TRIBOLOGICAL COMPARISON OF TRADITIONAL AND ADVANCED FIREARM COATINGS

A Thesis
Presented to
the Faculty of California Polytechnic State University,
San Luis Obispo

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Engineering
with Specializations in Materials Engineering

by
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June 2010

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ABSTRACT

Tribological Comparison of Traditional and Advanced Firearm Coatings

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The objective of this project is to find which type of coating has the best performance characteristics for finishing firearms. This is accomplished by measuring and comparing several performance characteristics, such as: adhesion, hardness, wear resistance, friction control, and corrosion resistance. Appearance is not a factor since any exterior coating that is flashy can be subdued or camouflaged with special purpose paints, which have proven durable enough for such purposes. Cost will not be a limiting factor for this experiment, but will be discussed in the conclusion as a secondary concern. This data will be used to identify the best coating for steel and aluminum firearm parts. The goal is to lengthen a firearm's life cycle while increasing performance and reliability by applying the best coating.

Keywords: firearms, coatings, tribology, adhesion, hardness, wear resistance, friction, corrosion.

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Chapter 1: Introduction

The added benefits of advanced coatings are of interest to the global firearms market. The ArmaLite model 15 rifle (AR15) is the perfect candidate for analysis. Analyzing newer coating techniques for the application of firearm coating will provide the information necessary to deliver firearm parts that are more resistant to catastrophic failure. This will provide the firearm industry a solution to improving performance and reliability, while lengthening the firearms lifecycle. This is beneficial for the military for the same reasons. Furthermore, the application of such information will greatly benefit and potentially save the lives of soldiers.

Which type of firearm has the largest percentage of the firearm market? Of all the types of firearms on the market (pistols, shotguns, long rifles, assault rifles, carbines, machine guns, sub machine guns), which owner would be most interested in an extremely durable firearm coating? With over 100 million in production, the Russian made Automatic Kalashnikov model 47 (AK47) owns the largest percentage of the worldwide market for assault rifles. Sure enough, the AK47 was designed by Mikhail Kalashnikov who was a former engineer for the Soviet military. Since the AK47 is inexpensive ($300 or less), non-democratic and undeveloped countries favor them. The production cost is low because the receiver is stamped sheet aluminum and the rifle is manufactured with relatively large tolerances, which makes the firearms extremely reliable. The reliable design and loose tolerances of the AK47 results in a decline of accuracy and precision compared to other rifles in its class. The loose tolerances that allow parts to move around despite dust and debris without jamming also makes for an inaccurate shot.

Conversely, the AR15 is more expensive because the receiver is forged aluminum and made with smaller tolerances. Thus, the gun is more accurate, but less reliable. These weight saving materials make the AR15 weigh in at 3.86 kg (8.5 lb.) while the AK47 weighs 4.98 kg (11 lb.). The AR15 is also inherently considered a “dirty” rifle because it is gas powered, where gas cycles from the igniting gun powder back into the breach of the rifle to cycle the bolt. The gas carries debris and carbon from burnt gunpowder (fouling), which interferes with the internal moving parts. Additionally, fouling adds to the reliability issue of the AR15; however, this can be solved by cleaning the gun regularly and properly.

The number of AR15s that have been produced is difficult to determine, since versions of the AR15 are now made by a large number of manufacturers. There are no reports of how many AR15 variants are in the United States of America, but it is possible to get a close approximation. The best selling ammunition in America is the .223/5.56 caliber bullet, which is standard fodder for AR15 variants. (4) The U.S. and Canada together have produced more than 8 million M16s and sold them around the world.

The large number of aftermarket AR15 parts and gunsmithing services allows the owner to create a very accurate and highly adaptable rifle or carbine. The advantage of having a weapon in long use by specialized military units and police special teams is that the top tactical minds of our generation have figured out the best ways to use AR15 variants in a variety of scenarios. Recent military activity and the consumer market for the use of AR15s for hunting or sport shooting has driven a slew of new products. The AR15’s accuracy, modularity, and versatility create a market demand that is unmatched, which makes it the ideal candidate for analysis.

Not only is there a large consumer market for weapon finishes, but the military is also looking for a self-lubricating finish. In September 2004, TACOM-ARDEC began identifying sources capable of providing a lubricious coating for critical small arms weapon components. Currently, most weapon parts are steel coated with either hard chrome or phosphate and maintained with wet lubrication. Lubricants are used in weapon systems to modify frictional characteristics of gun parts to provide better operation. The drawbacks of current lubricants are: (1) they contain various degrees of hazardous materials, (2) they must be applied in quantities that collect sand and dust, (3) they have poor cold weather performance, and (4) lubricants separate and partially solidify as they age. Self-lubricating coatings are expected to function without need for external lubrication in adverse conditions to include: sand, dust, extreme heat 204-427°C (400-800°F), extreme cold -54°C (-65°F), rain, mud, salt water, Nuclear-Biological-Chemical (NBC) decontamination solvents, etc.

Dry rifles function better at colder temperatures (-28°F to -58°F) than in temperatures above -10°F. Dry M16A1s experienced less malfunctions than lubricated M16A1s in colder temperatures (-28°F to -58°F). (7) However, at ambient temperatures lubricated weapons outperform dry weapons.

A self-lubricating firearm finish would reduce the large number of lubricants that are used throughout the Department of Defense (see Table 1.1). By switching to self-lubricating coatings for its firearm coatings, the government can eliminate several lubricants from its inventory. This could be of enormous savings to the government; similar to when the U.S. Secretary of Defense Robert McNamara pushed for the consolidation of weapon systems across all branches of the military by issuing the AR15.

Table 1.1 Current weapon systems lubricants.

Common Name	Mil-spec	Official Name	Application
LSA	MIL-L-46000C	Lubricating oil, semi-fluid (automatic weapons)	M2MG, M9/M11, M24, M60MG, M240MG
LSA-T	MIL-L-46150	Lubricating oil, semi-fluid (high load carrying)	M2MG, MK19GvG, M296MG, M134MG
CLP	MIL-PRF-63460	Cleaner, Lubricant, Preservative	M2MG, M4, M9/M11, M16A1, M16A2, M24, M296SAW
LAW	MIL-L-14107C	Lubricating oil, weapons, low temperature	M2MG, M4, M16A1, M16A2, M24, M60MG, M34MG
LAW-AW	DOD-L-85336A	Lubricating oil, general purpose	M197AC
PL-S	VV-L-800	Lubricating oil, weapons	M240MG
Black grease	MIL-G-21164D	Grease molybdenum disulfide	M230
TW-25B	-	Lubricating oil, weapons	M3PMG, M234MG
GAA	MIL-G-10924D	Grease, automotive and artillery	-
GAI	MIL-G-	Grease, aircraft and instrument	-
Red grease	MIL-G-	Grease, aircraft	M230

Chapter 2: Background

In order to avoid any potential pitfalls, design constraints must be identified based on the stakeholders' values. Stakeholders that would have an interest if the information gathered from this project were commercialized are: customers, employees, investors, business competitors, environmental groups, and government regulatory agencies. Based on potential stakeholders, the identified limitations of design are health and safety issues, sustainability concerns, and engineering codes and standards.

Without doubt, health and safety issues are of major concern for society. Coating facilities often require the use of chemicals that may be a health risk to employees. For example, the inhalation or physical contact of certain solvents, lacquers, varnishes, and other coating specific chemicals can pose a variety of health problems. Aluminum chloride is used in some paints, which is highly volatile with water and when reacted with water will let off noxious fumes. Additionally, the disposal of used hazardous chemicals must be done according to the regulations created by the California Environmental Protection Agency (EPA) Department of Toxic Substance Control. The Occupational Health and Safety Administration (OSHA), which falls under the US Department of Labor requires that chemicals must be stored and labeled properly and that appropriate safety equipment and clothing should be provided by all employers. (8) Hazardous material safety is greatly stressed by both of these organizations.

Not only do these hazardous chemicals present potential health risks, but there are environmental risks that cannot be undermined. Advanced coatings can benefit the environment and society by making products more durable. In turn, increasing the life cycle of products must be weighed against the potential environmental hazards. The EPA and other environmental groups could potentially bankrupt a company that did not take the time to analyze and mitigate potential environmental catastrophe. Even better than putting a band-aid on this problem would be to follow the EPA's lead in the Green Chemistry Initiative, which would help look for alternative chemicals that are less toxic. (9) The United States Environmental Protection Agency's scientific advisory board found in 2005 that perfluorooctanoic acid (PFOA), a chemical compound used to make Teflon, is a "likely carcinogen." (10) DuPont has paid over $300 million in lawsuit settlements and federal penalties based on groundwater pollution from this chemical. PFOA is still not regulated by the EPA. DuPont has agreed to stop releasing this chemical from its plants by 2015, but PFOA will still be used for production. A successful business must be prepared to avoid any accidents that may result in an ecological disaster.

Electroplated hard chromium is widely used to protect the barrel and barrel extension of an M16 rifle against tribological wear. Hexavalent chromium (Cr^{+6}) is a known human carcinogen and is present in the electroplating and rinse baths. The EPA has stipulated strict procedures for handling and disposal of chromium electroplating solutions and the rinse water used in the process. Stricter emission control regulations are also in place if one wishes to continue chromium electroplating. Therefore, there is an urgent need to replace hard chromium electroplate with an environmentally acceptable and also effective protective coating for high strength steel components. In order to comply with current Army policies and DOD directives, all new Army acquisition must be hexavalent chromium free. (11)

Engineering codes and standards will play a significant role during this project's development, and for coating companies during its implementation. The National Institute of Standards and Technology (NIST) manual, *Surface Engineering Measurement Standards for Inorganic Materials*, references many engineering standards organizations such as the American Society for Testing & Materials (ASTM), the Society of Automotive Engineers (SAE), and the International Organization for Standardization (ISO). Military Specifications (Mil-spec) were also used to identify materials, tolerances, and criticality of the critical parts. Mil-specs are United States Defense Standards that are set forth by the Department of Defense (DOD). The primary concern of potential customers and investors would be accuracy. If accuracy in data collection and production are imprecise, then the coating that they purchase may not meet all of the desired characteristics. The end result is an unhappy customer. To ensure accuracy, it is in a company's interest to work with the aforementioned certifying standards organizations. Some coating businesses may be in direct market competition with a company that could sell the coatings identified in this thesis. Many coating businesses still use antiquated coating techniques, such as electrochemical conversion coatings. The technical information from this project could be used to modernize the firearm coating industry. This project may, in fact, threaten companies that make proprietary coatings whom may attempt to discredit this thesis if specific engineering codes and standards are not correctly abided.

There is a powerful interconnection between the design and stakeholders. For example, the financial concerns of an investor are extremely dependent on customer satisfaction, and both of these are affected by design constraints. Therefore, the importance of these constraints cannot be over-emphasized. A handful of coatings need to be identified out of the hundreds available; the various metals and alloys typically used in firearms need to be identified. Once the metals and coatings have been found, specific health and safety issues, environmental concerns, and engineering codes and standards can be accurately pinpointed. More importantly, a more environment friendly coating system may result.

Chapter 3: Critical Firearm Parts

The goal of this project is to lengthen a firearm's life cycle while increasing performance and reliability by applying a better firearm coating than those currently in use. Before deciding on a finish, the parts desired to be finished and the materials that they are made of must be identified. To increase reliability, the malfunctions associated with the AR15 must be examined. The most dangerous malfunctions are those with the smallest number of permissible malfunctions, see Table 3.1. The *All Other Malfunctions* category covers issues related to fire control, where zero malfunctions are permitted.

Table 3.1 Malfunctions permitted in 6,000 rounds. (12)

Malfunction	**Description**	**# Malfunctions Permitted**
Failure of Bolt to Lock[a]	Failure of bolt to fully close and rotate to the locked position in the barrel extension.	2
Failure to Fire	Failure of the rifle to fire the cartridge, when the cartridge has been fully chambered; bolt has been locked in the battery position, and the trigger has been pulled.	2
Failure to Feed	Failure of the bolt to completely strip the next round from the magazine.	4
Failure to Eject	Failure of the rifle to eject a round from the rifle, when the cartridge has been fired and the cartridge case has been completely extracted from the magazine.	2
Failure to Chamber	Failure of the rifle to chamber a cartridge that has been completely stripped from the magazine.	3
Failure to Extract	Failure of the rifle to remove a cartridge case or unfired cartridge from the chamber.	1
Bolt Fails to Hold to the Rear	Failure of the bolt to remain in the rearward position after the last round in the magazine has been fired.	3
All Other Malfunctions[b]	Failure of the pawl of the forward assist assembly to engage or remain engaged with the bolt carrier serrations during manual attempt to lock the bolt, when the bolt fails to lock on return to the battery position.	0
Total Malfunctions	Number of permissible malfunctions for every 6,000 rounds fired.	9

a. In the event of any *Failure of Bolt to Lock* malfunction, the forward assist assembly shall be operated. Failure of the forward assist assembly to remain engaged with the bolt carrier assembly during manual attempt to lock bolt shall be considered an additional malfunction in the category of *All Other Malfunctions*.

b. *All Other Malfunctions* includes, but is not limited to: occurrence of doubling (two shots fired with a single trigger pull) during semi-automatic firing; failure to immediately stop firing when the trigger is released (uncontrolled fire) during burst firing; failure to fire three shots on a complete trigger pull in burst mode other than in the first trigger pull (when fresh magazine is inserted or when selector is switched to "Burst") or last trigger pull (when magazine is emptied); and failure of forward bolt assist assembly to remain engaged with bolt carrier assembly during manual attempt to lock the bolt, etc.

Failure to Fire malfunctions can be due to improper headspace, faulty ammunition, excessive fouling on the firing pin, or from a worn firing pin. Excessive fouling on the bolt carrier group, and barrel locking lugs may also cause this malfunction. The least likely cause for this malfunction is a non-functioning trigger assembly, but the trigger assembly is not likely to ever fail under normal use. If this malfunction occurs, remedial action should be applied and do not apply immediate action.

The next most important malfunction is *Failure to Extract*, which is potentially lethal. *Failure to Extract* malfunctions are usually due to short recoil cycles and fouled or corroded rifle chambers. A damaged extractor or a weak or broken extractor spring can also cause this malfunction. Short recoil is usually caused by excessive fouling in the bolt carrier or gas tube. This is considered an extremely serious malfunction, requiring the use of tools to clear the rifle. A live round can be left in the chamber and accidentally discharged. If a second live round is fed into the primer of the chambered live round, the rifle could explode and cause personal injury.

All subsequent malfunctions can be potentially remedied with immediate action, which is a series of actions used to quickly correct any stoppage without performing troubleshooting procedures to determine the actual cause. The Army teaches immediate action with the acronym/mnemonic SPORTS:

- Slap the magazine to ensure it is fully seated
- Pull the charging handle to the rear to clear the chamber
- Observe the chamber for a live round or expended cartridge
- Release the charging handle to allow the bolt to move forward
- Tap the forward assist to ensure bolt closure
- Squeeze the trigger to fire the rifle

Immediate action is only applied once to clear a stoppage. If the rifle fails to fire a second time for the same malfunction, apply remedial action. Remedial action is the continuing effort to determine the cause of a stoppage or malfunction and to try to clear the stoppage once it has been identified. For remedial action, first attempt to place the weapon on safe, then clear the weapon and place it on safe if you were unable to the first time. Refer to the field manual for detailed information on conducting remedial action for a specific malfunction. Remedial action is much more time consuming, which endangers the lives of soldiers and members of law enforcement.

A catastrophic malfunction is any malfunction that injures the operator, is untreatable with immediate action, or endangers the operator's life. If failure of a firearm part results in a catastrophic malfunction, the part will be deemed a "critical part" and selected for analysis. In AR15 variants, catastrophic malfunctions can be caused by barrel, chamber, and bolt carrier group malfunctions. Despite the large number of parts, the only critical parts in AR15 variants are: the barrel, upper receiver, lower receiver, bolt, bolt carrier, and the extractor (see Appendix A). While failure of other parts may also result in the rifle failing to function properly, they will not cause a catastrophic malfunction. Also, other parts are not prone to failure since they are not repeatedly subjected to extreme pressures and temperatures (unlike the critical parts). All springs, washers, detents, screws, and pins were not considered for coating analysis because (1) they are inexpensive, (2) are easily replaceable, (3) do not experience significant wear, and (4) would not result in catastrophic failure of the rifle. Samples of steel and aluminum used to make the aforementioned critical parts will be coated and analyzed.

Parts can be made more reliable by taking into account the operating environment caused by the caliber of ammunition. All coatings intended for use within a firearm must withstand the high temperatures and pressures associated with igniting a cartridge. The critical parts of AR15 variants include: the receivers, barrel, barrel extension, bolt carrier, bolt, and the extractor. Erosion in rifles is typically caused by a combination of high temperatures from burning of the nitrocellulose powder, the mechanical rubbing of the projectile on the lands of the rifling, and the cutting effect of gases moving at high velocities. (1) To understand how to make these parts more durable, one must first determine the temperature and pressure of the operating environment prior to identifying what makes these critical parts unserviceable.

High temperatures can cause the cartridges to detonate on their own and can even cause the barrel to fail catastrophically. A cook-off is the firing of a round due to the heat of a hot barrel, but not due to the firing mechanism. The average rifle and pistol cartridge will cook-off at high 93°C (200°F) to low 149°C (300°F). (20) Exceeding the sustained rate of fire of 12-15 rounds per minute generates enough heat to cause the barrel to melt and rupture. During testing, the M16A2 and M4 barrel had a maximum temperature of 871°C (1599°F) and 893°C (1639°F). (21) Firearm coatings should be capable of withstanding temperatures between 93°C (200°F) and 871°C (1599°F). Ideally, testing should be conducted between 38-93°C (100-200°F) in order to simulate the operating environment.

The instantaneous pressure created by the propellant combustion is 414 MPa (60,045 psi). (17) This pressure is dissipated as the bullet travels down the barrel and as the bolt retracts. At standard temperature and pressure, the chamber pressure for the M16A2 is reported to be 358.5 MPa (52,000 psi) (see Appendix B). The firing of a round from the M16 typically creates a chamber pressure in the range of 345 to 393 MPa (50,000 to 57,000 psi) depending on the temperature and pressure of the environment. If the chamber pressure is exceeded, over-pressure problems such as difficult extraction, flowing brass, or popped primers may occur. Drastically exceeding the chamber pressure could damage or destroy the rifle. Deviation from standard daytime temperature of 15°C (59°F) affects chamber pressure. (22) As air temperature increases, so does the chamber pressure. Ultimately this increases the initial velocity of the bullet. Chamber pressure does not affect trajectory as much as the air resistance. Cold air is denser than warm air meaning the bullet must travel through more tightly packed air particles. This causes the bullet to lose velocity resulting in the impact being lower than the intended point of impact. Therefore, the chamber pressure is more essential to the reliability than accuracy of the firearm.

The design of the cartridge and its interaction with the chamber determine the chamber pressure of the firearm. There are some common misconceptions concerning the cartridge for the AR15 regarding: what size caliber it is capable of firing, the difference in casing design and its effect on pressure, and at what locations the chamber pressures are measured. These misconceptions are due to the many evolutionary steps this cartridge underwent. Most AR15 variants are chambered for both .223 caliber and 5.56mm cartridges. In 1957, Eugene Stoner tweaked the .222 Remington round to fit the Infantry Board's requirements and created the .222 Special (later designated .223 caliber to avoid confusion). Testing indicated that the .222 Remington cannot achieve the required velocity without excess chamber pressure. The .223 caliber Remington cartridge was standardized by the American Sporting Arms and Ammunition Manufacturers' Institute (SAAMI). SAAMI is an association of American firearms and ammunition manufacturers focused on standardizing the field. The North Atlantic Treaty Organization (NATO) uses the 5.56 mm, which is very similar to the .223 caliber cartridge and can fit into the M16A2. The 5.56 mm cartridge was standardized by the European equivalent of SAAMI, which is the Commission Internationale Permanente (CIP) pour l'Epreuve des Armes à Feu Portatives (permanent international commission for testing portable firearms).

While the 5.56 mm and .223 cartridges are very similar, they are not identical. The dimensions of the casing and the bullet of the 5.56 mm and .223 cartridges are also different (see Appendix C). The casings of the 5.56 mm cartridge are thinner and contain more gunpowder, resulting in a greater chamber pressure compared to the .223 caliber cartridge. Military cases are made from thicker brass than commercial cases, which reduces the powder capacity (an important consideration for handloaders), and the NATO specification allows a higher chamber pressure. The difference is largely limited to the freebore, the cylindrical space in front of the case mouth, and the leade, the distance between the mouth of the cartridge and the tapered region that eases the bullet into full engagement with the rifling. The SAAMI chamber features less freebore and a tighter leade, which normally provide better bullet fit and match-grade accuracy than the NATO chamber. The .223 chambering, known as the "SAAMI chamber", is allowed to have a shorter leade, and is only required to be proof tested to the lower SAAMI chamber pressure. That means that advertised pressure of 58,000 psi for 5.56 mm NATO, is around 78,000 psi tested in .223 Remington test barrels (SAAMI .223 Remington proof maximum average pressure (MAP) is 78,500 psi so every 5.56 mm round fired is a proof load). A 5.56 mm cartridge used in a rifle chambered for the .223 caliber cartridge could damage the rifle. (23) Some aftermarket barrels are chambered to accept either .223 caliber or 5.56 mm cartridges. All coatings should be able to withstand pressures up to 100,000 psi (689,475,700 Pa).

Despite working together, there is not a consensus on what location to measure chamber pressure from. The difference in the location of the pressure measurement gives different results when measuring chamber pressure. Test barrels made for 5.56 mm NATO measure chamber pressure at the case mouth, as opposed to the SAAMI location. This difference accounts for upwards of 20,000 psi difference in pressure measurements. Thus, chamber pressures reported by CIP for the 5.56 mm cartridge can be much greater by SAAMI standards.

Chapter 4: Experimental Procedures

It is extremely important to outline the goal of the experiment and to structure a systematic approach of how to arrive at that goal. After determining what weapon system will be evaluated, the specific parts and their current coatings also needed to be determined. The characteristics that will be evaluated, and the laboratory equipment and standards that will be used to quantify them are also required. The following is the methodology used for this research.

Since the majority of AR15 variants are M16s, the sample substrate materials should be chosen based on the material outlined by M16 Mil-specs. Since these materials are proprietary, the critical parts must first be examined using elemental and quantitative analysis techniques. The bolt, bolt carrier, and extractor are all made of the same unknown high-carbon steel, which is kept by companies as proprietary information. Mil-specs call for forged aluminum receivers for use in M16s. Thus, cast receivers sold as aftermarket parts will not be examined (casted parts are generally of poorer quality compared to forged parts). The exact type of material can be determined by purchasing the parts and analyzing them using the Energy Dispersive X-Ray Spectrometer (EDS). These results will be verified using the portable X-Ray Florescence Spectrometer (XRF).

While searching for advanced coatings that have not yet been applied to firearms, it is imperative to examine traditional firearm coating techniques. Historically, the firearm industry uses trade names for commonly used finishes, such as: hard-chrome plating (chromium electro-deposition), bluing (oxide film-forming), parkerizing (phosphating), nickel plating (electroless nickel plating), Teflon coating, and anodizing (type 3 hard anodizing). To determine the type of advanced coating that has suitable performance characteristics, current reports, specifications, and articles were gathered and studied. Gunsmithing forums provided firsthand experience of people successfully applying coatings and their performance results.

Once the metals and coatings have been identified, the next vital step would be to determine necessary laboratory equipment. There are multiple tests using different equipment to test the same properties. Depending on the laboratory equipment available, the goal is to decide which experiments to conduct. The NIST manual on *Surface Engineering Measurement Standards for Inorganic Materials* references various standards organizations for coatings, quality control, measurements, and testing. (14) Table 4.1 lists all the general standards that can be studied to become familiar with terminology, testing procedures, and other industry standards. Once a variety of coatings are selected and the availability of potential laboratory equipment is determined, the NIST manual can serve as a guide as to which specific standards to use. Each standard will specify the variable that represents each performance characteristic. This will allow you to measure and compare each performance characteristic.

Table 4.1 General surface engineering standards for inorganic materials.

Specification #	**Title**
ASTM A902	Standard Terminology Relating to Metallic Coated Steel Products
ASTM D4417	Standard Test Methods for Field Measurement of Surface Profile of Blast-Cleaned Steel
ASTM E3	Standard Guide for Preparation of Metallographic Specimens
ASTM E140	Standard Hardness Conversion Tables for Metals; Relationship Among Brinell Hardness, Vickers Hardness, Rockwell Hardness, Superficial Hardness, Knoop Hardness, and Scleroscope Hardness
ASTM E673	Standard Terminology Relating to Surface Analysis
ISO 2064	Metallic and Other Inorganic Coatings – Definitions and Conventions Concerning the Measurement of Thickness
ISO 2079	Surface Treatment and Metallic Coatings – General Classification of Terms
ISO 3274	Geometrical Product Specification (GPS) – Surface Texture: Profile Method – Nominal Characteristics of Contact (Stylus) Instruments
ISO 4288	Geometrical Product Specification (GPS) – Surface Texture: Profile Method – Rules and Procedures for the Assessment of Surface Texture
ISO 8785	Geometrical Product Specification (GPS) – Surface Imperfections – Terms, Definitions, and Parameters
SAE J358	Nondestructive Tests
SAE J417	Hardness Tests and Hardness Number Conversions
SAE J448a	Surface Texture (SAE Standard)
SAE J449a	Surface Texture Control (SAE Recommended Practice)

After sample preparation, the next step is to measure the following performance characteristics: adhesion, hardness, wear resistance, friction control, and corrosion resistance. The standard testing methods for each performance characteristic is outlined in Table 4.2. Adhesion will be measured using either the Bend Test, Draw Test, Heat-Quench Test, or Scribe-Grid Test as outlined in *ASTM B571 Adhesion Testing* standard. Wear resistance will be determined by conducting the *ISO 3878 Hardmetals: Vickers Hardness* test using a hardness tester. Friction control will be tested using the *ASTM/ASM Friction and Wear Source Book*. Corrosion resistance will be examined using *ISO 10289 Methods for Corrosion Testing*, which will require a small bath of salt water for the samples to sit in. By comparing the results of the critical parts and the sample metal substrates, the experiment will ultimately be validated through replication.

All of the performance characteristics will be prioritized into a design decision matrix. The importance of adhesion, hardness, wear resistance, friction control, and corrosion resistance will be assigned a weighted value. The coating with the highest total value for all performance characteristics will be selected as the best coating for each specific metal substrate. The conclusion will identify the best coatings for each type of metal, and highlight if any coating is better suited for a critical part. The optimum result would be to find a coating that increases a products durability, performance, and reliability. Increasing a product's life-cycle reduces waste in our environment, provides a superior product for consumers, and reduces replacement or maintenance costs. The goal of this experiment will be kept in mind during all measures.

Table 4.2 Surface engineering testing and measurement standards for inorganic materials.

Property	Document #	Title	Year
Thickness	ASTM B487	Standard Test Method for Measurment of Metal and Oxide Coating Thickness by Microscopical Examination of a Cross-Section	2002
Thickness	ASTM B659	Standard Guide For Measuring Thickness of Metallic and Inorganic Coatings	2003
Thickness	ISO 1463	Metallic and Oxide Coatings – Measurement of Coating Thickness – Microscopical Method	2003
Adhesion	ASTM B571	Standard Practice for Qualitative Adhesion Testing of Metallic Coatings	2003
Adhesion	-	Industry Standard Scratch Adhesion Test	2005
Wear	ASTM G190	Standard Guide for Developing and Selecting Wear Tests	2006
Wear	ASTM G171	Standard Test Method for Scratch Hardness of Material Using a Diamond Stylus	2003
Wear	ASTM D7027	Standard Test Method for Evaluation of Scratch Resistance of Polymeric Coatings and Plastics Using an Instrumented Scratch Machine	2005
Wear	ASTM D7187	Standard Test Method for Measuring Mechanistic Aspects of Scratch/Mar Behavior of Paint Coatings by Nanoscratching	2005
Hardness	ASTM B578	Standard Test Method for Microhardness of Electroplated Coatings	1999
Hardness	ASTM E18	Standard Test Mehods for Rockwell Hardness and Rockwell Superficial Hardness of Metallic Materials	2003
Hardness	ASTM E384	Standard Test Method for Microindentation Hardness of Materials	1999
Hardness	ISO 3878	Hardmetals – Vickers Hardness Test	1983
Hardness	ISO 6507	Metallic Materials – Vickers Hardness Test	2005
Hardness	ISO 14577-1	Metallic Materials – Instrumented Indentation Test for Hardness and Materials Parameters, Part 1: Test Method	2002
Friction	ASTM/ASM	Friction and Wear Testing: Source Book of Selected References From ASTM Standards and ASM Handbook	1997
Friction	ASTM D4417	Standard Test Methods for Field Measurement of Surface Profile of Blast-Cleaned Steel	2003
Friction	ISO 4288	Geometrical Product Specification (GPS) – Surface Texture: Profile Method – Rules and Procedures for the Assessment of Surface Texture	1996
Friction	SAE J448a	Surface Texture (SAE Standard)	1963
Friction	SAE J449a	Surface Texture Control (SAE Recommended Practice)	1963
Corrosion	ASTM B117	Standard Practices for Operating Salt Spray (Fog) Apparatus	2003
Corrosion	AMS 2438	Chromium Plating, Thin, Hard, Dense, Deposit (referenced by XADC – Armology)	
Corrosion	ISO 9227	Corrosion Tests in Artificial Atmospheres – Salt Spray Tests	2006
Corrosion	ISO 10289	Methods for Corrosion Testing of Metallic and Other Inorganic Coatings on Metallic Substrates – Rating of Test Specimens and Manufactured Articles Subjected to Corrosion Tests	1999

Coating performance is partly intrinsic to the coating, but also depends on its interaction with the substrate. The substrates of all the critical parts were examined for elemental composition, microstructure, and coating thickness using the equipment outlined in Table 4.3.

Table 4.3 The purpose and sample requirements of necessary laboratory equipment.

Equipment	**Purpose**	**Sampling Area**	**Sampling Depth**	**Sensitivity**	**2D/3D Resolution**	**Sample Description**
Tungsten thermal FEI Quanta scanning electron microscope (SEM)	Image the surface to visualize the roughness.	10 x 10 μm^2	1-3 µm	-	10-100 nm	The sample should not be any greater than 3½ cm in length and 2 cm in height.
Energy dispersive x-ray spectroscope (EDS)	Elemental analysis of coatings and bulk material of the critical parts.	10 nm^2	-	1000 ppm	0.01 µm / 1-3 µm	The sample should not be any greater than 3½ cm in length and 2 cm in height.
X-ray florescence spectroscope (XRF)	Compare with EDS results. Can't detect carbon, among other elements.	15 mm^2	1-10 µm	500 ppm	Energy dispersive: 150 eV Wavelength dispersive: 15 eV	No sample preparation required.
X-ray photoelectron spectroscope (XPS)	Measure elemental & chemical bonding between the coating and the metal substrate, which requires angle resolved analysis and films 2-3 µm thick.	50 μm^2	1-8 nm	500 ppm	10 µm / 50 Å	The sample should not be any greater than 1 x 1 cm^2, and the thickness should be about 5 mm. The sample needs a surface roughness of < 100nm. The UHV environment should be 10-8 torr.
Physical Electronics 6650 Dynamic Secondary Ion Mass Spectrometry (D-SIMS)	Depth profiling of coatings, allowing a determination of elemental composition (H-U) as a function of depth.	-	8 µm	1 ppb	10 µm / 30 Å	The Phi 6650 DSIMS system can handle two different size sample holders, 25mm & 60mm dia. It can hold a ~7mm thick sample with a flat sample holder, and a ~12mm thick sample with a recessed holder. The UHV environment can be as low 10-6 torr

Chapter 5: Substrate Material Composition

All of the AR15 critical parts were manufactured by Colt Defense, since they are the largest Department of Defense (DOD) supplier of AR15 variants. The exact type of material was determined by purchasing the parts and analyzing them using the Energy Dispersive X-Ray Spectroscopy (EDS). Since EDS does not detect light elements, therefore X-Ray Photoelectron Spectrometer (XPS) will be used to determine the carbon content. These results will be verified using the portable X-Ray Florescence Spectrometer (XRF). The following standard will be used for this portion of the experiment: *ASTM E3 – Standard Guide for Preparation of Metallographic Specimens*. This standard outlines how to observe structure and composition of metals and alloys by light or electron microscopy.

The receivers used in M16s are made of forged 7075-T6 aluminum, and are Type III hard anodized. Cast receivers will not be examined since Mil-specs call for a forged receiver. The receiver was sectioned as shown in Figure 5.1. The scan locations on each sample are illustrated in Figure 5.2, and the composition of each scan location is shown in Tables 5.1, 5.2, and 5.3. A characteristic micrograph illustrates the elemental composition of one scan location (see figure 5.3).

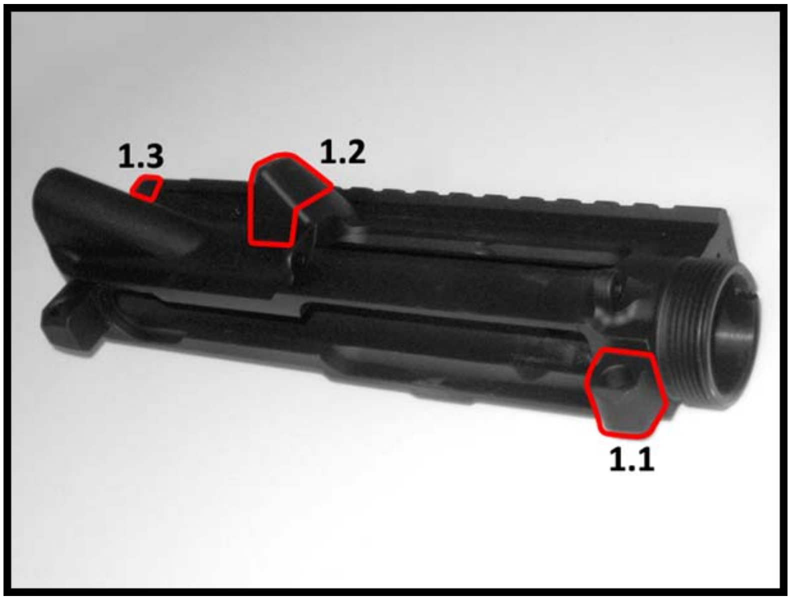


Figure 5.1 Sample sections of a Colt manufactured M4A1 upper receiver.

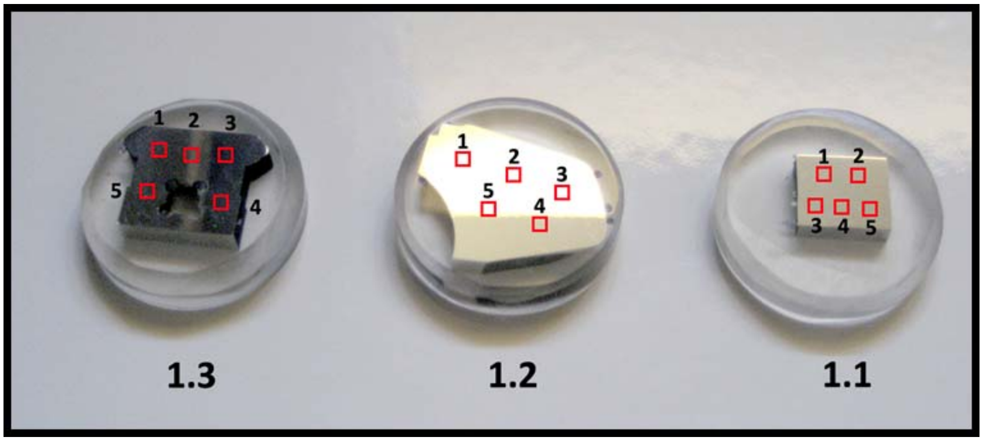


Figure 5.2 Scan locations on receiver samples.

Table 5.1 Weight percentages of each element present in the receiver sample 1.1.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	2.66	±0.60	3.02	±0.59	3.09	±0.59	3.12	±0.60	3.17	±0.59	3.01	±0.20
O	1.26	±0.21	1.25	±0.21	1.02	±0.21	1.27	±0.21	1.34	±0.21	1.23	±0.12
Mg	2.64	±0.05	2.58	±0.05	2.62	±0.05	2.57	±0.05	2.64	±0.05	2.61	±0.03
Al	84.45	±0.56	84.12	±0.55	84.16	±0.56	84.11	±0.56	83.79	±0.55	84.13	±0.23
Si	0.10	±0.05	0.12	±0.05	0.11	±0.05	0.03	±0.05	0.11	±0.05	0.09	±0.04
Cr	0.20	±0.02	0.22	±0.02	0.20	±0.02	0.19	±0.02	0.19	±0.02	0.20	±0.01
Mn	0.07	±0.02	0.06	±0.02	0.05	±0.02	0.09	±0.02	0.05	±0.02	0.06	±0.02
Fe	0.16	±0.03	0.19	±0.03	0.17	±0.03	0.13	±0.03	0.17	±0.03	0.16	±0.02
Cu	1.29	±0.04	1.25	±0.04	1.28	±0.04	1.28	±0.04	1.25	±0.04	1.27	±0.02
Zn	5.74	±0.08	5.73	±0.08	5.76	±0.08	5.66	±0.08	5.69	±0.08	5.72	±0.04
Ag	1.44	±0.07	1.46	±0.07	1.54	±0.07	1.54	±0.07	1.60	±0.07	1.52	±0.07

Table 5.2 Weight percentages of each element present in the receiver sample 1.2.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	2.43	±0.60	1.81	±0.60	2.78	±0.57	2.91	±0.58	2.40	±0.59	2.47	±0.43
O	1.22	±0.21	1.08	±0.21	1.15	±0.21	1.16	±0.21	1.04	±0.21	1.13	±0.07
Mg	2.67	±0.05	2.63	±0.05	2.60	±0.05	2.62	±0.05	2.68	±0.05	2.64	±0.03
Al	84.59	±0.56	85.27	±0.56	84.36	±0.54	84.22	±0.55	84.90	±0.56	84.67	±0.42
Si	0.08	±0.05	0.06	±0.05	0.08	±0.05	0.09	±0.05	0.08	±0.05	0.08	±0.01
Cr	0.18	±0.02	0.21	±0.02	0.23	±0.02	0.20	±0.02	0.24	±0.02	0.21	±0.02
Mn	0.05	±0.02	0.05	±0.02	0.07	±0.02	0.05	±0.02	0.03	±0.02	0.05	±0.01
Fe	0.19	±0.03	0.19	±0.03	0.21	±0.03	0.17	±0.03	0.20	±0.03	0.19	±0.01
Cu	1.28	±0.04	1.28	±0.04	1.21	±0.04	1.26	±0.04	1.23	±0.04	1.25	±0.03
Zn	5.69	±0.08	5.83	±0.08	5.74	±0.08	5.80	±0.08	5.69	±0.08	5.75	±0.06
Ag	1.60	±0.07	1.59	±0.07	1.58	±0.07	1.53	±0.07	1.52	±0.07	1.56	±0.04

Table 5.3 Weight percentages of each element present in the receiver sample 1.3.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	3.91	±0.60	4.15	±0.58	3.36	±0.59	4.22	±0.58	4.33	±0.58	3.99	±0.39
O	0.94	±0.21	1.47	±0.21	1.44	±0.21	1.39	±0.21	1.24	±0.21	1.30	±0.22
Mg	2.57	±0.05	2.52	±0.05	2.57	±0.05	2.54	±0.05	2.58	±0.05	2.56	±0.03
Al	83.33	±0.56	82.72	±0.54	83.24	±0.55	82.60	±0.54	82.47	±0.54	82.87	±0.39
Si	0.12	±0.05	0.11	±0.05	0.16	±0.05	0.16	±0.05	0.16	±0.05	0.14	±0.02
Cr	0.17	±0.02	0.20	±0.02	0.20	±0.02	0.24	±0.02	0.21	±0.02	0.20	±0.03
Mn	0.06	±0.02	0.08	±0.02	0.05	±0.02	0.04	±0.02	0.04	±0.02	0.05	±0.02
Fe	0.17	±0.03	0.15	±0.03	0.19	±0.03	0.15	±0.03	0.20	±0.03	0.17	±0.02
Cu	1.29	±0.04	1.32	±0.04	1.30	±0.04	1.33	±0.04	1.34	±0.04	1.32	±0.02
Zn	5.94	±0.08	5.88	±0.08	5.98	±0.08	5.84	±0.08	5.93	±0.08	5.91	±0.05
Ag	1.51	±0.07	1.41	±0.07	1.52	±0.07	1.49	±0.07	1.49	±0.07	1.48	±0.04

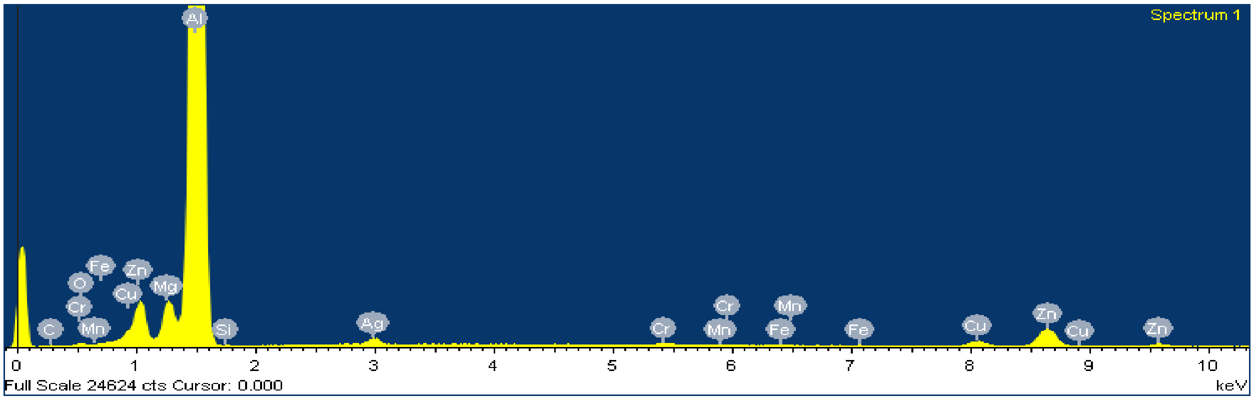


Figure 5.3 EDS micrograph of a receiver sample (Spot Size = 6.0, Voltage = 30 kV).

The barrel is made out of ORD 4150 steel, ORD 4150 resulfurized steel, and chrome-moly-vanadium steel.[9] The finish machined surface of the barrel should not exceed a roughness height rating of 40 micro-inches, which are in accordance with the barrel Mil-specs. Since 1971, M16A1 rifles were manufactured with chromed bores and chambers. Previously, only the chambers were chromed. According to military specifications, the barrel should be made of the alloys listed in Table 5.4. The barrel was sectioned as shown in Figure 5.4 and 5.5. The scan locations on each sample are illustrated in Figure 5.6, and the composition of each scan location is shown in Tables 5.5, 5.6, and 5.7. A characteristic micrograph illustrates the elemental composition of one scan location (see Figure 5.7).

Table 5.4 Military specifications for the chemical composition of M16 barrels.[1, 2, 3] (16)

Element	ORD 4150	ORD 4150 Resulfurized	Chrome-Moly-Vanadium
Carbon	0.48 - 0.55	0.47 – 0.55	0.41 – 0.49
Manganese	0.75 – 1.00	0.70 – 1.00	0.60 – 0.90
Phosphorus	0.040	0.040	0.040
Sulfur	0.040	0.05 – 0.09	0.040
Silicon	0.20 – 0.35	0.20 – 0.35	0.20 – 0.35
Chromium	0.80 – 1.10	0.80 – 1.15	0.30 – 0.40
Molybdenum	0.15 – 0.25	0.15 – 0.25	0.30 – 0.40
Vanadium	-	-	0.20 – 0.30
Iron	Balance	Balance	balance

1. Chemical ranges and limits based on ladle analysis.
2. Maximum except where indicated as a range.
3. Steels, containing elements not designated, in excess of the following amounts shall be subjected to rejection: copper 0.35 percent and aluminum 0.040 percent.

Figure 5.4 Sample sections of a Colt manufactured M4 barrel.

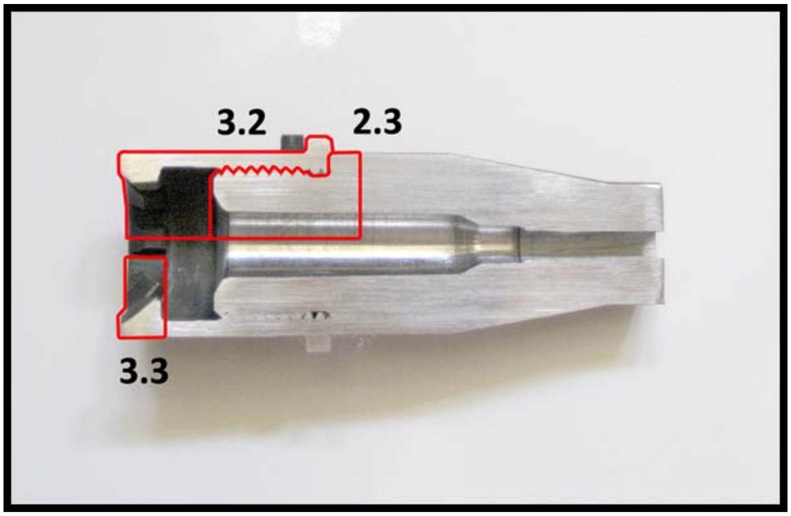


Figure 5.5 Sample sections of a Colt manufactured M4 barrel & barrel extension cross-section.

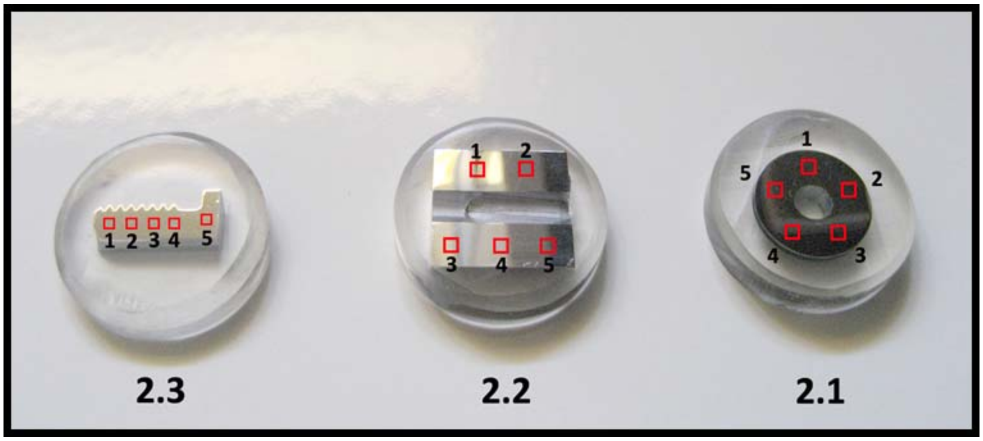


Figure 5.6 Scan locations on barrel samples.

Table 5.5 Weight percentages of each element present in the barrel sample 2.1.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	3.00	±0.45	4.67	±0.50	4.91	±0.53	4.61	±0.53	4.93	±0.61	4.42	±0.81
Si	0.53	±0.05	0.59	±0.06	0.57	±0.06	0.57	±0.06	0.62	±0.07	0.58	±0.03
P	0.05	±0.05	-0.01	±0.05	0.00	±0.05	-0.05	±0.05	0.04	±0.06	0.01	±0.04
S	0.06	±0.09	0.08	±0.10	0.18	±0.10	0.18	±0.10	-0.01	±0.11	0.10	±0.08
V	0.26	±0.03	0.27	±0.03	0.27	±0.03	0.25	±0.03	0.22	±0.03	0.25	±0.02
Cr	1.07	±0.03	1.08	±0.03	1.02	±0.03	1.05	±0.03	1.04	±0.03	1.05	±0.02
Mn	0.80	±0.04	0.74	±0.04	0.76	±0.04	0.77	±0.04	0.74	±0.05	0.76	±0.02
Fe	93.80	±0.52	92.19	±0.56	92.00	±0.60	92.52	±0.59	91.76	±0.67	92.45	±0.80
Mo	0.43	±0.27	0.42	±0.28	0.29	±0.30	0.11	±0.29	0.66	±0.33	0.38	±0.20

Table 5.6 Weight percentages of each element present in the barrel sample 2.2.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	1.48	±0.23	1.30	±0.23	1.33	±0.23	1.02	±0.22	1.40	±0.23	1.31	±0.17
Si	0.33	±0.03	0.33	±0.03	0.35	±0.03	0.32	±0.03	0.33	±0.03	0.33	±0.01
P	0.01	±0.03	0.04	±0.03	0.04	±0.03	0.01	±0.03	-0.01	±0.03	0.02	±0.02
S	0.04	±0.05	0.04	±0.05	0.08	±0.05	0.08	±0.05	0.03	±0.05	0.05	±0.02
V	0.24	±0.02	0.24	±0.02	0.25	±0.02	0.24	±0.02	0.25	±0.02	0.24	±0.01
Cr	1.05	±0.02	1.04	±0.02	1.08	±0.02	1.05	±0.02	1.06	±0.02	1.06	±0.02
Mn	0.80	±0.03	0.75	±0.03	0.77	±0.03	0.72	±0.03	0.78	±0.03	0.76	±0.03
Fe	95.77	±0.28	95.97	±0.27	95.88	±0.28	96.38	±0.27	95.78	±0.27	95.96	±0.25
Mo	0.30	±0.15	0.30	±0.15	0.23	±0.15	0.18	±0.15	0.37	±0.15	0.28	±0.07

Table 5.7 Weight percentages of each element present in the barrel sample 2.3.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	2.48	±0.25	2.37	±0.25	2.29	±0.24	2.77	±0.25	2.36	±0.25	2.45	±0.19
Si	0.32	±0.03	0.39	±0.03	0.33	±0.03	0.36	±0.03	0.35	±0.03	0.35	±0.03
P	-0.01	±0.03	0.02	±0.03	0	±0.03	0.04	±0.03	0.04	±0.03	0.02	±0.02
S	0.01	±0.05	0.04	±0.05	0.03	±0.05	0.04	±0.05	0.05	±0.05	0.03	±0.02
V	0.27	±0.02	0.25	±0.02	0.26	±0.02	0.26	±0.02	0.26	±0.02	0.26	±0.01
Cr	1.04	±0.02	1.04	±0.02	1.03	±0.02	1.06	±0.02	1.07	±0.02	1.05	±0.02
Mn	0.79	±0.03	0.75	±0.03	0.79	±0.03	0.78	±0.03	0.74	±0.03	0.77	±0.02
Fe	94.72	±0.29	94.85	±0.29	94.97	±0.28	94.38	±0.28	94.81	±0.29	94.75	±0.22
Mo	0.37	±0.15	0.3	±0.15	0.3	±0.15	0.32	±0.15	0.32	±0.15	0.32	±0.03

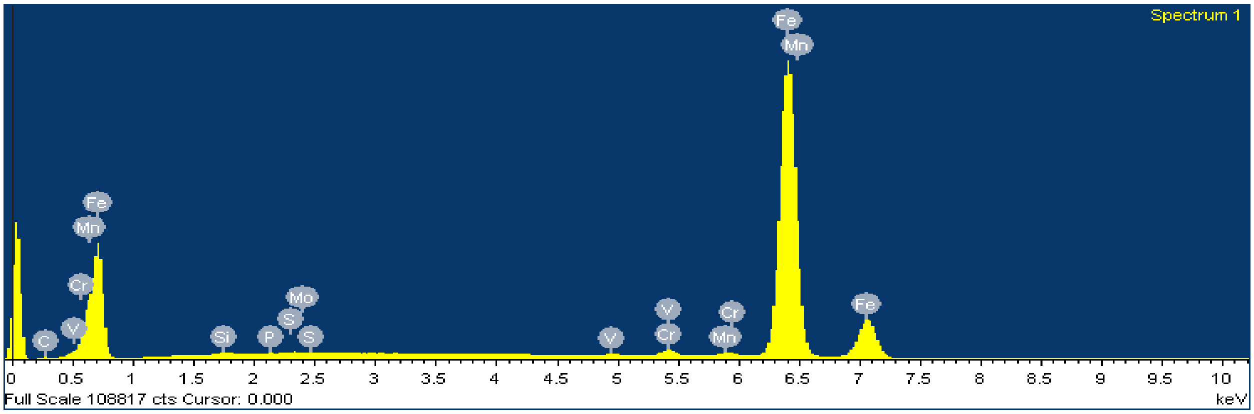


Figure 5.7 EDS micrograph of a barrel sample (Spot Size = 6.0, Voltage = 30 kV).

The barrel-extension was sectioned as shown in Figure 5.4 and 5.5. The scan locations on each sample are illustrated in Figure 5.8, and the composition of each scan location is shown in Tables 5.8, 5.9, and 5.10. A characteristic micrograph illustrates the elemental composition of one scan location (see Figure 5.9).

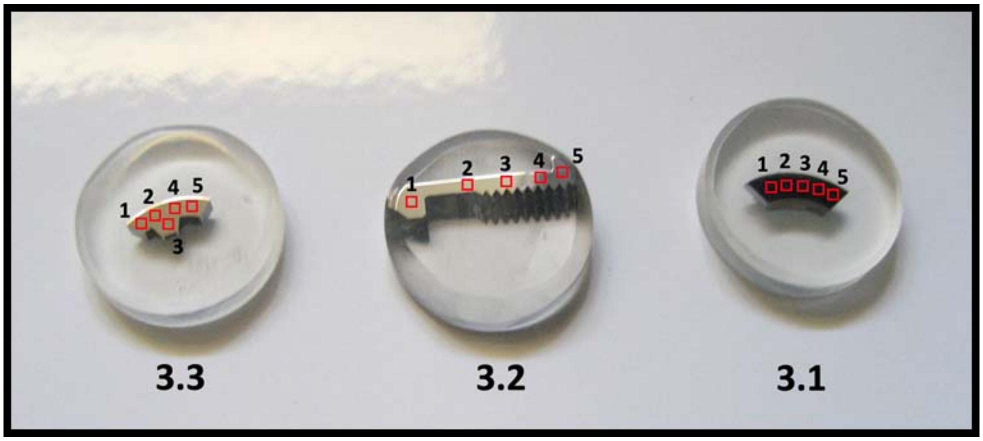


Figure 5.8 Scan locations on barrel-extension samples.

Table 5.8 Weight percentages of each element present in the barrel-extension sample 3.1.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	2.97	±0.30	2.84	±0.270	2.45	±0.26	2.33	±0.25	2.04	±0.25	2.53	±0.38
Si	0.27	±0.04	0.29	±0.030	0.31	±0.03	0.29	±0.03	0.35	±0.03	0.30	±0.03
Cr	0.57	±0.02	0.52	±0.020	0.55	±0.02	0.55	±0.02	0.51	±0.02	0.54	±0.02
Mn	0.85	±0.03	0.85	±0.030	0.85	±0.03	0.9	±0.03	0.88	±0.03	0.87	±0.02
Fe	94.38	±0.31	94.56	±0.280	95.01	±0.27	94.88	±0.26	95.25	±0.26	94.82	±0.35
Ni	0.51	±0.04	0.45	±0.040	0.49	±0.04	0.53	±0.04	0.47	±0.04	0.49	±0.03
Cu	0.2	±0.04	0.22	±0.040	0.15	±0.04	0.22	±0.04	0.2	±0.04	0.20	±0.03
Mo	0.25	±0.08	0.25	±0.070	0.18	±0.07	0.3	±0.07	0.3	±0.07	0.26	±0.05

Table 5.9 Weight percentages of each element present in the barrel-extension sample 3.2.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	2.29	±0.26	2.57	±0.26	2.36	±0.27	2.97	±0.27	3.15	±0.28	2.67	±0.38
Si	0.3	±0.03	0.29	±0.03	0.31	±0.03	0.28	±0.03	0.33	±0.03	0.30	±0.02
Cr	0.54	±0.02	0.54	±0.02	0.56	±0.02	0.54	±0.02	0.53	±0.02	0.54	±0.01
Mn	0.91	±0.03	0.89	±0.03	0.85	±0.03	0.88	±0.03	0.83	±0.03	0.87	±0.03
Fe	94.87	±0.27	94.83	±0.27	94.95	±0.28	94.37	±0.28	94.27	±0.29	94.66	±0.31
Ni	0.46	±0.04	0.39	±0.04	0.45	±0.04	0.48	±0.04	0.47	±0.04	0.45	±0.04
Cu	0.32	±0.04	0.21	±0.04	0.22	±0.04	0.2	±0.04	0.22	±0.04	0.23	±0.05
Mo	0.32	±0.07	0.28	±0.07	0.3	±0.07	0.27	±0.07	0.2	±0.07	0.27	±0.05

Table 5.10 Weight percentages of each element present in the barrel-extension sample 3.3.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	2.75	±0.29	2.51	±0.29	2.25	±0.29	2.66	±0.29	2.64	±0.28	2.56	±0.19
Si	0.36	±0.04	0.36	±0.04	0.34	±0.04	0.33	±0.04	0.35	±0.03	0.35	±0.01

Cr	0.52	±0.02	0.54	±0.02	0.56	±0.02	0.57	±0.02	0.55	±0.02	0.55	±0.02
Mn	0.87	±0.03	0.88	±0.03	0.87	±0.03	0.83	±0.03	0.86	±0.03	0.86	±0.02
Fe	94.49	±0.30	94.67	±0.30	94.97	±0.30	94.7	±0.30	94.81	±0.29	94.73	±0.18
Ni	0.4	±0.04	0.49	±0.04	0.48	±0.04	0.43	±0.04	0.42	±0.04	0.44	±0.04
Cu	0.28	±0.04	0.22	±0.04	0.16	±0.04	0.2	±0.04	0.17	±0.04	0.21	±0.05
Mo	0.34	±0.08	0.33	±0.08	0.37	±0.08	0.29	±0.08	0.22	±0.07	0.31	±0.06

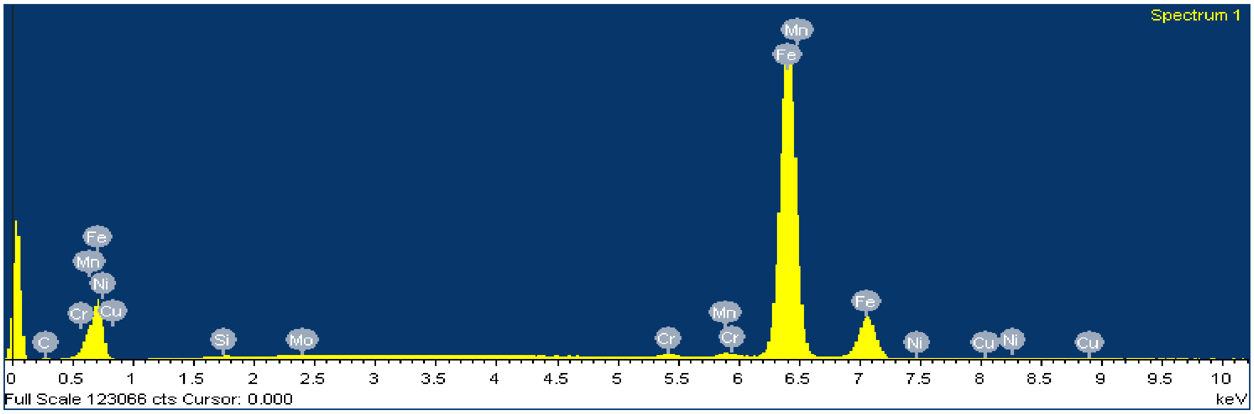


Figure 5.9 EDS micrograph of a barrel-extension sample (Spot Size = 6.0, Voltage = 30 kV).

The bolt-carrier was sectioned as shown in Figure 5.10. The scan locations on each sample are illustrated in Figure 5.11, and the composition of each scan location is shown in Tables 5.11, 5.12, and 5.13. A characteristic micrograph illustrates the elemental composition of one scan location (see Figure 5.12).

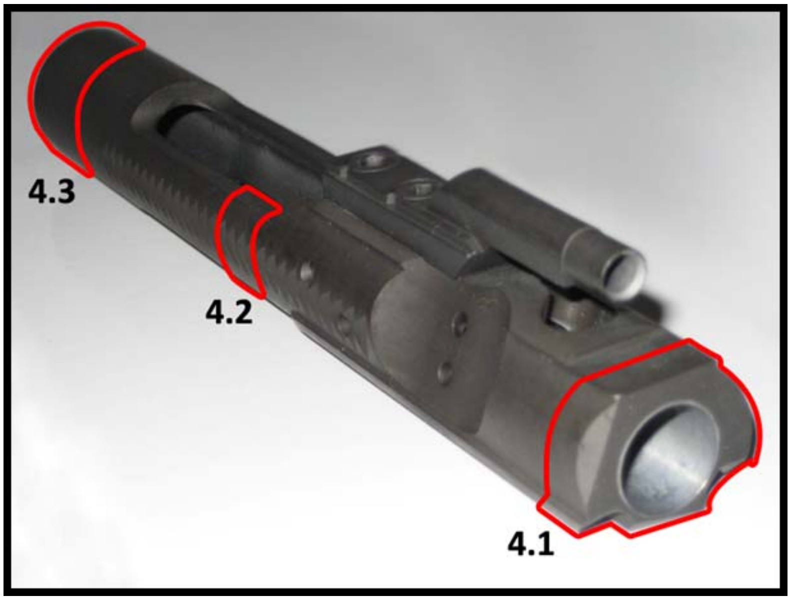


Figure 5.10 Sample sections of a Colt manufactured M16 bolt carrier.

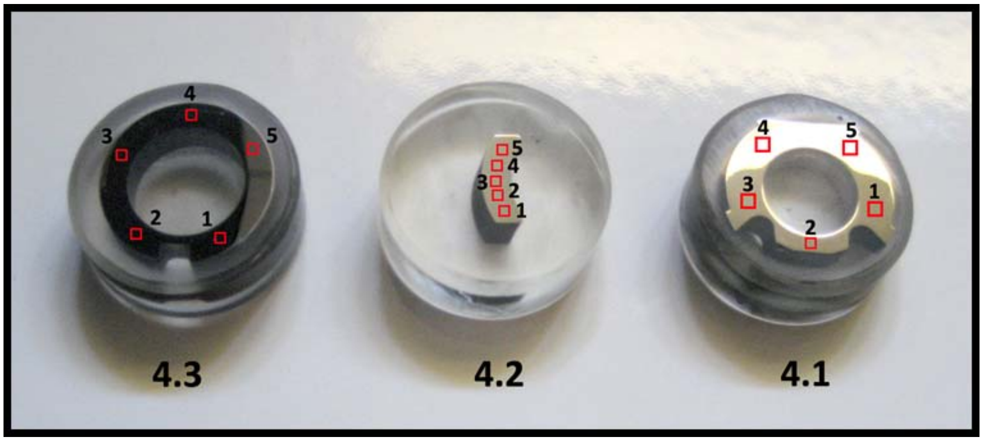


Figure 5.11 Scan locations on bolt-carrier samples.

Table 5.11 Weight percentages of each element present in the bolt-carrier sample 4.1.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	1.55	±0.22	2.16	±0.22	1.82	±0.22	1.85	±0.22	1.99	±0.22	1.87	±0.23
Si	0.31	±0.03	0.34	±0.03	0.33	±0.03	0.25	±0.03	0.27	±0.03	0.30	±0.04
Cr	0.53	±0.02	0.53	±0.02	0.51	±0.02	0.52	±0.02	0.53	±0.02	0.52	±0.01
Mn	0.86	±0.03	0.86	±0.03	0.87	±0.03	0.86	±0.03	0.88	±0.03	0.87	±0.01
Fe	95.57	±0.23	94.78	±0.23	95.25	±0.23	95.31	±0.23	95.10	±0.23	95.20	±0.29
Ni	0.75	±0.03	0.76	±0.03	0.73	±0.03	0.73	±0.03	0.73	±0.03	0.74	±0.01
Cu	0.18	±0.03	0.25	±0.03	0.23	±0.03	0.25	±0.03	0.18	±0.04	0.22	±0.04
Mo	0.26	±0.06	0.32	±0.06	0.27	±0.06	0.23	±0.06	0.32	±0.06	0.28	±0.04

Table 5.12 Weight percentages of each element present in the bolt-carrier sample 4.2.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	2.68	±0.23	2.76	±0.23	2.43	±0.22	2.34	±0.22	2.55	±0.23	2.55	±0.17
Si	0.31	±0.03	0.30	±0.03	0.30	±0.03	0.25	±0.03	0.31	±0.03	0.29	±0.03
Cr	0.54	±0.02	0.49	±0.02	0.53	±0.02	0.54	±0.02	0.52	±0.02	0.52	±0.02
Mn	0.87	±0.03	0.83	±0.03	0.88	±0.03	0.84	±0.03	0.86	±0.03	0.86	±0.02
Fe	94.45	±0.24	94.38	±0.24	94.64	±0.23	94.70	±0.23	94.57	±0.24	94.55	±0.13
Ni	0.75	±0.03	0.74	±0.03	0.73	±0.03	0.80	±0.03	0.73	±0.03	0.75	±0.03
Cu	0.17	±0.03	0.20	±0.03	0.21	±0.03	0.23	±0.03	0.17	±0.03	0.20	±0.03
Mo	0.23	±0.06	0.29	±0.06	0.29	±0.06	0.29	±0.06	0.29	±0.06	0.28	±0.03

Table 5.13 Weight percentages of each element present in the bolt-carrier sample 4.3.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	2.09	±0.22	1.95	±0.22	1.96	±0.22	2.06	±0.27	1.91	±0.22	1.99	±0.08
Si	0.29	±0.03	0.28	±0.03	0.27	±0.03	0.29	±0.04	0.30	±0.03	0.29	±0.01
Cr	0.53	±0.02	0.53	±0.02	0.50	±0.02	0.52	±0.02	0.50	±0.02	0.52	±0.02
Mn	0.85	±0.03	0.86	±0.03	0.87	±0.03	0.89	±0.03	0.87	±0.03	0.87	±0.01
Fe	94.95	±0.23	95.09	±0.23	95.06	±0.23	94.92	±0.28	95.23	±0.23	95.05	±0.12
Ni	0.75	±0.03	0.77	±0.03	0.78	±0.03	0.78	±0.04	0.79	±0.03	0.77	±0.02
Cu	0.25	±0.03	0.21	±0.03	0.24	±0.03	0.19	±0.04	0.17	±0.03	0.21	±0.03
Mo	0.29	±0.06	0.31	±0.06	0.32	±0.06	0.34	±0.08	0.23	±0.06	0.30	±0.04

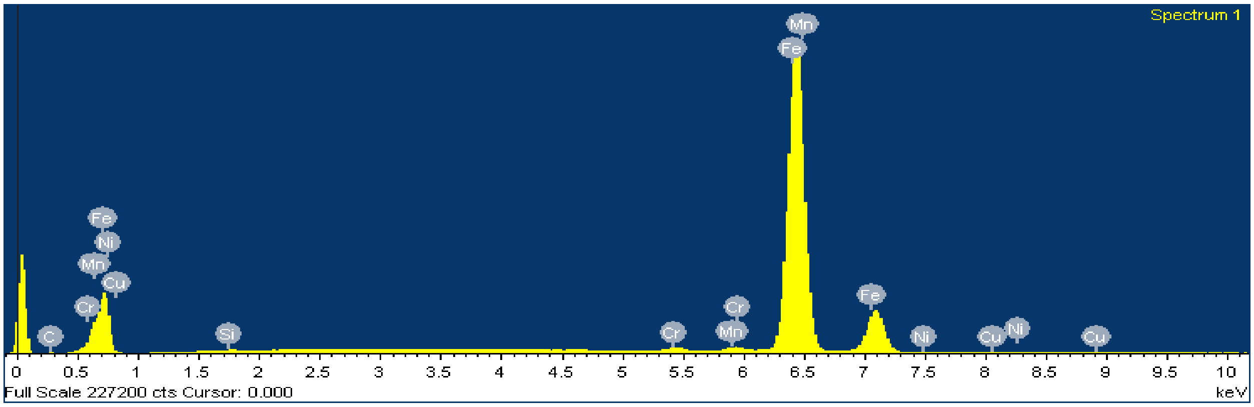


Figure 5.12 EDS micrograph of a bolt-carrier sample (Spot Size = 6.0, Voltage = 30 kV).

The bolt was sectioned as shown in Figure 5.13. The scan locations on each sample are illustrated in Figure 5.14, and the composition of each scan location is shown in Tables 5.14, 5.15, and 5.16. A characteristic micrograph illustrates the elemental composition of one scan location (see Figure 5.15).

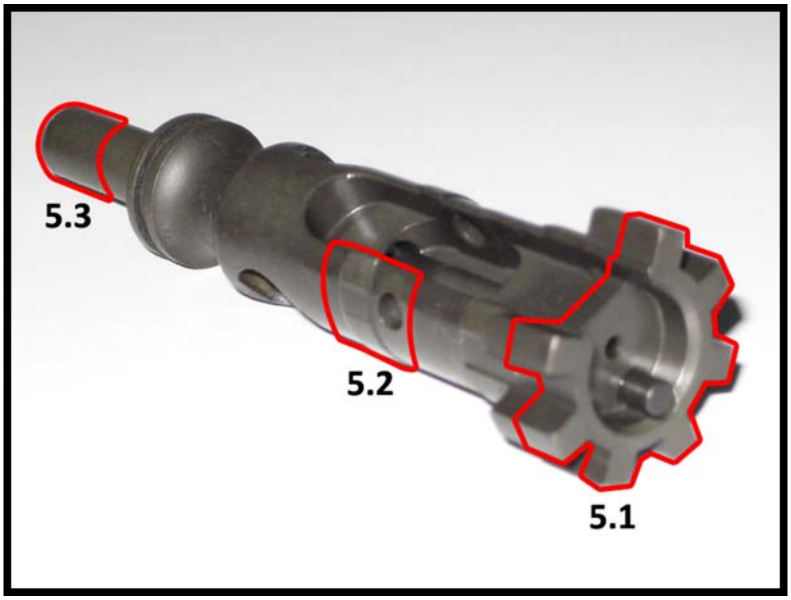


Figure 5.13 Sample sections of a Colt manufactured M16 bolt.

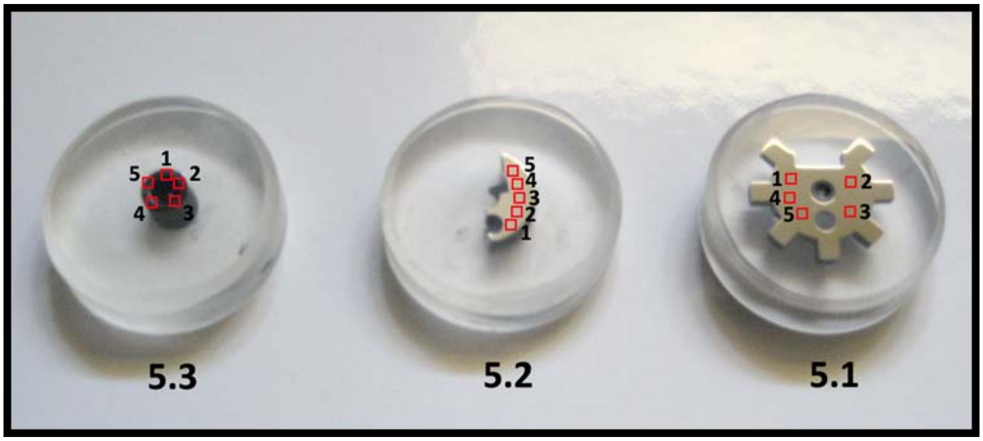


Figure 5.14 Scan locations on bolt samples.

Table 5.14 Weight percentages of each element present in the bolt sample 5.1.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	0.66	±0.16	1.16	±0.17	1.14	±0.16	0.80	±0.16	0.51	±0.16	0.85	±0.29
Si	0.39	±0.03	0.40	±0.03	0.39	±0.03	0.42	±0.03	0.43	±0.03	0.41	±0.02
Cr	1.72	±0.02	1.64	±0.03	1.64	±0.02	1.64	±0.02	1.65	±0.02	1.66	±0.03
Mn	0.54	±0.03	0.53	±0.04	0.56	±0.03	0.56	±0.03	0.56	±0.03	0.55	±0.01
Fe	93.35	±0.16	92.99	±0.17	92.88	±0.16	93.24	±0.16	93.49	±0.16	93.19	±0.25
Ni	3.34	±0.04	3.29	±0.06	3.39	±0.04	3.34	±0.04	3.37	±0.04	3.35	±0.04

Table 5.15 Weight percentages of each element present in the bolt sample 5.2.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	1.95	±0.18	1.45	±0.17	1.34	±0.17	1.09	±0.17	0.83	±0.16	1.33	±0.42
Si	0.36	±0.03	0.41	±0.03	0.40	±0.03	0.37	±0.03	0.39	±0.03	0.39	±0.02
Cr	1.65	±0.02	1.66	±0.02	1.66	±0.02	1.66	±0.02	1.66	±0.02	1.66	±0.00
Mn	0.57	±0.03	0.55	±0.03	0.58	±0.03	0.56	±0.03	0.60	±0.03	0.57	±0.02
Fe	92.11	±0.18	92.60	±0.17	92.68	±0.17	92.97	±0.17	93.17	±0.16	92.71	±0.40
Ni	3.36	±0.04	3.33	±0.04	3.34	±0.04	3.35	±0.05	3.34	±0.04	3.34	±0.01

Table 5.16 Weight percentages of each element present in the bolt sample 5.3.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	2.17	±0.17	2.22	±0.17	3.01	±0.18	1.45	±0.16	1.84	±0.17	2.14	±0.58
Si	0.37	±0.03	0.40	±0.03	0.38	±0.03	0.40	±0.03	0.36	±0.03	0.38	±0.02
Cr	1.63	±0.02	1.65	±0.02	1.61	±0.02	1.63	±0.02	1.65	±0.02	1.63	±0.02
Mn	0.56	±0.03	0.56	±0.03	0.60	±0.03	0.57	±0.03	0.56	±0.03	0.57	±0.02
Fe	92.04	±0.17	91.97	±0.17	91.13	±0.18	92.66	±0.16	92.32	±0.17	92.02	±0.57
Ni	3.22	±0.04	3.21	±0.04	3.27	±0.04	3.30	±0.04	3.27	±0.04	3.25	±0.04

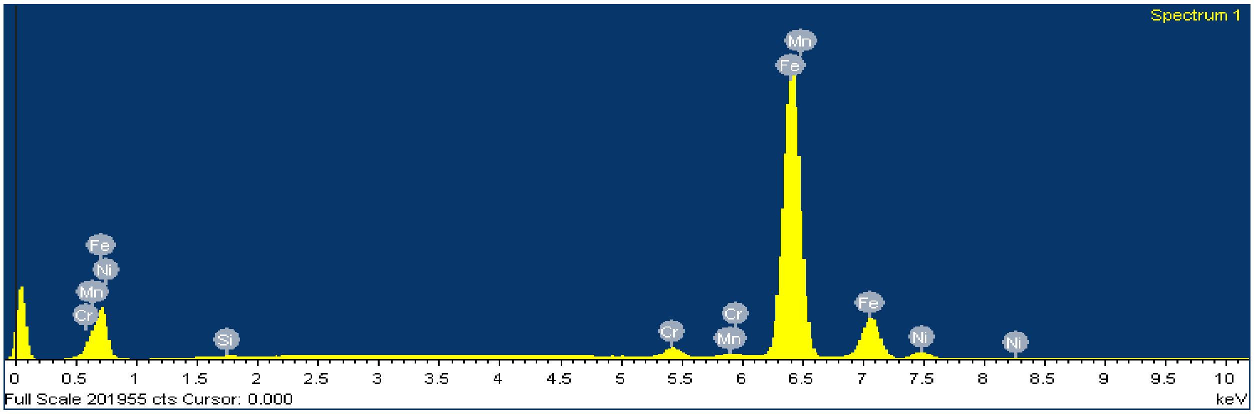


Figure 5.15 EDS micrograph of a bolt sample (Spot Size = 6.0, Voltage = 30 kV).

The bolt is the most important and highly stressed part of a firearm. It is important that every step of its production is highly scrutinized. A comparison of the material composition specifications and the chemical analysis results show accuracy within a tenth of the weight percentage (see Table 5.17).

Table 5.17 Chemical composition of M16 bolts. (17)

Element	Carpenter Steel 158	Chemical Analysis Results
Carbon	0.10	0.185
Silicon	0.30	0.22
Nickel	3.50	3.43
Manganese	0.50	0.45
Chromium	1.50	1.39
Iron	balance	balance

The extractor was sectioned as shown in Figure 5.16. The scan locations on each sample is illustrated in Figure 5.17, and the composition of each scan location is shown in Tables 5.18, 5.19, and 5.20. A characteristic micrograph illustrates the elemental composition of one scan location (see Figure 5.18).

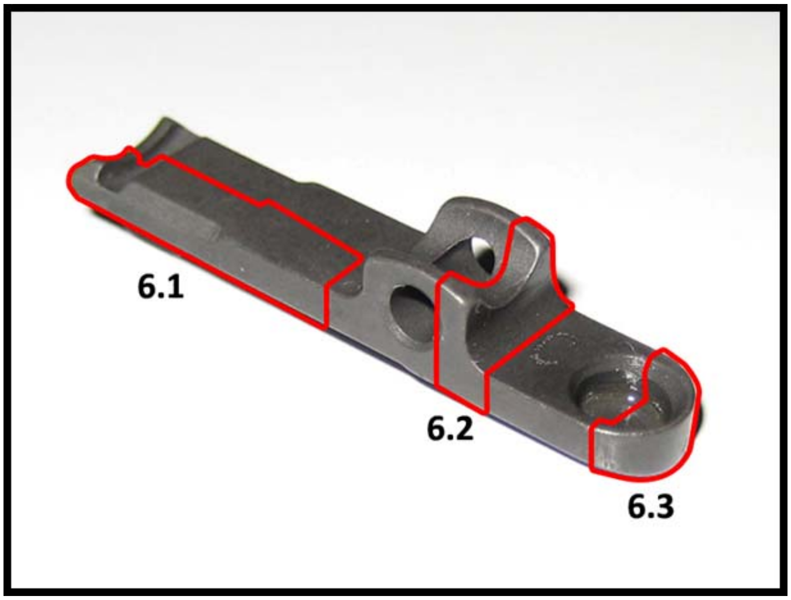


Figure 5.16 Sample sections of a Colt manufactured M16 extractor.

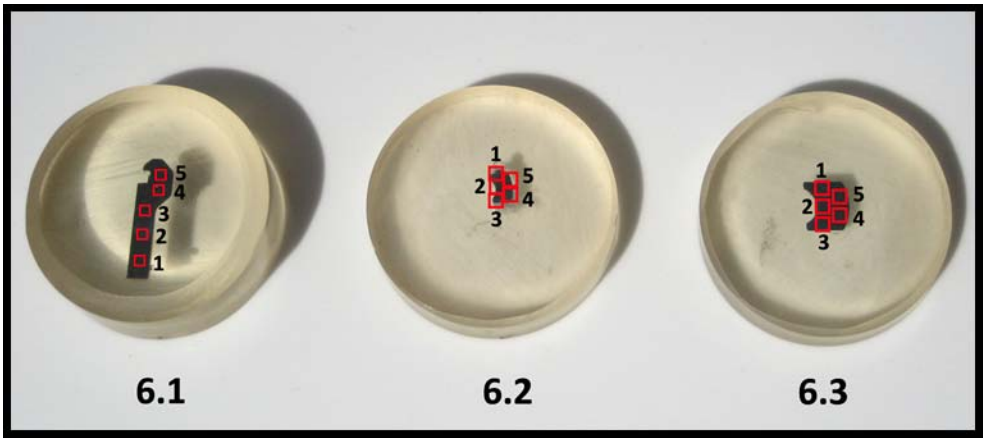


Figure 5.17 Scan locations on extractor samples.

Table 5.18 Weight percentages of each element present in the extractor sample 6.1.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	4.67	±0.77	5.03	±0.73	4.88	±0.72	3.66	±0.73	5.01	±0.72	4.65	±0.57
Si	0.44	±0.11	0.37	±0.11	0.31	±0.11	0.19	±0.11	0.44	±0.11	0.35	±0.10
Cr	1.15	±0.08	1.10	±0.08	1.04	±0.07	1.02	±0.08	0.98	±0.07	1.06	±0.07
Mn	0.81	±0.11	0.87	±0.11	0.74	±0.11	0.81	±0.11	0.91	±0.10	0.83	±0.06
Fe	92.93	±0.76	92.63	±0.73	93.03	±0.72	94.32	±0.73	92.66	±0.72	93.11	±0.70

Table 5.19 Weight percentages of each element present in the extractor sample 6.2.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	5.42	±0.89	5.69	±0.88	4.94	±0.87	4.75	±0.89	5.30	±0.87	5.22	±0.38
Si	0.26	±0.12	0.28	±0.12	0.25	±0.13	0.31	±0.13	0.29	±0.12	0.28	±0.02
Cr	1.03	±0.09	1.06	±0.09	1.05	±0.09	1.10	±0.09	1.07	±0.09	1.06	±0.03
Mn	0.84	±0.12	0.85	±0.12	0.88	±0.12	0.75	±0.12	0.86	±0.12	0.84	±0.05
Fe	92.44	±0.89	92.12	±0.88	92.87	±0.87	93.09	±0.89	92.48	±0.87	92.60	±0.38

Table 5.20 Weight percentages of each element present in the extractor sample 6.3.

Element	Scan Location										Average Weight %	σ
	1	σ_1	2	σ_2	3	σ_3	4	σ_4	5	σ_5		
C	4.91	±0.87	4.61	±0.85	6.10	±0.87	5.73	±0.85	4.48	±0.84	5.17	±0.71
Si	0.22	±0.12	0.44	±0.12	0.29	±0.12	0.24	±0.12	0.10	±0.12	0.26	±0.12
Cr	0.93	±0.09	0.97	±0.08	1.04	±0.09	0.95	±0.09	1.15	±0.09	1.01	±0.09
Mn	0.80	±0.12	0.82	±0.12	0.73	±0.12	0.84	±0.12	0.79	±0.12	0.80	±0.04
Fe	93.15	±0.87	93.16	±0.85	91.84	±0.86	92.24	±0.85	93.47	±0.84	92.77	±0.70

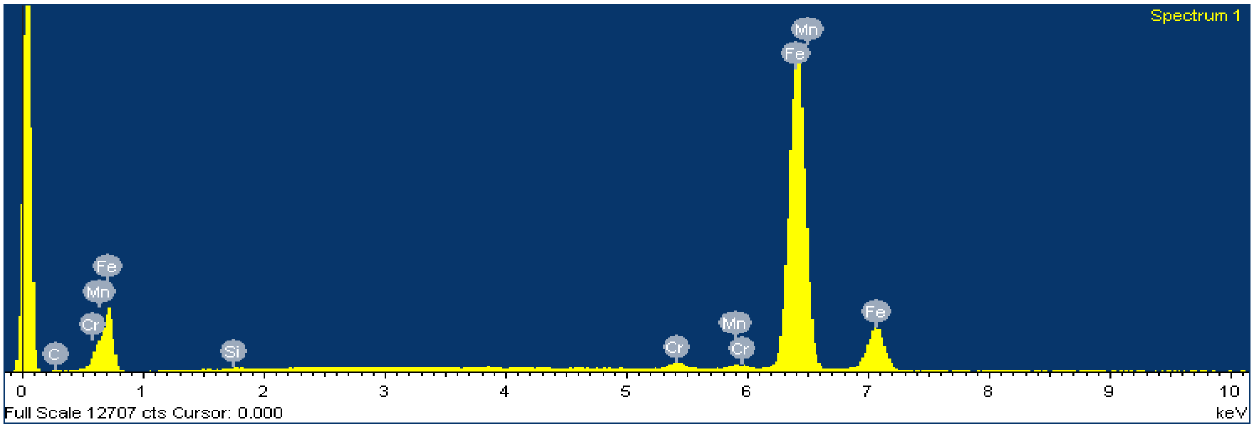


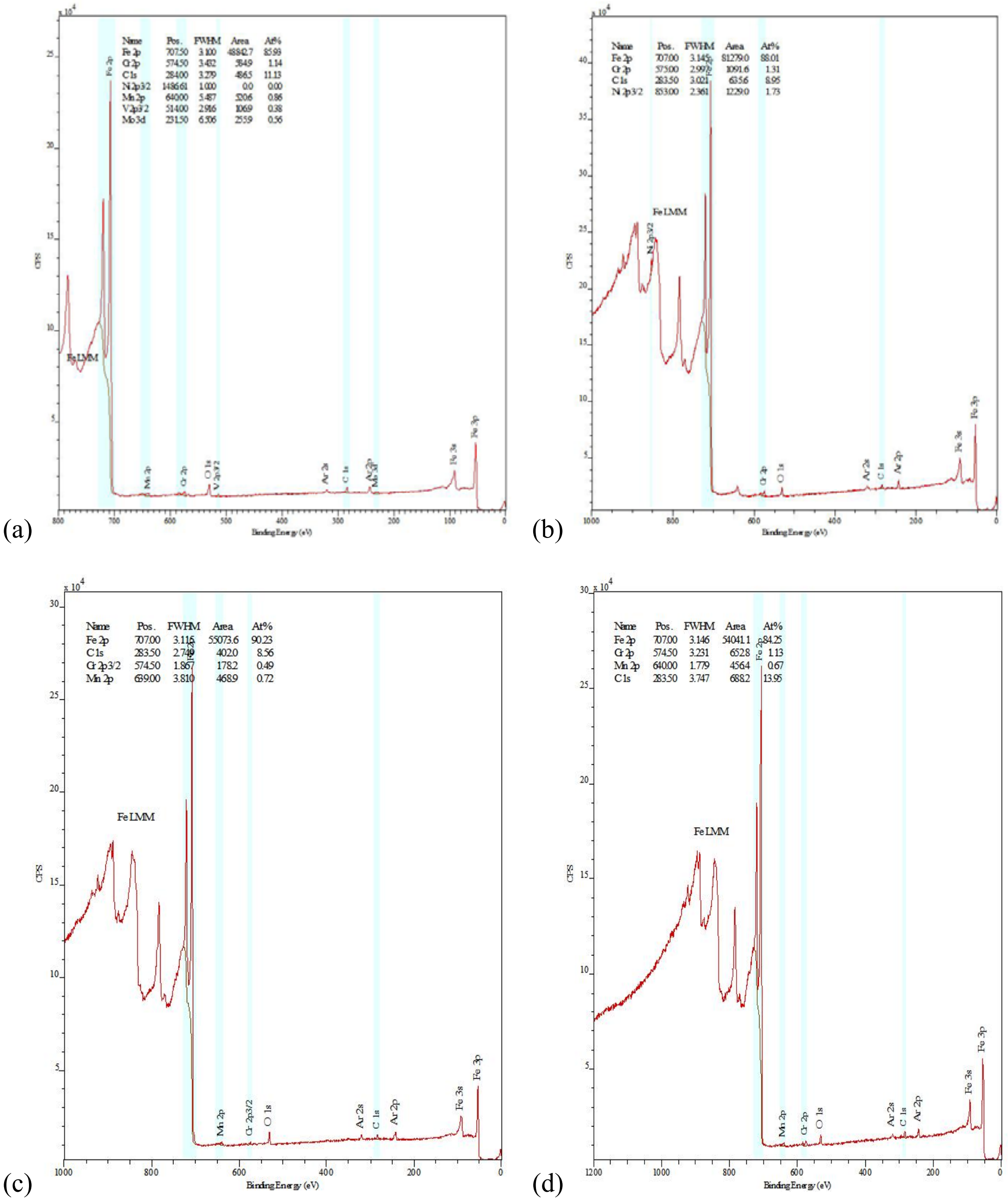
Figure 5.18 EDS micrograph of an extractor sample (Spot Size = 6.0, Voltage = 30 kV).

To sum up the results of the elemental composition analysis using EDS, Table 5.21 shows

Table 5.21 EDS element measurements of average weight percentages of each critical part.

	Receiver		**Barrel**		**Barrel Extension**		**Bolt Carrier**		**Bolt**		**Extractor**	
Element	Average Weight %	σ of SOI	Average Weight %	σ of SOI	Average Weight %	σ of SOI	Average Weight %	σ of SOI	Average Weight %	σ of SOI	Average Weight %	σ of SOI
C	3.16	±0.73	2.45	±1.41	2.59	±0.31	2.14	±0.34	1.44	±0.69	5.01	±0.59
O	1.22	±0.16	-	-	-	-	-	-	-	-	-	-
Mg	2.60	±0.05	-	-	-	-	-	-	-	-	-	-
Al	83.89	±0.85	-	-	-	-	-	-	-	-	-	-
Si	0.10	±0.04	0.36	±0.19	0.32	±0.03	0.29	±0.03	0.39	±0.02	0.30	±0.10
P	-	-	0.01	±0.06	-	-	-	-	-	-	-	-
S	-	-	0.08	±0.08	-	-	-	-	-	-	-	-
V	-	-	0.25	±0.27	-	-	-	-	-	-	-	-
Cr	0.21	±0.02	1.05	±0.10	0.54	±0.02	0.52	±0.02	1.65	±0.02	1.04	±0.07
Mn	0.06	±0.02	0.77	±30.47	0.87	±0.02	0.86	±0.02	0.56	±0.02	0.82	±0.05
Fe	0.18	±0.02	94.39	±31.34	94.73	±0.28	94.93	±0.34	92.64	±0.63	92.83	±0.61
Ni	-	-	-	-	0.46	±0.04	0.75	±0.02	3.31	±0.05	-	-
Cu	1.28	±0.04	-	-	0.21	±0.04	0.21	±0.03	-	-	-	-
Zn	5.79	±0.10	-	-	-	-	-	-	-	-	-	-
Mo	-	-	0.33	±0.12	0.28	±0.05	0.29	±0.01	-	-	-	-
Ag	1.52	±0.06	-	-	-	-	-	-	-	-	-	-

After mounting and polishing the samples, the elements heavier than silicon in the samples were confirmed using a portable x-ray florescence (XRF) spectrometer. Since the XRF and EDS are not capable of accurately detecting light elements, the x-ray photoelectron spectrometer (XPS) was used to obtain a more accurate reading of the lighter elements, and the values were compared alongside the EDS results (see Table 5.22). This is particularly important in regards to the carbon content of the steel samples, since the strength of steel is partly dependent on carbon. Prior to analyzing the surfaces using the XPS, the surfaces were blasted with an argon beam to etch away any contaminants. Some of the trace elements that were detected with the EDS were not detected with the XPS, this is attributable to the human error in assigning elements to the peaks detected by the EDS software and to the sensitivity of the EDS for detecting those peaks. These discrepancies are not of major significance since most metals purchased from fabricators will contain a small level of impurities, and half of a weight percent is not significant amount of impurity.



Name	Pos.	FWHM	Area	At%
Fe 2p	707.50	3.100	48842.7	85.93
Cr 2p	574.50	3.432	584.9	1.14
C 1s	284.00	3.279	486.5	11.13
Ni 2p3/2	1486.61	1.000	0.0	0.00
Mn 2p	640.00	5.487	520.6	0.86
V 2p3/2	514.00	2.916	106.9	0.38
Mo 3d	231.50	6.506	255.9	0.56

Name	Pos.	FWHM	Area	At%
Fe 2p	707.00	3.145	81279.0	88.01
Cr 2p	575.00	2.997	1091.6	1.31
C 1s	283.50	3.021	635.6	8.95
Ni 2p3/2	853.00	2.361	1229.0	1.73

Name	Pos.	FWHM	Area	At%
Fe 2p	707.00	3.115	55073.6	90.23
C 1s	283.50	2.749	402.0	8.56
Cr 2p3/2	574.50	1.867	178.2	0.49
Mn 2p	639.00	3.810	468.9	0.72

Name	Pos.	FWHM	Area	At%
Fe 2p	707.00	3.146	54041.1	84.25
Cr 2p	574.50	3.231	652.8	1.13
Mn 2p	640.00	1.779	456.4	0.67
C 1s	283.50	3.747	688.2	13.95

Figure 5.19 XPS counts measured at each binding energy to determine the atomic weight percentage of each element in an M16 barrel (a), bolt (b), bolt carrier (c), and extractor (d).

Table 5.22 Comparison of EDS and XPS weight percentages of elements present in critical parts.

	Barrel		**Bolt Carrier**		**Bolt**		**Extractor**	
Element	EDS Weight %	XPS Weight %	EDS Weight %	XPS Weight %	EDS Weight %	XPS Weight %	EDS Weight %	XPS Weight %
C	2.45	2.6	2.14	2.0	1.44	2.1	5.01	3.4
Si	0.36	-	0.29	-	0.39	-	0.30	-
P	0.01	-	-	-	-	-	-	-
S	0.08	-	-	-	-	-	-	-
V	0.25	0.4	-	-	-	-	-	-
Cr	1.05	1.3	0.52	0.6	1.65	1.5	1.04	1.2
Mn	0.77	0.9	0.86	0.8	0.56	-	0.82	0.7
Fe	94.39	93.7	94.93	96.7	92.64	94.5	92.83	95.0
Ni	-	-	0.75	-	3.31	1.9	-	-
Cu	-	-	0.21	-	-	-	-	-
Mo	0.33	1.1	0.29	-	-	-	-	-

All critical parts except for the receiver were made primarily of iron with varying amounts of other alloys. The Bolt Carrier and the Barrel Extension were both similar to 90XX series steel except for the presence in the hundredths of a percent of boron, phosphorous, and sulfur. The bolt was almost an exact match for 40XX series steel, but the bolt contained copper. Compared to the bolt carrier and barrel extension, the bolt has the addition of nickel to change its microstructure from ferrite to austenite. This makes the bolt more ductile and tougher. The addition of nickel is common to maraging steels to improve their toughness. Unlike the other steel components, molybdenum and copper are missing from the extractor since a high strength to weight ratio is not critical for this small part, unlike the bolt carrier and barrel extension. Table 5.23 summarizes the materials and coatings used to make the critical parts.

Table 5.23 Critical parts materials and coatings.

Part	**Material**	**Typical Coating**
Receivers	·7075-T6 Aluminum	·Anodized Type III Hardcoat
Barrel	·ORD/AISI/SAE 4150 ·ORD/AISI/SAE 4150 Resulfurized ·4140 Chrome-Moly Steel ·Chrome-Moly-Vanadium Steel	·Manganese Phosphate ·Hard Chrome Bore and Chamber
Barrel-Extension	·90XX Series Steel	·Parkerized Exterior ·Hard Chrome Interior
Bolt	·40XX Series Steel	·Parkerized ·Hard Chrome
Bolt Carrier	·90XX Series Steel	·Parkerized ·Originally Chrome Plated
Extractor	·40XX Series Steel	·Parkerized

Chapter 6: Substrate Material Surface Treatments & Microstructure

Modification of the superficial layer after machining by heat treatment (e.g., quench and tempering, induction hardening, flame hardening, laser hardening, and electron beam hardening), thermochemical treatment (e.g., carburizing, carbonitriding, nitriding, nitrocarburising, and boriding) or implantation (e.g., of nitrogen ions) is commonly used to improve properties such as hardness as seen in Figure 6.1. In many cases the superficial layer formed by machining is improved; usually it is strengthened by other surface treatment operations, significantly changing its properties. These treatments are used to harden the substrate prior to coating, but the coating hardness provides the majority of the protection.

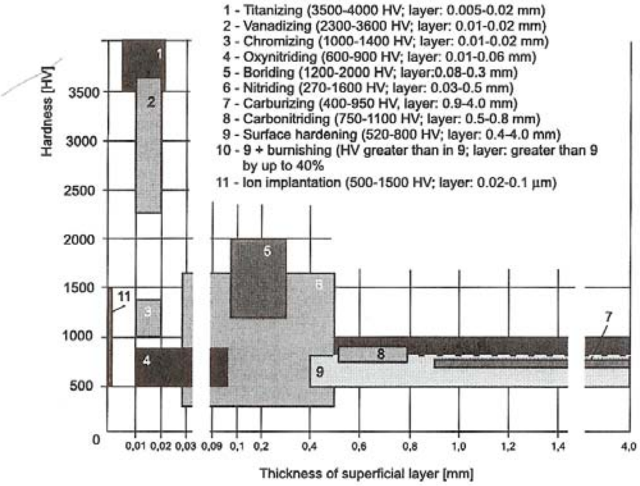
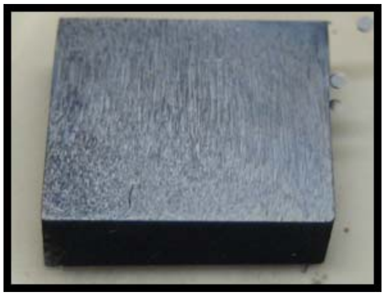
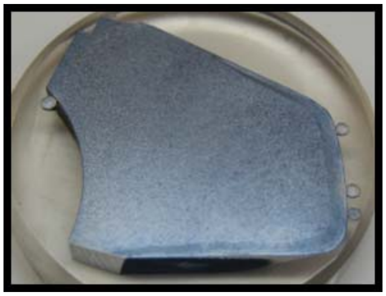


Figure 6.1 Orientation values of thickness and hardness of some superficial diffusion layers. (15)

To determine which parts received surface treatment operations after fabrication, each of the critical parts were etched. The steel samples were etched using a two percent Nital solution and the aluminum samples were etched using Keller's Solution. Etching revealed that the bolt, bolt carrier, and barrel extension received a surface treatment, which can be seen as the faint ring around the sectioned parts (see Figures 6.4, 6.5, and 6.6). This is interesting since these three parts are in direct contact with the cartridge as it undergoes combustion, and are the most highly stressed parts in this system. It is a significant advantage to harden the superficial layer prior to coating these critical parts.





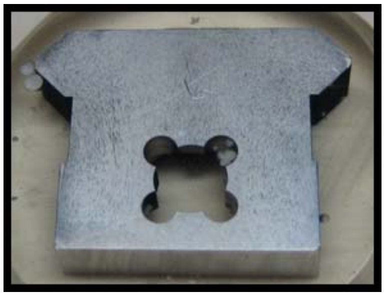


Figure 6.2 Receiver Samples 1.1, 1.2, and 1.3

Figure 6.3 Barrel Samples 2.1, 2.2, and 2.3

Figure 6.4 Barrel Extension Samples 3.1, 3.2, and 3.3

Figure 6.5 Bolt Carrier Samples 4.1, 4.2, and 4.3

Figure 6.6 Bolt Samples 5.1, 5.2, and 5.3

Figure 6.7 Extractor Samples 6.1, 6.2, and 6.3

Structure plays an important role in mechanical behavior, especially tribological behavior. Structure depends first on chemical composition and then on mechanical and thermal processing (sintering, casting, hot working, machining, and heat treatments of all kinds). Such chemical composition and processing steps influence tribological properties by their effect on phase, concentration of ingredients and their gradients, inclusions, voids, metastable phases, dispersed phases, and lattice imperfections of different kinds. (19) Ideally, the hardness of the substrate and the coating would be maximized without the material becoming too brittle or suffering from adhesion issues. The hardness of traditional oxide coatings used on firearms is significantly less than diamond coatings.

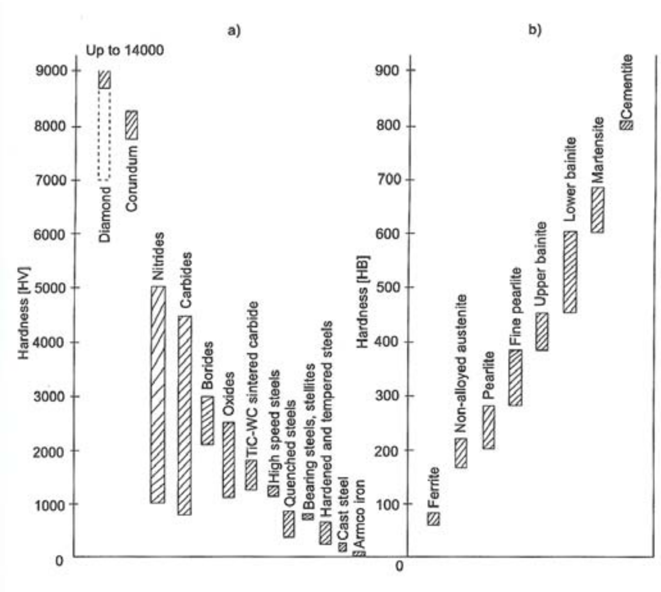


Figure 6.8. Hardness of (a) various coating materials and (b) steel microstructures. (15)

A hard substrate generally provides a lower coefficient of friction and longer wear life than a soft one. (18) The hard substrate provides a firmer support, thereby maintaining the true contact area and minimizing the tendency of the coating to spall or crack as a result of repeated flexing. During service, the superficial layer's thickness and properties may undergo changes as a result of oxidation, friction, corrosion, and fatigue. Due mainly to the rise of temperature caused by friction, the depth of migration of the nitrogen ion layer exceeds its initial thickness by a factor of several tens.

The etched samples were then viewed under a microscope, which revealed the metal's microstructure and the last of the manufacturing details of the critical parts. The images of the microstructure of the 7075-T6 aluminum are consistent with that found in literature. The receivers show no signs of surface treatment or grain refinement. The microstructure of the 40XX and 90XX series steel parts are predominantly a combination of austenitic and martensitic as seen in Figures 6.11 through 6.15, with the exception of the barrel extension which is completely martensitic. The austenitic regions can be clearly seen as the polygonal formations, while the lenticular shapes of the martensitic structures are more apparent in some images than others due to the orientation of the grains caused by the angle of the plane that steel part was cut at. Figure 6.12 (b) shows the change in grain structure along the surface treatment boundary. The highly refined grains are in the darker portion of the steel sample.

A hardness and microhardness test of each critical part shows that the aluminum receivers are the softest, followed by the barrel, extractor, bolt, bolt carrier, and barrel extension (see Figure 6.9). The three hardest parts also show increased hardness around the outer edges, confirming that these parts had received surface treatment as indicated by the outlines revealed by etching. The barrel extension and bolt carrier were expected to have a more similar hardness profile since these parts had the same elemental composition, but they appear to have different microstructures or may have received different surface treatments.

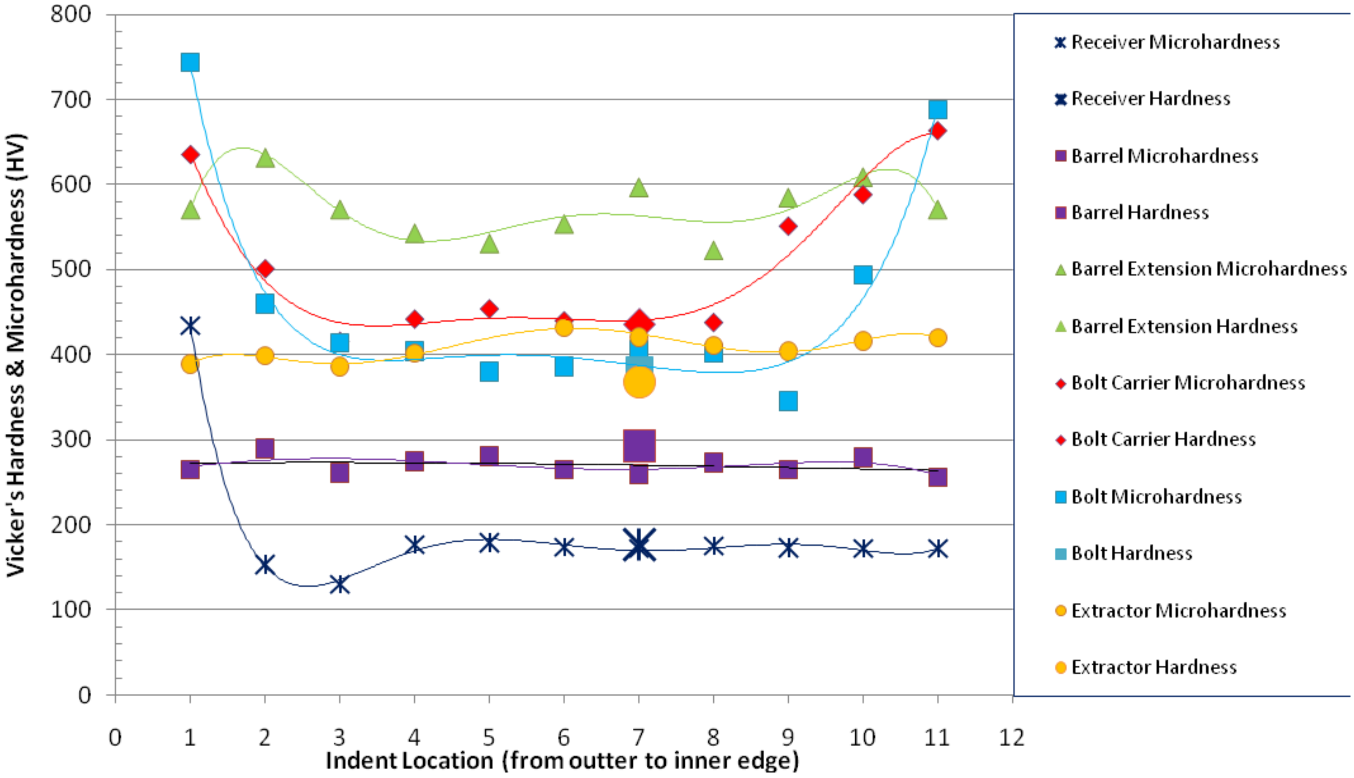


Figure 6.9 M16A2/M4 Critical Part Hardness Compared to Microhardness

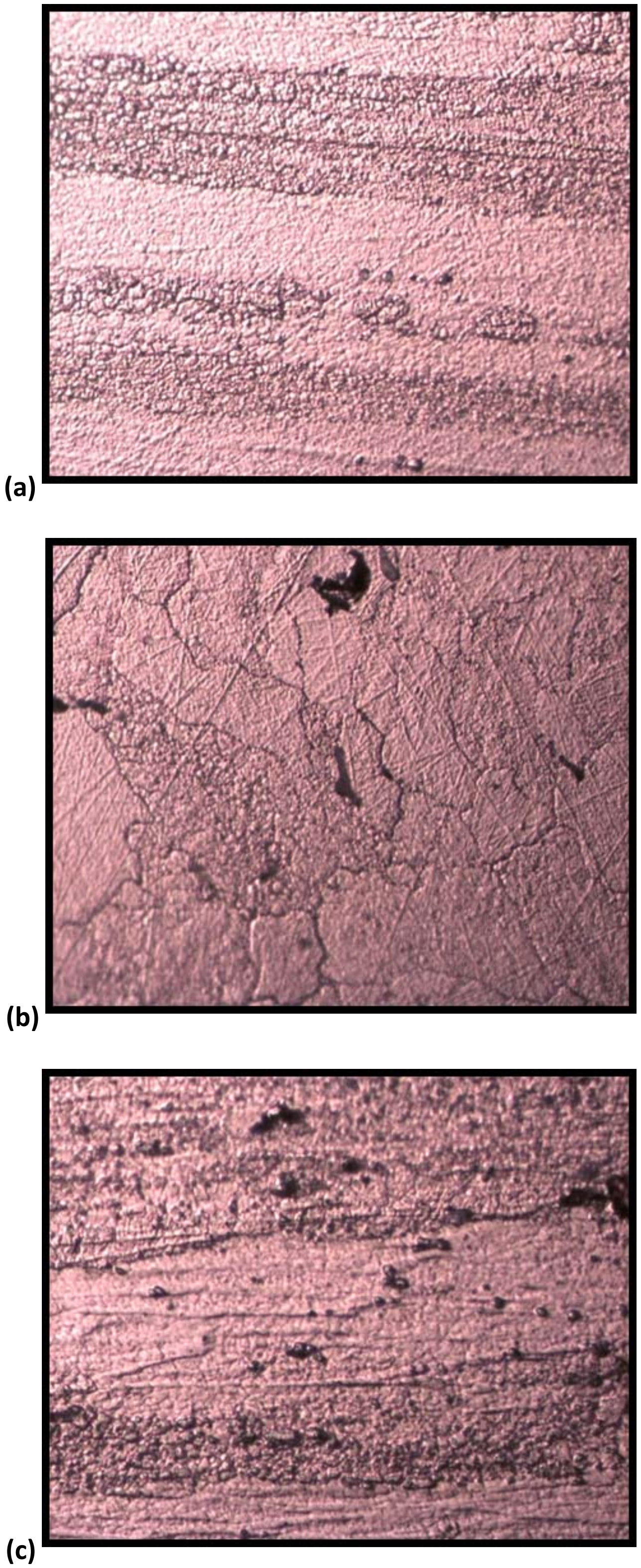


Figure 6.10 Receiver Samples 1.1 (a), 1.2 (b), and 1.3 (c) in Keller's Solution at .75x

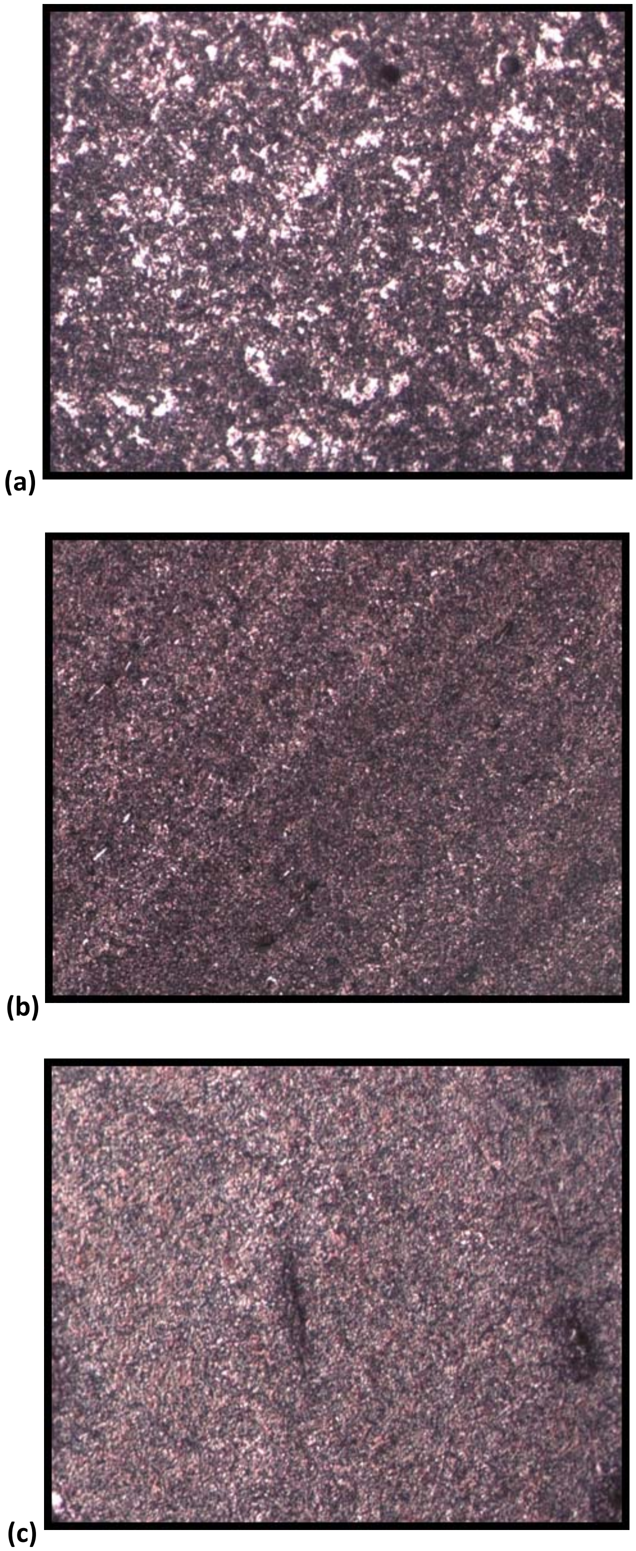


Figure 6.11 Barrel Samples 2.1 (a), 2.2 (b), and 2.3 (c) in a 2% Nital Solution at .75x

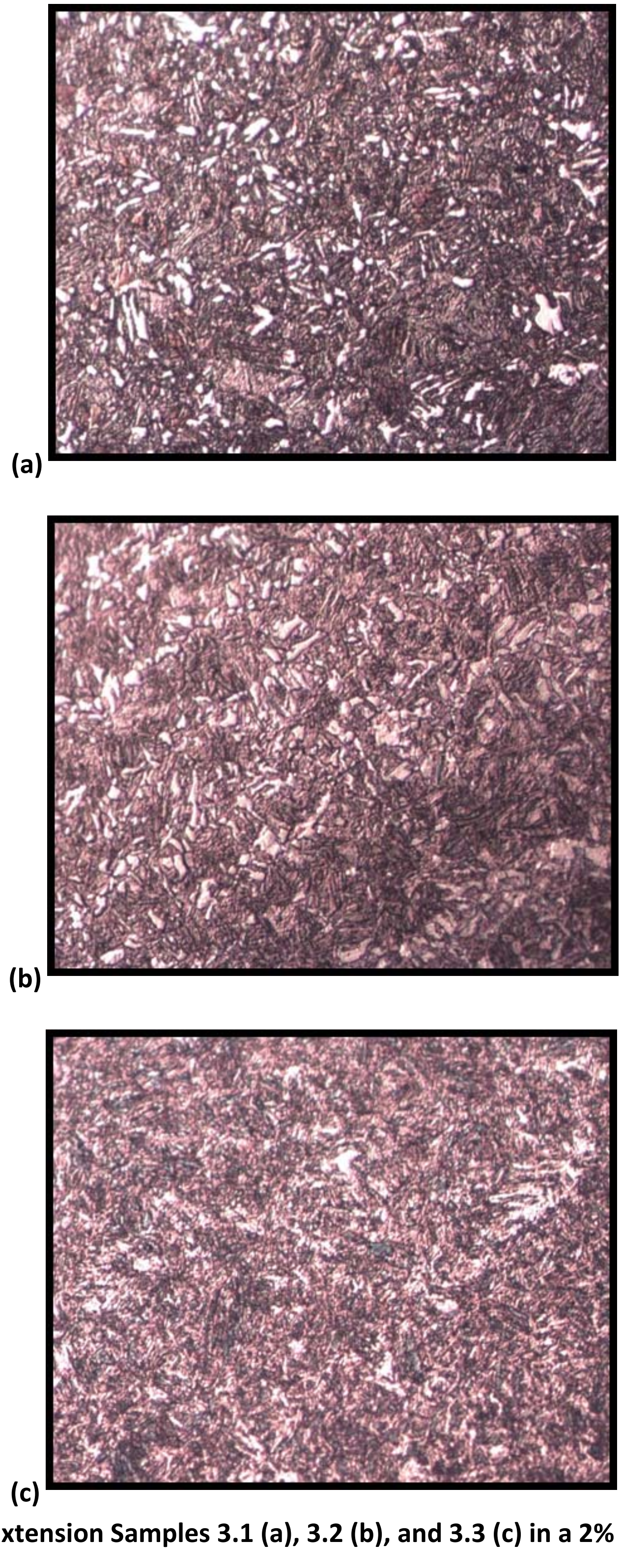


Figure 6.12 Barrel Extension Samples 3.1 (a), 3.2 (b), and 3.3 (c) in a 2% Nital Solution at .75x

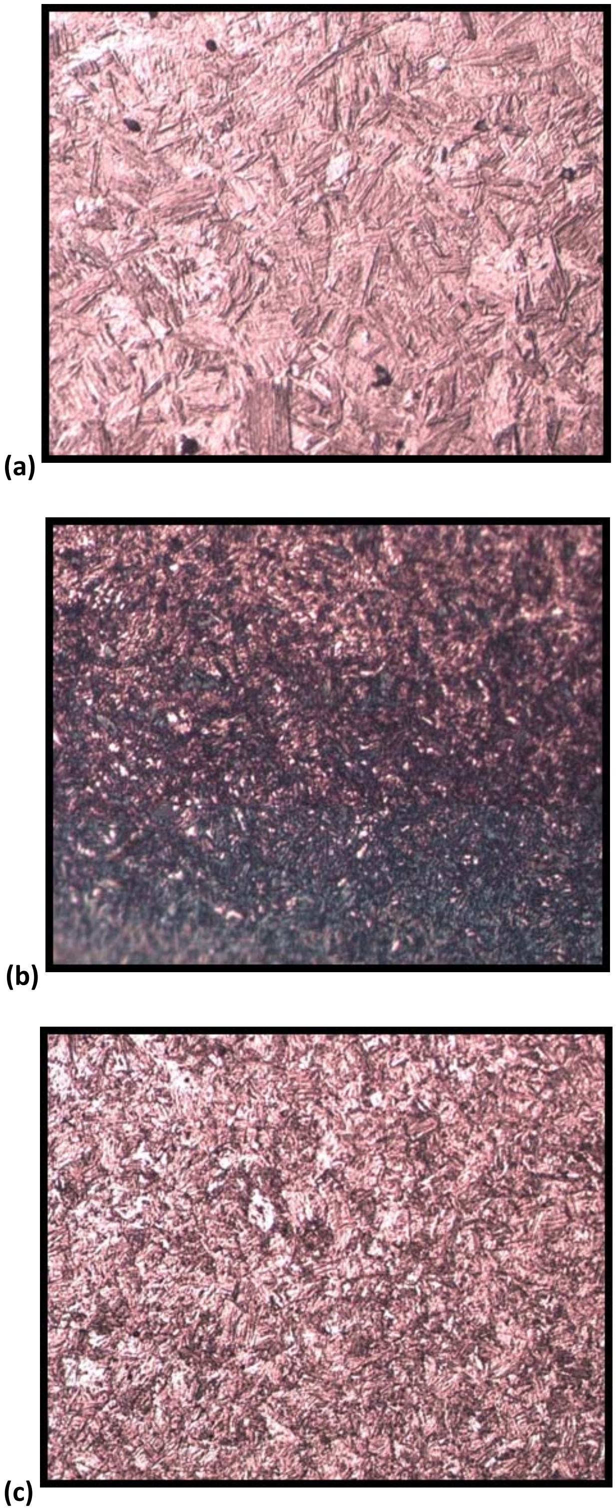
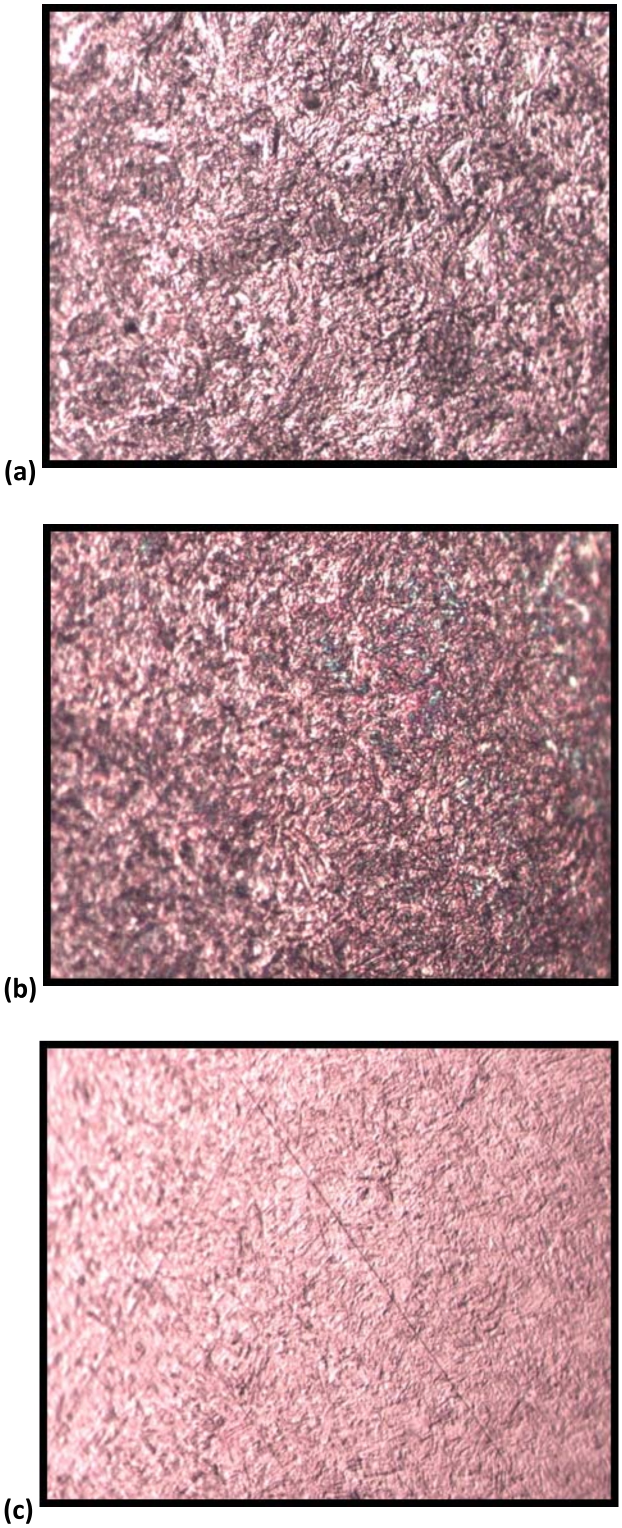


Figure 6.13 Bolt Carrier Samples 4.1 (a), 4.2 (b), and 4.3 (c) in a 2% Nital Solution at .75x


(a)

(b)

(c)

Figure 6.14 Bolt Samples 5.1 (a), 5.2 (b), and 5.3 (c) in a 2% Nital Solution at .75x

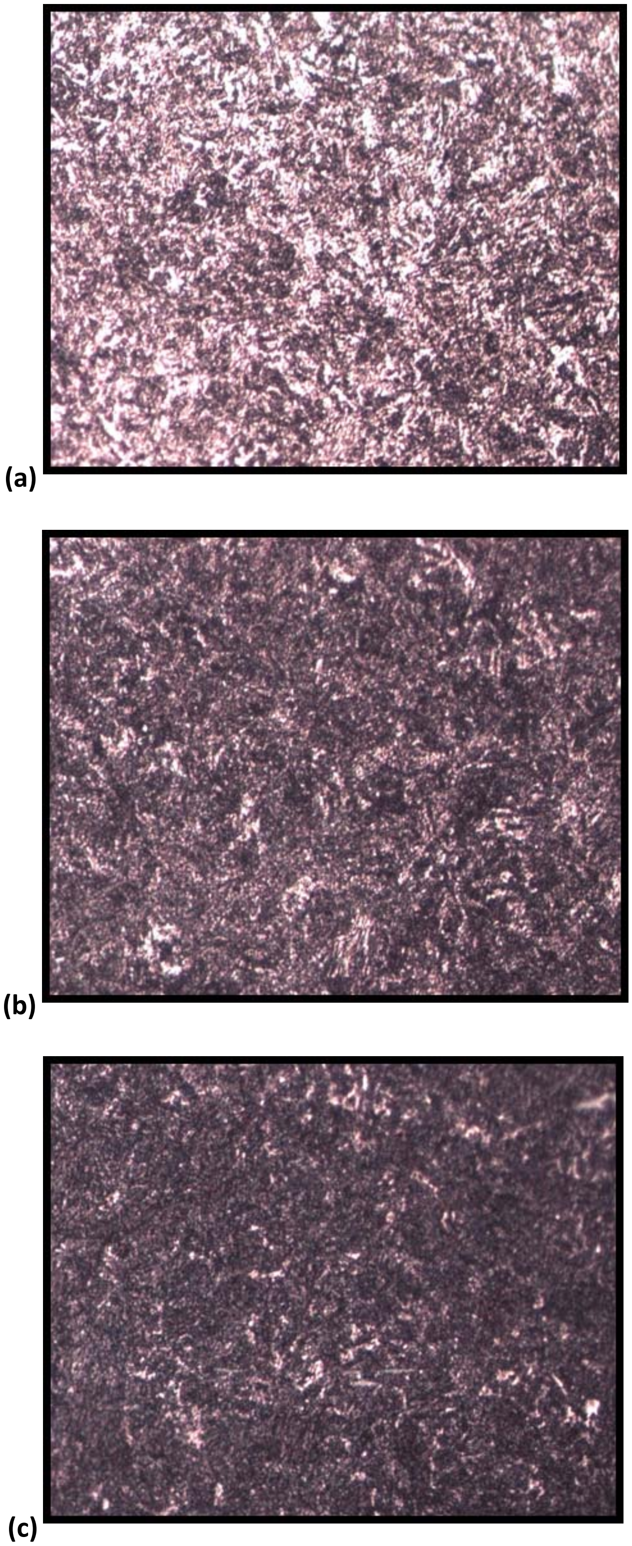


Figure 6.15 Extractor Samples 6.1 (a), 6.2 (b), and 6.3 (c) in a 2% Nital Solution at .75x

Chapter 7: Failure Modes of Critical Parts

When looking at the failure modes of firearm coatings, corrosion is the greatest cause for unserviceability. The mechanism of deterioration includes the embrittlement of the surface layers of the bore by reaction with hydrogen, nitrogen, and carbon at the elevated pressure and temperature during propellant combustion. The ultimate result is crack formation, crack propagation, and crack intersection. Each critical part has criteria for determining if the quantity or location of the corrosion is acceptable.

General rifle inspection should include satisfactory metal surfaces ranging from black to light gray. A rifle should be refinished when its worn shiny metal surface is capable of reflecting light. All rear sights must have a dull gray or black finish on all surfaces that could cause a glare. Minor loss of finish (shiny spots, nicks, scratches) on the exterior surfaces of the barrel and flash suppressor are not cause for rejection.

Large variations occur in the useful life of the barrels due to variations in manufacturing, ammunition, and firing rate. The typical rate of erosion is about one-thousandth of an inch per thousand rounds of fire. Erosion increases and useful-life of the weapon decreases with increase in rate of fire. The useful-life may be approximated with the following equation:

$$L = a_f^{-2/3}$$

Where L is the useful-life in minutes, and a_f is the firing rate in rounds per minute. (25) The firing rate has not been used extensively as a parameter in wear predictions possibly because it is variable and unpredictable in actual combat conditions; nevertheless, it is recommended that this parameter should be used at least in laboratory controlled experiments in order to formulate a successful model of wear. Even if an empirical function were used to simulate the average firing rate in combat conditions, the useful-life would still only be an approximation. Even under the same testing conditions barrel useful-life varies from 7,124 to 29,058 rounds for 9 inches extreme spread criteria. (25) This large variation is due to the barrels coming from various manufacturers, and the large variation between guns from the same manufacturer. The useful-life of the weapon system has an even greater variation not only due to the aforementioned variants, but also due to different types of ammunition from various manufacturers and various firing rates. While the useful-life can be approximated, it is impossible to calculate precisely.

Barrel erosion results in loss of muzzle velocity. The barrel should be free of any: pits in bore, burrs, broken or worn locking lugs, surface cracks, and defects. Pits in the bore as wide as a land or groove and 3/8 inch (0.953 cm) or less in length are allowable (see Figure 7.1). Uniformly fine pits in a densely pitted area of the bore are allowable. The barrel should be replaced if it contains surface cracks, broken or burred locking lugs, or pits larger than those mentioned above. The chamber should be free of any pitting. Fine pits are allowable, but pits 1/8 inch (0.318 cm) in length are cause for rejection. Pits in the chamber are allowable if they do not cause extraction difficulties. Tool marks are acceptable regardless of length. Flaking or fine cracks of chromium plate in barrels or chambers will not be cause for rejection, unless accompanied by pitting to the degree that extraction difficulties are encountered or accuracy is unacceptable. Stripping of lands and grooves shall not be cause for rejection unless so determined by the barrel erosion gage. Lands in the barrel that appear dark due to gliding metal from projectiles coating the barrel interior are not cause for rejection. Damage or missing teeth of the barrel nut is not cause for rejection provided the proper torque value can be obtained during installation.(24) While service manuals instruct to check the barrel for erosion using a barrel erosion gauge for chrome lined barrels, erosion gauges have been shown to be inaccurate.

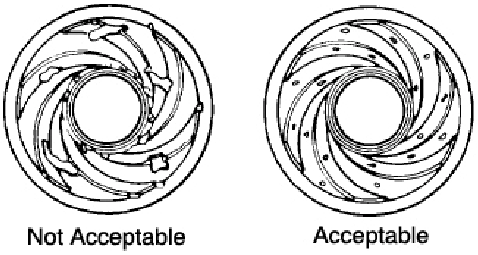


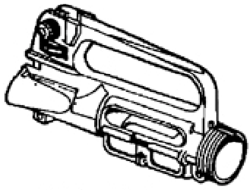
Figure 7.1 Bore inspection for serviceability due to pitting.

The firing accuracy depends upon the true shape of the bore and not just the bore diameter at the origin of rifling. Changes in radius and symmetry of the barrel will affect the muzzle velocity and extreme spread. (25) Better results are received when attempting to predict accuracy for rifles of a particular manufacturer, but these results are still far from being desirable. The limit for extreme spread for overseas use is 7 inches. (26) Extreme spread is the most commonly used predictor of barrel serviceability, while a method thought to be more accurate and complicated would be to measure the mean radius. Neither method has been conclusively proven to be the most reliable indicator of barrel accuracy. (1)

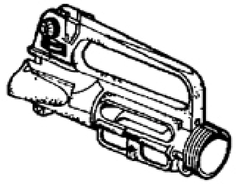
The relationship between accuracy and breech bore wear was used to create a gauge for M16A1 reliability testing, which has been experimentally proven to be inaccurate 38-70% of time, depending on barrel manufacturer. (26) However, there are three types of gauges used to determine barrel serviceability: “Go,” “Field,” and “No-go” gauges (in increasing length). (27) With the go gauge, the bolt should close and lock with the gauge in the chamber. If the action does not close on the go gauge, the chamber has not been set to the correct depth or the bolt is oversized. A rifle that will not accept a go gauge may also be prone to slam fires when the chamber becomes somewhat fouled; cartridges hang-up in the chamber and the floating firing pin then hits the primer with extra force, firing the cartridge. Changing the bolt with a shorter bolt may help, but the problem is typically with the chamber size. The no-go gauge measures the maximum head-space of the chamber. The bolt should not close on this gauge. It the bolt does lock, then the chamber is too deep or the bolt is undersized. You may be able to correct the problem with a longer bolt. It is also possible that a barrel which chambers the no-go gauge is set at the maximum chamber length. This type of barrel could be used, but maximum loads should not be fired in it since they might quickly create a dangerous condition of excessive headspace in the chamber. Brass fired from a rifle with the maximum headspace will stretch quite a bit, greatly shortening the reloading life of the empties. To determine whether a rifle with excessive headspace (one-that accepted the no-go gauge) is safe, use the field gauge. If the bolt turns on the field gauge, do not ever fire a round in this barrel. If the chamber allowed the bolt to close on the no-go gauge but not the field gauge, it would be safe to fire the rifle with regular loads. It would be wise, however, to check the chamber with the field gauge every few hundred rounds to be sure it has not enlarged sufficiently to be dangerous.

Gas cutting (from a too small bullet), friction (from the bullet), stripping (when a bullet does not accept the rifling and strips out the lands), and corrosion (rust) are all enemies of barrel steel. The greatest enemy of barrel steel is the heat generated by shooting. If you want to burn out a barrel quickly, just shoot it as fast as you can and let it get good and hot. Flash heat, such as that developed by powder and gas, is much hotter than the melting point of steel. Fortunately, this heat is of very short duration. When you fire a shot, the heat actually melts a bit of the barrel's surface metal, but it is very quickly cooled by the mass of cool metal underneath. (13) Quick melting and quenching causes microscopic surface cracks and loosens tiny flakes of steel. The next shot removes the flakes. Ballisticians call this erosion. The hotter and bigger the cartridges are, the shorter the barrel life.

Inspect the upper and lower receiver assemblies for cracks, corrosion, wear, or damage that would prevent the weapon from functioning properly. Small dents or gouges that do not affect functioning will not be cause for rejection. If the upper and lower receiver assemblies contain cracks or holes, then replace the receiver assembly. Inspect the lower receiver lobes of the pivot area or hinge pin area. If extensive corrosion appears in these areas, the receiver will not be repaired and the rifle will be replaced (see Figures 7.2 and 7.3).



Shiny Surfaces
(Repairable)



Corroded
(Repairable)

Figure 7.2 Upper receiver inspection for serviceability due to corrosion.

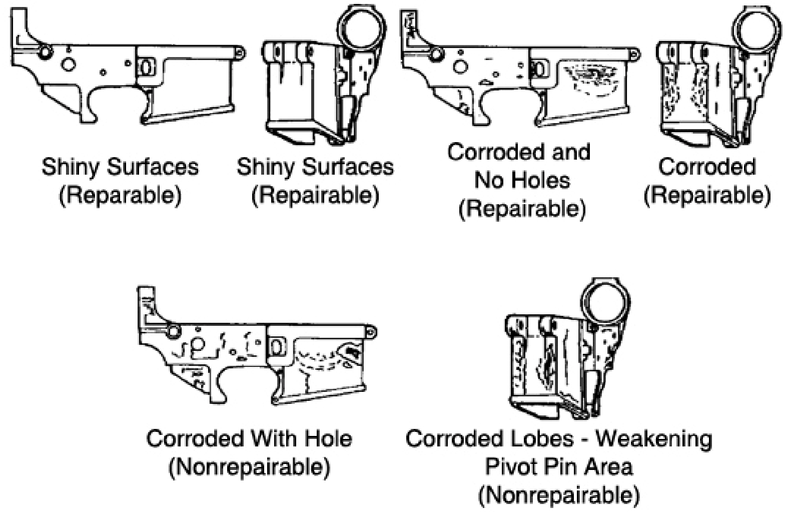


Figure 7.3 Lower receiver inspection for serviceability due to corrosion.

Inspect the bolt carrier group for pits, burrs, and wear. Bolt faces with a cluster of pits which are touching or tightly grouped, covering an area measuring approximately 1/8 inch (0.31 cm) across and appear to be more than 0.010 inches (0.0254 cm) deep, will be rejected and replaced. Bolts which contain individual pits or a scattered pattern will not be cause for rejection (see Figure 7.4). Bolts that contain pits extending into the firing pin hole will not be rejected unless the firing pin hole gauging check determines excess wear. Rings on the bolt face (machine tool marks), grooves, or ridges less than approximately 0.010 inches (0.0254 cm) will not be cause for rejection. Inspect the bolt for cracks in the locking lugs and cam pin hole area. Replace the bolt if any cracks are detected. Particular attention must be given to the area where the lugs meet the bolt body and around the side walls of the cam pin hole.

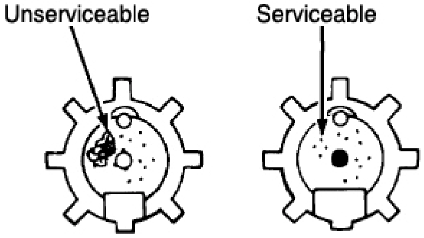


Figure 7.4 Bolt face inspection for serviceability due to pitting.

Inspect the extractor for pits, burrs, and wear. The cartridge engaging surfaces on extractors must not be chipped or deformed. Due to numerous catastrophic fractures of the M16 rifle bolt under firing conditions at an unspecified United States Army installation, a failure analysis of the M16 rifle bolt was conducted at the United States Military Academy. The analysis used (1) fractured bolts to gather metallurgical evidence, (2) new bolts to conduct a controlled experiment, and (3) geometric finite element analysis to analyze stress locations. The highest stress concentrations were present in the locking lugs which were immediately adjacent to the extractor (see Figure 7.5). The base metal exposed due to the wear makes this area susceptible to corrosion pitting. It was discovered that the fracture initiated at a localized corrosion pit and propagated by fatigue. The fractures of the M16 bolt are a result of the cumulative effect of high stress concentrations at the fillet radius and the additional stress concentration imposed by the presence of localized pitting at the surface. The primary cause for failure was coating wear. One possible countermeasure to prevent wear is to case harden the material. Disparities between microhardness profiles near the fillet region and 10 mm away from this region revealed that the bolt may not have been uniformly case hardened. The softer, less carburized region near the fillet contributes to the formation of a wear area after firing just 1800 rounds. (17)

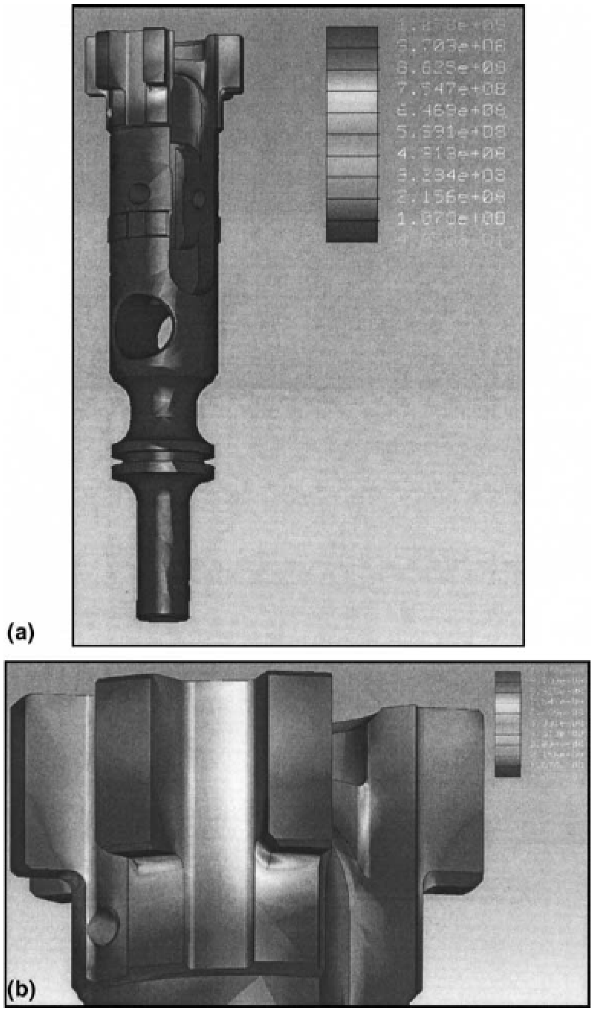


Fig. 7.5 (a) Model of von-Mises stress distribution in M16 bolt (stress values in Pa). (b) Model of von-Mises stress distribution in fillet region of locking lugs adjacent to extractor (stress values in Pa). (17)

These critical parts are subjected to high temperatures and pressures that can cause a catastrophic malfunction if operated under unserviceable conditions. A firearm's first layer of defense against corrosion is its coating. While this is the coating's primary purpose, it must also provide good adhesion, hardness, wear resistance, and friction control to continue to ensure successful operation.

Chapter 8: Coating Theory

The goal of this project is to lengthen a firearm's life cycle while increasing performance and reliability by applying a better firearm coating than those currently in use. This is accomplished by measuring the following performance characteristics: adhesion, hardness, wear resistance, friction control, and corrosion resistance (see Appendix D). The architecture of the coating and how it is built upon its substrate are important to understand.

The substrate, in other words, the coated object, or, in stricter terms, its superficial layer, constitutes one phase of the system. The coating constitutes the second phase. Between the coating and the substrate there exists an interface in the form of an intermediate layer of certain volume, with transitional properties, usually facilitating adherence of the coating to the substrate. In some cases it is difficult to distinguish between the coating and the superficial layer, particularly when the diffusion layers are incremental.

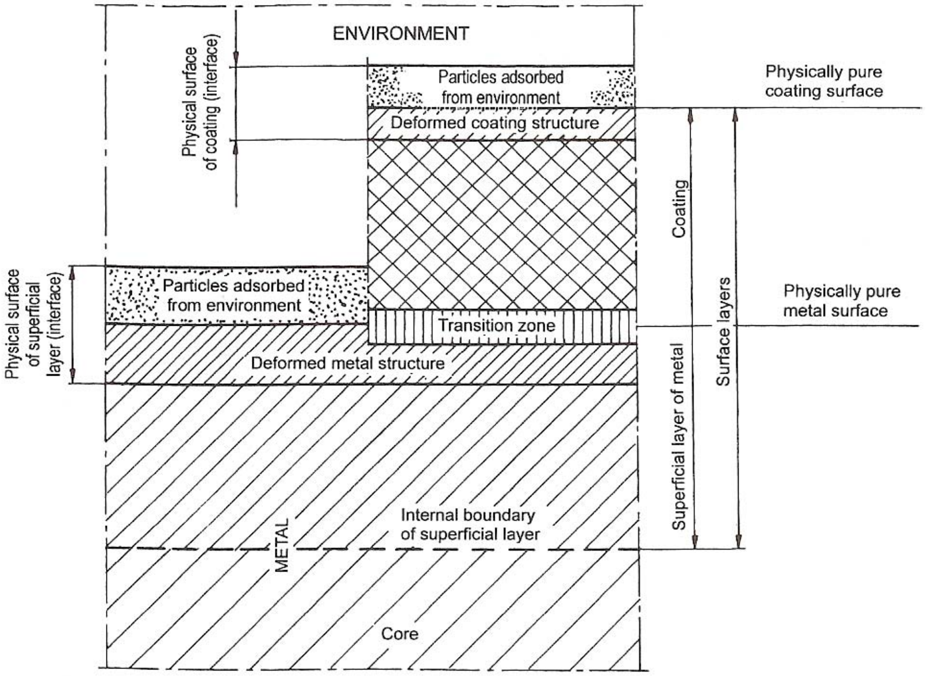


Figure 8.1 Schematic of surface layers. (15)

In the first phase of the system, the majority of commonly used metals in firearms (iron, tin, nickel, cobalt, chromium, zinc, manganese, etc.) are thermodynamically unstable in conditions of practical usage. These metals and alloys exhibit a natural tendency to pass from a state of practical application, artificially created by man, to that of a thermodynamically stable one (i.e. as they occur in the earth's crust in the form of ores). The transition of the metal from the thermodynamically unstable to the stable state is a process of natural destruction of that which man created artificially and is known as corrosion of metals. Factors initiating or accelerating the process of corrosion are based on the surrounding environment.

The first phase of the system is protected from the environment by the second phase. In principle, coatings may be manufactured from all metals, non-metals, and composites. However, not all coatings are applicable in practice on account of their properties and technological difficulties in their manufacture.

Coatings are usually divided into two groups, metals and non-metals. Generally, the structure of metallic coatings may be crystalline (similarly to most metals and alloys) or amorphous (a very small group of specially developed solid metals and alloys). However, as opposed to the crystalline structure of solid metals and alloys, the crystalline structure of coatings is characterized by both finer grain size and greater amount of defects.

Coatings can also be divided according to hardness:

1. Hard (<40 GPa) coatings are characterized by a high plastic deformation increasing with decreasing hardness up to about 70% got $H \approx 10$ GPa.
2. Superhard (≥40 GPa) coatings are characterized by a high elastic recovery increasing with increasing hardness up to about 85% for $H \approx 10$ GPa. Compared to a large number of hard materials, there are only a few superhard materials (i.e. cubic boron nitride (c-BN), amorphous diamond-like carbon (DLC), amorphous carbon nitride (a-CN_x) and polycrystalline diamond. Moreover, these superhard materials are thermodynamically unstable. (27)

The structure of the coating is dependent on chemical composition, and affects many of the coating's properties. Even when depositing the same coating material on the same substrate, the structure of the coating will differ depending on deposition method used and deposition parameters. The same object coated with the same type of coating, exhibits different corrosion resistance in different environments. For that reason, a generalization of the problem of corrosion resistance is extremely difficult. It depends most significantly on: chemical composition, structure of the coating, three-dimensional structure of coating surfaces, on defects, residual stresses, type and condition of the substrate, type and intensity (temperature and concentration) of the corrosive medium and time of exposure. In general, thick coatings offer better protection than thin ones.

Some finishes are better suited for exterior or interior parts based on their physical characteristics. Except for the hot-dip bluing, none of the other finishes should be used on the interior of your rifle. Metal platings do not typically migrate into holes well. Even if they did, your bore and chamber have already been manufactured to the correct dimensions. The chrome-plated bore of an AR15 barrel is made slightly oversized and then plated to its correct dimension. Otherwise, the 1 mm (0.0004 in.) thickness of the plating would greatly increase pressures. The Parkerizing process is so rough that the bore and chamber must be plugged to keep them from being roughened to the point of being useless. According to military specifications, the only acceptable finish for bolt carriers is a phosphate coating. Although, there are aftermarket bolts and bolt carriers with various other finishes, bolts can be both phosphated and chrome plated. (13)

Traditional Metallic Coatings

One of the most fundamental types of coatings is metallic coating, which has been used for hundreds of years as decoration, protection against corrosion, and wear-resistance. Plating is applied using one of two methods, electroplating or electroless plating. The most popular metallic coatings are electroplated chromium, also known as chrome, and electroless nickel.

With electroplating, the cleaned article to be plated is connected as the cathode (negative pole) in a solution known as the electrolyte. Direct current is introduced through the anode (positive pole) which usually consists of the metal to be deposited. Metal dissolves from the anode and deposits on the cathode. Under ideal conditions, the same weight of metal dissolves from the anode as is deposited on the cathode and the overall composition of the bath remains constant. Ideal conditions are never fully realized, and the bath composition changes and must be adjusted at intervals. If the anode efficiency exceeds the cathode efficiency, the metal content of the solution increases and the pH of the solution increases (and vice versa). With chromium plating, insoluble anodes are used and metal must be added periodically to the solution by means of soluble compounds such as chromic acid. The exact chemicals, currents, voltages, temperatures, and general procedure will vary with the kind of metal being plated and the type of method being used. Electrodeposited metals are crystalline in character, and according to the conditions of deposition the deposit may have a fine or course grained structure. Fine grains are preferable in every way. They have better corrosion resistance, greater uniformity and adhesion, polish more readily, and are aesthetically more desirable. The chief factors influencing the character of a deposit are cathode current density, concentration of the electrolyte, nature of the basis-metal, temperature, and the presence of colloidal matter. (33) Electrodeposited coatings are subject to hydrogen embrittlement. Hydrogen embrittlement during plating may be avoided by the use of vacuum deposited coatings. (32)

In electroless plating of metallic objects, metallic coatings of various types, such as nickel, copper, etc., are deposited on solid catalytic surfaces through the process of chemical reduction. As the name implies, no electric current is required. Under the right conditions, positive ions (cations) will be freed from the solution and the reduced metal will form a metallurgical material. This is sometimes referred to as metallic glass because it has no crystal structure. Electroless plating of nickel produces a uniform coating regardless of the shape of the surface being plated. The result is a hard, semi-bright, even, thin layer that is almost free of pores. (33)

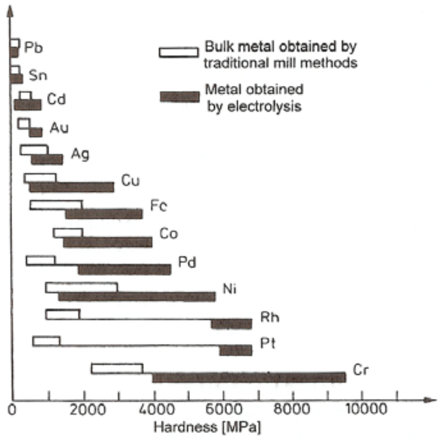


Figure 8.2 Comparison of hardness of metals obtained by traditional metal mill methods (annealed or rolled) with that of electrolytically deposited. (15)

Although nickel has been the traditional favorite, other metals used have included gold, silver, brass, and chrome. Of the different metallic coatings, chromium has the largest surface hardness (see Figure 8.2). This is why chromium is typically used to protect automotive parts for harsh corrosion causing environments. When chrome is applied to metal gun parts, it provides a surface harder than the hardest steel. Chrome protects the base metal, reduces wear, lessens friction and, at the same time, provides an attractive appearance. Clearly the very hard metals such as chromium find application in wear-resistant applications in engineering machinery while certain softer metals may be used as bearing surfaces. Metals having high internal stress, which may lead to micro-cracking, are not necessarily limited in scope (see Table 8.1). For example, hard chromium of 0.01-0.07 mm thickness is cracked in many separate layers and the cracks give rise to valuable lubricating properties. (30) While nickel is not as hard as chromium, it does offer more corrosion resistance. This makes electroless nickel another popular alternative.

Table 8.1 Mechanical properties of electrodeposits.[15]

Material	UTS kg/mm^2	Elongation %	Hardness 100g Knoop	Internal Stress kg/mm^2
Ag	25-35	10-20	55-80	5-10 tensile
Cd			15-60	5-10 compressive
Cr	10-15	0	400-1000	20-60 tensile
Cu	10-40	2-40	35-190	20-50 tensile
Fe	20-50	2-40	130-380	10-20 tensile
Ni	35-150	0-30	120-600	15-35 tensile
Zn	3-25	0-50	45-120	10-20 t. and c.

The electroplating process produces coatings with distinct advantages: (31)

- The workpiece will not undergo distortion or metallurgical changes because the operating temperature of the bath does not exceed 100 °C (212 °F).
- Plating condition can be adjusted to modify hardness, internal stress, and metallurgical characteristics of the coating.
- Coatings are dense and adherent to the substrate.
- The thickness of the coating is proportional to the current density and length of time of the deposition, and there is no limit to the thickness of electrodeposists.
- Although deposition rate seldom exceeds 75 μm/h (3 mils/h), it can be accelerated by forced circulation of the electrolyte and can be as high as 150 or 200 μm/h (6 or 8 mils/h) for some metals in high-speed plating.
- Application of coatings is not confined to the line of sight. Although throwing power may be limited, the freedom of anode design and location is helpful.
- Areas not requiring deposition can be masked.
- Only the tank size of the bath limits the dimensions of the part, although large parts such as gun barrels can be the tank itself; as another alternative, brush plating can be used.
- The process is suitable for automation and has economic advantages over other coating processes.

A main drawback in electroplating is the inability of achieving uniform deposition, which is related to the throwing power of the electrolyte. Throwing power is substrate-shape dependent and also depends on the anode/cathode configuration and the current density, as well as on the composition and conductivity of the electrolyte. A second difficulty is that not all metallic elements can be deposited. Another problem with electroplating is evolution of hydrogen at the electrodes when the cathode efficiency is less than 100%. If a ferrous substrate is to be plated, absorbed atomic hydrogen can cause embrittlement of the part. Unless the parts are heat treated to remove the absorbed hydrogen, they will be brittle and unusable for any application involving elastic strain. (31)

Military specifications provide temperature limitations for some commonly used metal coatings to prevent the coating from softening due to the heat generated by combustion. The low temperature limits for softer metals prevents their use as a firearm coating (see Table 8.2).

Table 8.2 Temperature limitations for common metallic coatings. (31)

Coating	Temperature
Silver[1]	649°C (1,200°F)
Nickel	538°C (1,000°F)
Metallic ceramic[2]	510°C (950°F)
Aluminum[2]	496°C (925°F)
Zinc	260°C (500°F)
Cadmium[3]	232°C (450°F)
Tin-lead[4]	177°C (350°F)
Tin-cadmium[4]	174°C (345°F)
Tin[4]	166°C (330°F)

1. Shall not be used on titanium parts or in contact with titanium parts exposed to temperatures over 288°C (550°F) in service.
2. Above 510°C (950°F) there may be an unfavorable effect upon the fatigue strength of the steel base metal due to diffusion.
3. Cadmium coatings shall not be used on titanium parts or fasteners, or in contact with titanium. Under certain conditions, titanium can be embrittled by contacting cadmium or silver components.
4. Pure tin or tin containing materials which undergo a solid –state transformation shall not be used for parts which are for use at subzero temperatures.

The finishing of metals to be placed in intimate contact when assembled presents a special problem, since dissimilar metal contact results in electrolytic couples which promote corrosion through galvanic action. Table 8.3 lists metals and alloys by galvanic potential. To provide corrosion resistance intermetallic couples shall be selected so that there is 0.25 volts or less potential between the two metals or alloys. The proper selection of metals in the design of equipment will result in fewer intermetallic contact problems caused by corrosion at the contact points.

Table 8.3 Galvanic potentials of metals in sea water. (32)

Anodic End (Less noble, reactive)	
	Potential (V) – Relative to saturated calomel electrode at 25°C
Magnesium	-1.80
Magnesium alloys	-1.60
Zinc	-1.10
Zinc – hot dip, galvanized steel	-1.05
Aluminum – cast, other than silicon type	-0.95
Cadmium – plated and chromate	-0.80
Aluminum – wrought, other than copper type	-0.75
Aluminum – cast, silicon type	-0.75
Iron – wrought carbon or low alloy steels gray or malleable cast iron	-0.70
Aluminum – wrought copper type	-0.60
Steel, stainless – 13% chromium, active	-0.55
Lead – solid or plated, high lead alloys	-0.55
Steel, stainless – 18% chromium, 8% nickel	-0.50
Tin – plate, terneplate, tin-lead solders	-0.50
Chromium – plated	-0.45
Steel, stainless – 13% chromium, passive	-0.45
Brass – yellow, naval, cartridge, muntz metal	-0.40
Brass – red, gliding	-0.35
Copper – solid or plated	-0.30
Nickel – solid or plated	-0.30
Monel	-0.30
Steel, stainless – 18% chromium, 8% nickel, passive	-0.20
Silver, solder	-0.20
Steel, stainless – 18% chromium, 12% nickel, 3% molybdenum, passive	-0.20
Titanium, commercial	-0.15
Hastelloy C	-0.10
Silver – solid or plate, high silver alloys	0.0
Rhodium	0.20
Graphite	0.25
Gold – solid or plated, high gold alloys	0.25
Platinum – wrought, high platinum alloys	0.25
Cathodic End (More noble, unreactive)	

Traditional Solid Lubricants

Solid film lubricants can generally be defined as materials that provide lubrication to two relatively moving surfaces under essentially dry conditions. The study of solid lubricants, as they are now known, is a relatively new field of lubrication. No systematic study of these materials began until a considerable time after they were introduced in the aircraft industry. Three basic phenomena are involved in the friction of unlubricated solids: (34)

1. The area of real contact between the sliding surfaces.
2. The type of strength of bond that is formed at the interface where contact occurs.
3. The way in which the material in and around the contacting regions is sheared and ruptured during sliding.

The technology of solid lubrication has advanced rapidly in the past four decades, responding primarily to the needs of modern industries. Solid film lubricants have been used for more than 100 years, but it was not until the 1950's, with the development of the jet engine, a number of research laboratories began a systematic study of solid lubrication for high temperatures. Most of the work was directed towards defining the required characteristics of solid lubricants. In the 1960's, the need for lubrication in space prompted increased research into solid lubrication with emphasis on the role of atmosphere. Ways of using solid lubrication, with emphasis on the role of atmosphere, were explored. By the early 1970's, when many of the problems had been resolved and their limitations defined, most of the research stopped. (19) The new direction in recent years is the extended use of solid lubrication in the automotive, metal working, and computer/office machine industries. Solid lubricants have been tested in the early 1990's for use in automobile engines, and demonstrated to have coefficients of friction that were close to a properly lubricated metallic interface, but a wear rate that is two to three orders of magnitude higher. (35) Alas, the mechanical stresses in an engine were too high for these undeveloped solid lubricants.

The coating technology developed for the automotive industry can be easily adapted for use in firearms. Laminar solids are efficient lubricants from room temperature to about 450°C. The internal combustion, temperatures, and pressures in engines are analogous to firearms. In recent years, new solid lubricant-containing coatings have been developed with oil-resistant binders. (34) These oil-compatible coatings protect metal surfaces from wear and reduce friction under boundary lubricated conditions in the presence of oil. These coatings are well suited to provide substantially improved lubrication for firearm components under adverse environmental conditions.

Basic solid lubricants are generally classified in two categories, i.e. soft and hard coatings, depending on whether the hardness value is lower or higher than ≈ 10 GPa. (37) This classification, even though arbitrary, is the result of their higher wear resistance when compared with softer lubricants. Hard coatings include oxides, carbides, nitrides, borides, and some carbon-based compositions (diamond, low hydrogenated diamond-like carbon (DLC). Soft coatings include polymers, soft metals, halides, and sulfates of alkaline earth metals, some carbon-based compositions (highly hydrogenated DLC) and the well-known lamellar solids, including transition-metal dichalcogenides and graphite. (29)

A number of materials are used to form solid lubricants, and sometimes combinations of several materials, each contributing specific properties to the film, are used. The most common dry solid lubricants are diamond, graphite, molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), and polytetrafluorethylene (PTFE). Of the most common dry solid lubricants, diamond outperforms MoS_2 in regards to coefficient of friction, wear, and wear rate (see Table 7.4). The use of MoS_2 as a lubricating solid also began in the 1940's, and MoS_2 is now used in more applications than any other lubricating solid. (19) MoS_2 differs from graphite mainly in that its low friction is an inherent property and does not depend on the presence of adsorbed vapors. Apart from oxidation it is stable with most chemicals but is attacked by strong oxidizing acids and alkalis. There is currently no evidence that MoS_x films have a crystalline structure. They are either amorphous or too thin (~110 nm thick), or the crystal domain size is beyond the limits of detection using XRD. MoS_2 is unsuitable as a dry lubricant in air because it reacts with oxygen and/or water vapor to form corrosive products. (19) A useful MoS_2 film can be obtained by:

1. Simply rubbing or burnishing MoS_2 powder onto a substrate material
2. Dipping, brushing, or spraying with a dispersion of MoS_2 in a volatile solvent or water and allowing the liquid to evaporate
3. Using a binder material (resin, silicate, phosphate, or ceramic)
4. Vacuum sputtering

Solid lubricants can be applied in several forms: lubricating powders, bonded films, lubricant composites (metal and plastic based), and lubricating coatings and films. The following are commercially developed, affordable dry solid film lubricants:

1. Bonded molybdenum disulfide (MoS_2), the most widely used
2. Magnetron-sputtered MoS_2
3. Ion-plated silver
4. Ion-plated lead
5. Magnetron-sputtered diamond-like carbon (MS DLC)
6. Plasma-assisted, chemical-vapor-deposited diamond-like carbon (PACVD DLC)

The coefficient of friction provided by solid lubricants are low (typically on the order of 0.04-0.25), they are not as low as those provided by hydrodynamic films (typically on the order of 0.001-0.003). (18) However, the coefficients of friction provided by solid lubricants can be lower than those provided by oils operating under conditions of boundary lubrication. They have finite wear lives, and replenishment of lubricant is more difficult.

Table 8.4 Tribological properties for selected solid lubricating films in sliding contact with 440C stainless steel balls (19)

Film	Steady-state coefficient of friction	Film wear (endurance life)[a]	Film wear rate [$mm^3/N\cdot m$]	Ball wear rate [$mm^3/N\cdot m$]
Bonded MoS_2	0.14	113,570	2.4×10^{-6}	8.1×10^{-8}
MS MoS_2	0.10	277,377	2.4×10^{-7}	1.5×10^{-7}
Ion-plated silver	0.43	8	5.5×10^{-5}	1.2×10^{-5}
Ion-plated lead	0.39	82	3.7×10^{-6}	3.6×10^{-7}
MS DLC	0.12	>1 million	1.7×10^{-7}	4.1×10^{-8}
PACVD DLC	0.07	>1 million	1.0×10^{-7}	6.4×10^{-6}

For solid lubricating films to be durable under sliding conditions, they must have low wear rates and high interfacial adhesion strength between the films and the substrates. The actual wear rates, wear modes, and interfacial adhesion strengths of solid lubricating films (e.g. MS MoS_2 films), however, are widely variable, depending on operating variables and substrate preparation. Their wear rates are also dependent on the binder used and its maximum use temperature (see Table 8.5).

Table 8.5 Common binders for solid lubricant coatings. (34)

Binders	Cure Temperature [K]	Max Use Temperature [K]
Phenolic Resins	423	478
Cellulosic Resins	343	338
Acrylic Resins	343	338
Epoxy Resins	448-478	588
Amide Resins	573	623
Inorganic Silicates	463-523	723
Inorganic Phosphates	338-473	773
Bohemite	723	873
Alkyd Resins	343	343
Silicone Resins	533	598

Solid film lubricants enhance oil lubrication and are less expensive than oil and grease lubrication systems for many applications. Solid film lubricants are useful under the following conditions: (36)

1. Where conventional lubricant are difficult to apply or retain.
2. Where sliding motion is applied under conditions where heavy-load capacity, solvent resistance, and long term corrosion protection is needed.
3. Where dust and dirt contamination on lubricated surfaces is deleterious.
4. Where temperatures may range from -67°C to +93°C (-88.6°F to 199.4°F).
5. In mechanisms operated at infrequent intervals.
6. In mechanisms that are lubricated for the life of the mechanism.
7. Where long-term corrosion protection is required.
8. Where a dull, dark gray or black non-reflective surface is required.
9. Where a sacrificial lubricant is necessary to carry extremely heavy loads developed in the initial start-up of heavily loaded mechanism designed for fluid lubrication. In operations consisting of reciprocating motion, loaded to 15 psi (103 kPa) or less, where contamination with conventional fluid lubricants are probable.

Solid lubricant coatings provide the following benefits: (34)

1. Reduction of weight
2. Reduction of friction during boundary and mixed lubrication
3. Reduction of frictional temperature levels
4. Enlargement of the hydrodynamic lubrication regime
5. Elimination of stick-slip at low speeds
6. Prevention of wear-in damage through seizure
7. Reduction of noise during boundary lubrication
8. Increase of load carrying capacity
9. Reduction of shear stress in the area of frictional contact

Solid lubricants exhibit the following major shortcomings: (29)

1. Except for soft metals, most solid lubricants are poor thermal conductors; hence they cannot carry away heat from sliding interfaces.
2. Depending on the environment (water vapor, oxygen, temperature, pressure, etc.) and contact conditions, their friction coefficients may be high or fluctuate significantly.
3. Their wear lives are finite and their replenishment is more difficult than that of liquid lubricants.
4. The lubrication mechanisms are not exactly the same from one lamellar solid to another. For example, water vapor is necessary to lower the friction of graphite but rapidly inhibits the lubricating properties of MoS_2.

Polymers

An increasing number of polymer composites are now being used as sliding elements that were formerly composed of metallic materials only. They have been developed for special applications in which low friction, high wear resistance, and good thermal conductivity under sliding wear conditions against smooth steel counterparts were of great importance. Polymer lubricants are efficient lubricants between room temperature to about 300°C. (39) There are many compositions available on the commercial market. The use of external lubricants has been a simple and fairly successful technique to mitigate wear in metal parts and components. However, because polymers often swell in contact with liquid lubricants, the approach used for metals cannot be simply transferred. (51)

Plastics are successfully used in many applications involving friction and wear. Nylon, for example, has long been used for quiet-running gears, and Teflon is often used for sleeve bearings that operate dry with little friction. Many plastics have low coefficients of friction, even when run dry. As a result, plastic parts can operate under conditions where oils and greases could not be used. Although plastics can operate dry, their performance is greatly improved by lubrication. Some of the plastics have excellent impact strength. This has permitted them to be used for ball bearings for armored vehicle turrets, where the bearings must survive recoil and other heavy loads without appreciable wear. Plastics deform more readily than metals to conform to mating parts. Tolerances are less critical for plastics, and less accurate mounting and alignment are required. Plastics are abrasion resistant, and they allow contaminants to be embedded into them, thus preventing scoring of the mating part. This property makes sealing against contamination less critical with plastic components than with those fabricated from metal. Plastics are free from corrosion by most acids and other chemical agents. Plastics are compatible with oils, greases, and many chemicals so that such materials can be added for lubrication or to protect other parts against corrosion without harming the plastic components with which they come into contact. Many plastics retain their useful properties even at cryogenic temperatures, which are below those at which oils and greases become too viscous to be useful lubricants.

Tribologists often classify thermoplastic polymeric materials into three distinct groups according to their friction and wear behavior. These are (1) the normal polymers such as low-density polyethylene (LDPE), polypropylene (PP); (2) the amorphous polymers such as polyvinyl chloride (PVC), polymethylmethacrylate (PMMA); and (3) the ‘smooth molecular profile’ polymers such as polytetrafluoroethylene (PTFE) and ultra high molecular weight polyethylene (UHMWPE). Among them, the better frictional performance of the smooth molecular profile polymers can be explained by the easiness with which the long chain molecules shear across each other. (47)

Polymides and PTFE are the most important solid lubricants in the polymer group because of their excellent thermal stabilities and good friction characteristics. (39) Organic polymers such as PTFE and polymeric amides offer very low friction characteristics but generally exhibit low load carrying capacities. The load carrying capabilities can be drastically improved with fillers such as carbon, oxides, molybdenum disulfides and other polymeric binders. PTFE has excellent non-wetting properties and is widely used as a release agent. As a molded article it serves for many lightly loaded applications, and in conjunction with proper fillers and binders, as a solid lubricant film. In some applications, however, the use of these materials is limited by excessive cold flow under load (particularly at high temperature), poor thermal conductivity, high thermal expansion, low radiation stability, inability to dissipate heat efficiently, and lack of strength and dimensional stability.

According to generally accepted friction models, two mechanisms contribute to the friction force between a thermoplastic and steel: adhesion in the contact zone and deformation of the polymer. On rough surfaces the deformation component increases, while on smooth surfaces the adhesion becomes more important. The thin transfer film can lead to a considerable increase of the frictional adhesion component, because with the sliding between polymer/polymer pairs, contact is made between materials with the same atomic composition and molecular structure. However, in all the material combinations the thickness of the layer of transferred material decreases with increasing load because of greater compaction and the likelihood of loose material being detached from the surface. (48) Transfer rate is also dependent on the polymer's hardness, since the flexibility of the polymer chains increases for soft materials (reflected by a low elasticity modulus). However, in presence of oil, a transfer film is not observed. The PETP/PTFE transfer layer is thin and continuous, since its high rigidity (elastic modulus) prevents polymer chains from separating. Since the solid lubricant can penetrate into the sliding area more easily than oil does, friction and stick-slip is eventually reduced by the formation of a PTFE transfer layer. It has been reported that thin transfer films are beneficial for friction at low speeds, intermediate temperatures, and smooth surfaces. (48)

One of the traditional concepts for improvement in the friction and wear behavior of polymeric materials is to reduce their adhesion to the counterpart material and to enhance their hardness, stiffness, and compressive strength. This can be achieved quite successfully by using special fillers. Not all fillers are of benefit to the wear performance of composites. The wear resistance is increased when fillers decompose and generate reaction products which enhance the bonding between the transfer film and the counterface, whereas other fillers decrease the wear resistance because they generate more discontinuities in the material. It is thus important to understand the growth, bonding and loss of transfer films, which are strongly related to the wear mechanisms.

During the sliding of polymers against metal counterfaces, wear is mainly caused by a fatigue process due to the repeated action of tearing and crack-propagation, in opposite with metal on metal pairs where the cutting effect is more important. Therefore, the wear resistance mainly depends on the deformation ability of polymers (strength, hardness, and work of rupture) and chain rigidity (elasticity modulus). Brittle polymers show high wear rates, while tough polymers show higher plasticity and allow for better material transfer. On rough surfaces an increased toughness influences the wear rate in the same trend irrespective of the applied load. (48)

Microparticles and nanoparticles are being used to enhance the mechanical and tribological properties of polymers, this has been widely investigated in the past decade. Various kinds of microparticle filler, e.g. copper compounds (CuO, CuS, and CuF_2), SiC, TiO2, and ZrO2, were selected to reinforce different matrices, e.g. PEEK, polyamide (PA), and PPS. (49) Reducing the size of the particles improves the wear resistance. Not many efforts have been made to reduce wear by developing these types of composite materials.

The thermal conductivity of plastics is much lower than that of metals. They are less able to dissipate frictional heat generated at rubbing interfaces, and plastic parts run hotter than similar metal parts. This disadvantage can be overcome by using the plastic as a thin film over a metal substrate so that the metal can conduct the frictional heat away more efficiently. Bulk plastics cannot be used at as high of temperatures as can steels. They soften with heat and generally should not be used above 93 to 149°C (200 to 300°F), although polymides are useful up to 600°F for continuous service. (18) With respect to temperature on the wear rate of polymers, amorphous polymers show higher wear rates than either crystalline or semi-crystalline polymers. (34) Although temperature has an effect on the transfer of polymers, it is not uniform with all polymer structures. In the case of typical polymers having a spherulite structure, it is suggested that the size of the spherulite plays an important role in the magnitude of the wear rate. Polymers with smaller spherulites have lower wear rates. In addition, the tensile, strength and melting point do not seem to be controlling factors with respect to the wear rate. From wear tests on polymers with bulky molecules and large spherulites, it is also shown that the shear strength at high temperatures near the melting point plays an important role in determining the war rate. (34) The wear rate is seen to be, in general, higher when surface melting does not occur because of frictional heating than when it does occur. Although many physical, chemical, and mechanical properties are related to polymer wear, it is difficult to isolate the effect of any particular property because the wear process is complex and all effects are interrelated. (34)

Ceramic Coatings

Ceramics are assuming an ever-important position among the multitude of materials currently available for application in mechanical systems. Their wear properties, frictional characteristics, and their high temperature capabilities suit them particularly well for a number of applications. High hardnesses, corrosion resistance, strength at elevated temperatures, and high elastic moduli are attractive properties of ceramics. These properties are strongly driven by the bond type of the ceramic as seen in Tables 8.6, 8.7, 8.8, and 8.9. High-performance ceramic coatings include high-temperature glasses; high-temperature coatings based on oxides, carbides, nitrides, and silicides; and cermets. Ceramic coatings are applied to metals to protect them from oxidation and corrosion at room temperature and at elevated temperature. Special coatings have been developed for specific uses, including wear resistance, chemical resistance, high reflectivity, electrical resistance, and prevention of hydrogen diffusion.

Table 8.6 Properties of coating materials with metallic bonding (15)

Type of coating		Density [g/cm^3]	Hardness [HV]	Melting point [C]	Thermal conductivity [J/(cm·s·K)]	Coeff of linear exp. [10-6/K]	Young's Modulus [kN/mm2]	Resistivity [μW×cm]
Nitrides	TiN	5.40	2100-2400	2950	0.289	9.35-10.1	256-590	18-25
	VN	6.11	1560	2050-2177	0.113	8.1-9.2	460	85
	ZrN	7.32	1600-1900	2980	0.109	7.9	510	7-21
	NbN	8.43	1400	2200-2300	0.0374	10.1	480	58
	TaN	-	1300	2090	0.096	5.0	-	128
	HfN	-	2000	2700	0.113	6.9	-	28
	CrN	6.12	1100	1050	-	2.3	400	640
Carbides	TiC	4.93	2800-3800	3070-3180	0.172-0.35	7.61-8.6	460-470	51
	VC	5.41	2800-2900	2650-2830	0.043	6.5-7.3	430	60
	HfC	-	2700	3890	0.063	6.73-7.2	359	37
	ZrC	6.63	2600	3445-3530	0.205	6.93-7.4	355-400	42
	NbC	7.78	1800-2400	3480-3610	0.142	6.84-7.2	345-580	19-35
	WC	15.72	2000-2400	2730-2776	0.293	3.8-6.2	600-720	17
	W_2C	-	2000-2500	-	-	-	-	-
	TaC	14.48	1550-1800	3780-3985	0.22	6.61-7.1	291-560	15-20
	Cr_3C_2	6.68	1500-2150	1810-1890	0.188	10.3-11.7	400	75
	Mo_2C	9.18	1660	2517	-	7.8-9.3	540	57
Borides	TiB_2	4.50	3000	3225	-	7.8	560	7
	VB_2	5.05	2150	2747	-	7.6	510	13
	NbB_2	6.98	2600	3036	-	8.0	630	12
	TaB_2	12.58	2100	3037	-	8.2	680	14
	CrB_2	5.58	2250	2188	-	10.5	540	18
	Mo_2B_5	7.45	2350	2140	-	8.6	670	18
	W_2B_5	13.03	2700	2365	-	7.8	770	19
	LaB_6	4.73	2530	2770	-	6.4	400	15

Table 8.7 Properties of hard coating materials with covalent bonds (15)

Type of coating		Density [g/cm^3]	Hardness [HV]	Melting point [°C]	Thermal conductivity [J/(cm·s·K)]	Coeff of linear exp. [10-6/K]	Young's Modulus [kN/mm2]	Resistivity [μW×cm]
Nitrides	BN (cubic)	2.52	3000-5000	2730	-	-	660	10^{18}
	BN (FCC)	-	4700	1200-1500	1.8-2.01	-	-	-
	AlN	3.26	1230	2250	-	4.2-5.7	350	10^{15}
	Si_3N_4	3.19	1720	1900	-	2.5-3.9	210	10^{18}
Carbides	B_4C	2.52	3000-4100	2450	-	4.5-6.1	441	0.5×10^{6}
	C (diamond)	3.52	≈8000	3800	-	1.0	910	10^{20}
	SiC	3.22	2600	2760	-	5.3-6.1	480	10^{5}
Borides	B	2.34	2700	2100	-	8.3	490	10^{12}
	TiB_6	2.43	2300	1900	-	5.4	330	10^{7}
	AlB_{12}	2.58	2600	2150	-	-	430	2×10^{12}

Table 8.8 Properties of hard coating materials with ionic bonds (15)

Type of coating		Density [g/cm^3]	Hardness [HV]	Melting point [°C]	Thermal conductivity [J/(cm·s·K)]	Coeff of linear exp. [10-6/K]	Young's Modulus [kN/mm2]	Resistivity [μW×cm]
Oxides	Al_20_3	3.98	1800-2500	2047	0.301	8.4-8.6	400	10^{20}
	Al_2TiO_3	3.68	-	1894	-	0.8	13	10^{16}
	TiO_2	4.25	1100	1867	-	9.0	205	-
	ZrO_2	5.76	1200-1550	2677	-	7.6-11.1	190	10^{16}
	HfO_2	10.2	780	2900	-	6.5	-	-
	ThO_2	10.0	950	3300	-	9.3	240	10^{16}
	BeO_2	3.03	1500	2550	-	9.0	390	10^{23}
	MgO	3.77	750	2827	-	13.0	320	10^{12}
Borides		7.9	850-1100	1300	0.502	11.0-13.0	205	10^{5}

Table 8.9 Physico-chemical properties of hard coating materials (15)

Value	Hardness	Brittleness	Melting point	Stability	Coeff. of linear exp.	Adhesion to metallic substrate	Reactivity	Suitability for multi-layer system
High level	C	I	M	I	I	M	M	M
	M	C	C	M	M	I	C	I
	I	M	I	C	C	C	I	C
M – metallic; C – covalent; I – ionic bonds in materials								

Crystalline coatings are usually characterized by a significant variability of chemical composition which results in changes in the type of chemical bonds and morphology. Crystalline coatings are not low friction and do not provide any protection for the opposing surface. (39) Indeed, the coatings are very hard, and if the coated surface or the coating is rough, then they can cause abrasion and rapid wear of the opposing surface. If a particle of the ceramic coating breaks away, it becomes a source of abrasion within the mechanism. Among non-metallic coatings, very high hardness and excellent tribological properties are exhibited by nitride, oxide, carbide, and boride coatings deposited in a vacuum by physical vapor deposition (PVD) or chemical vapor deposition (CVD) techniques. Crystalline coatings are mainly compounds of transition metals (nitrides, carbides, oxides, borides, silicides, carbonitrides and aluminonitrides) or pure metals (e.g., aluminum). In the overwhelming majority of cases, deposited substrates are constituted by transition metals belonging to group IVb, Vb, and VIb of the periodic table (most common elements are Ti, V, Zr, Cr, Ta, Mo, W, Nb, and Hf), and reactive gases (usually nitrogen and oxygen).

There are over 600 ternary compounds known involving carbon and nitrogen with transition metals belonging to groups IVb, Vb, and VIb of the periodic table. Of these, the best researched compounds are solutions of nitrides: TiN, TiCN, TiAlN, VN, ZrN, NbN, HfN, TaN, WN, CrN, and MoN with TiC, VC, ZrC, NbC, HfC and TaC carbides. Compounds of carbides and nitrides usually together form solid solutions and as ternary and quaternary compounds feature better properties, especially tribological, than simple coatings. The obtaining of appropriate properties may be controlled, taking advantage of the broad range of mutual solubility of these compounds. Best researched and featuring best tribological properties is the titanium carbonitride Ti(C,N), as well as the titanium and aluminum alloy nitride (Ti, Al)N. (15) To date, titanium-based coatings have defined the benchmark of hard coatings. In an oxidation or corrosive environment Ti elements often forms a porous non-protective oxide scale, and therefore the oxidation and corrosion resistance of titanium-based coatings is limited. (38)

Technically, the oxide layer formed on a metallic surface from its interaction with air is nature's ceramic coating. The first stage in the reaction between a metal and oxygen is the chemisorptions of oxygen. As the rate of chemisorptions is very high, at normal temperatures the surface is almost instantaneously covered with a monomolecular layer of oxygen. The oxide layer is formed by the complete reaction between oxygen and atoms in the metal surface. Then, up to a thickness of several hundred Angström the increase in the thickness of the oxide layer takes place by the diffusion of the reactants in both directions. Pores or cracks usually occur with greater oxide thicknesses, facilitating access of oxygen to the metallic surface. (46)

Oxide coatings can form as several different oxides that are arranged so that the compound which is richest in oxygen lies at the solid-gas interface while the compound which is poorest in oxygen lies at the metal-oxide interface. If an alloy is subjected to oxidation, the reaction products occur either in the form of separate layers or as a heterogeneous mixture. In the latter case, a new mixed compound may form. If one of the oxides is in excess, it may impose its structure on other compounds present in smaller quantities. The structure of the main compound may be affected by the structure of the base metal. (46)

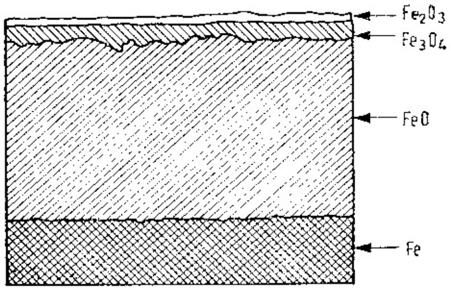


Figure 8.3 Formation of superposed oxide layers on an iron surface at 625°C after 24 h. (46)

Metal oxides are useful lubricants between 500 and 1000°C, though their performance is rather poor at lower temperatures, though their performance is rather poor at low temperatures. (45) Metals like nickel, chromium, aluminum, titanium, and the stainless steels have the ability to form thin invisible films of oxide (1-3nm thick) in a number of environments. (28) Although these metals are electrochemically active the films have a very marked effect on the rate of reaction. The ability of a metal to form a protective film is called passivity, and the passivation of a metal is one of the most important methods of corrosion control. Most oxides become highly lubricious and can provide fairly low friction at elevated temperatures. (29)

Carbides as ceramic coatings are principally used for wear and seal applications, in which the high hardness of carbides is an advantage. These applications include jet engine seals, metal-forming tools, hand tools, dies for ceramic and plastic processing, and other machine elements. (45) Carburization of firearm barrels reduces the melt temperature of the surface. Once the carbon concentration exceeds 2.1%, the material is considered cast iron. Erosion calculations have shown that the surface can saturate with carbon providing the best boundary source available for diffusion. This enables the formation of substrate iron carbide at the maximum rate possible. As the ballistic cycle progresses the surface temperature rises, all the while carbon is diffusing and creating the carbide Fe_3C. (41)

Nitrides are used for wear-resistant applications, most notably surface engineering of cemented carbide cutting tool steels. (45) The first practical application of crystalline coatings using vacuum deposition was in the 1960s when cutting tools were coated by titanium nitride for the first time in US industry. (15) It was not until the 1980's that physical vapor deposition coatings became commercialized with TiN coatings. (38) Since then, hard coatings based on transition metal nitrides have been successfully used for materials protection and particularly to improve cutting tools lifetime. Traditionally, hard coatings have mainly been applied to cutting tools to give good protection against abrasive wear, and thus lengthen tool life. Nowadays, new coatings have to be more and more multifunctional in order to meet industrial needs. Nitriding results in consistent wear and barrel life compared to chrome plating, which is sometimes less reproducible. Unfortunately, nitride barrels do not have the erosion life of chrome barrels. Pre-nitriding the surface of chromed or otherwise coated barrels would protect the interface between the coating and substrate steel from degradation when cracks occur. (40)

Borides have very high hardness values due to their nanocolumnar structure and the strong covalent bonds within the B network. (42) With increasing nitrogen content, hardness and modulus of the Cr-B-N coatings rapidly decrease.

The tribological mechanisms in contact with alumina (Al_2O_3), partially stabilized zirconia (PSZ), silicon carbide (SiC) and silicon nitride (Si_3N_4) sliding unlubricated on steel and on themselves were studied with a pin-on-disc tester. Of the material combinations investigated, only alumina and silicon carbide against themselves and possibly silicon carbide against steel are applicable in continuously operating unlubricated sliding contacts. (45) Strong formation of tribological transfer layers occurred in most of the material combinations studied, the direction of the material transfer being governed by the thermal chemical and mechanical conditions in the sliding interface. Ceramics, though very hard, also behave plastically under tribological conditions, although their brittleness and surface chemistry dominate the wear process. The coefficient of friction for these experimentally studied unlubricated ceramic and steel contacts were in the range of 0.37-0.82, which is quite high for applications involving continuous sliding. (45)

Since the maximum barrel temperature of an M4 and M16 is 871°C (1600°F), the current firearm design would benefit from the use of the ceramic materials. For temperatures of 1000°C (1832°F) and higher, metal structural materials and bearing materials are being replaced by ceramics. (34) These ceramics must either be self-lubricating or coated with a solid lubricant. Fortunately, the composition of ceramics, especially oxide ceramics, are easily modified and are therefore amenable to formulation tailored for specific properties. Ceramics may be made self-lubricating by incorporating lubricating components into their basic structure or by surface diffusion of the solid lubricant material into the surface layer of the ceramic. All of this will require a great deal of research to achieve the degree of lubrication required without being damaging to other properties such as strength and dimensional stability.

The US Army Research Laboratory is currently assessing the feasibility of ceramic gun barrels in an attempt to provide a significant increase in barrel life, a reduction in weight (primarily for smaller caliber systems), and enable the use of higher energetic propellants. This investigation spans a range of calibers from the 5.56-mm rifle to the 155-mm artillery system. The steel gun barrels currently used by the Army for these systems have a short lifecycle and cannot withstand many of the higher energy propellants that are currently available or under development. It is anticipated that ceramic gun barrel liners will provide a 50% increase in barrel life with sustained accuracy for direct and indirect fire, enable a 20% increase in muzzle kinetic energy for direct fire, and provide a 5-25% weight reduction (per unit length of barrel) owing to the combination of superior wear resistance, high temperature capability, and relatively low density that are inherent to ceramic materials. (46)

The current crop of commercial thermal coatings, applied on the inside of a jet engine consists of three unique layers, which are exposed to temperatures around 2,100°F during their operation. (43) The bond coat is applied directly on the alloy followed by a thermal oxide coating and a ceramic top coating on the bond coat. The best possible design for a coatings adhesion would be the formation of coating crystals, similarly oriented relative to the substrate's crystallographic orientation. If the lattice parameters do not differ by more than 10%, this is called epitaxial growth. (15) As opposed to many other techniques of coating deposition, those coatings which are deposited by PVD techniques are only in exceptional cases composed of pure evaporated material.

Diamond

Diamond is an allotrope of carbon, joining graphite and the fullerenes as the major pure carbon structures. Diamond has a unique combination of properties: hardness, thermal conductivity, chemical and thermal inertness, and abrasion resistance. These properties make diamond attractive for a wide range of tribological applications, including solid lubrication. Presently, modern diamonds fall into four distinct categories: natural, high-pressure synthetic, chemical vapor deposited, and diamond-like carbon.

Natural diamond is produced in volcanic shafts at high temperatures and pressures. In 1814 the English chemist H. Davy proved conclusively that diamond was a crystalline form of carbon. Since that time many attempts have been made to synthesize diamond by trying to duplicate nature. These attempts, spread over a century, were unsuccessful. It was not until 1955 that the first unquestioned syntheses were achieved in the United States (General Electric), in Sweden (AESA), and in the Soviet Union (Institute for High-Pressure Physics). More changes, like the recent development of chemical-vapor-deposited diamond and diamond-like carbon, will undoubtedly take place in the future. Low-pressure diamond synthesis was discovered in the 1970's. In the 1980's synthetic diamond was produced in coating form by using a variety of low-pressure, vapor-phase synthesis techniques under relatively benign conditions, it is known as diamond-like carbon (DLC). (19) Although DLC has properties similar to those of CVD diamond, it cannot be obtained as thick monolithic shapes, at least with present technology.

Diamond has two crystalline structures, one with cubic symmetry (by far the more common and stable) and one with hexagonal symmetry (found in nature as the mineral lonsdaleite). In diamond the light carbon atoms are densely packed, but the lattice is in many ways similar to those of other crystals, such as silicon, of the same structure. Materials with high hardness are usually brittle and diamond is no exception. Diamond behaves as a brittle solid and fractures along its cleavage planes (primarily along the {111} plane, but also along {211}, {110}, and {322}). (19) It is generally accepted that, for a material to be recognized as diamond, it must have all of the following characteristics:

1. A clear, sharp diamond peak at 1332 cm^{-1} in the Raman spectrum
2. A crystalline morphology visible by SEM or TEM
3. A single-phase diamond crystalline structure detectable by x-ray or electron diffraction

CVD diamond and DLC coatings offer a broader potential in the field of tribology than do natural and high-pressure synthetic diamond because size and eventually cost will be less of a limitation. Most CVD diamond is produced as films of polycrystalline diamond on ceramic or metal substrates. These films open the door to tribological technology and design engineering that can take full advantage of diamond's intrinsic properties to make solid-lubricating, wear-resistant, erosion- and corrosion-resistant, and protective coatings.

Diamond consists of light carbon atoms held together by strong forces, and this combination produces many extreme properties. Table 8.10 summarizes the general properties of CVD diamond and compares them to those of single-crystal diamond, such as type Ib. Because of the difficulty in testing, the effect of impurities and structural defects, and the differences between the various deposition processes, uncertainty and broad results have been found in the reported property values. The values in Table 7.6 should be viewed with caution. The tribological properties of CVD diamond are similar to those of natural and synthetic diamond. The coefficient of friction and wear resistance of CVD diamond are generally superior in the atmosphere.

Table 8.10 Properties of CVD Diamond (19)

Property	**CVD diamond**	**Single-crystal diamond**
Density [g/cm^3]	3.51	3.515
Thermal conductivity at 25°C [W/m°C]	2100	2200
Thermal expansion coefficient at 25 to 200°C [1/°C]	2.0×10^6	$(1.5 \text{ to } 4.8)\times10^6$
Tensile Strength [GPa]	1 to 5	4 to 6
Young's modulus [Pa]	$(7 \text{ to } 9)\times10^{11}$	10.5×10^{11}
Poisson's ratio [GPa]	0.1 or 0.07	0.1 or 0.07
Vicker's hardness range[a] [kg/mm^3]	5000 to 10000	5700 to 10400
Chemical properties	Both CVD and single-crystal diamonds are resistant to all liquid organic and inorganic acids, alkalis, and solvents at room temperature. One of the most chemically resistant materials.	
Band gap [eV]	5.45	5.45
Index of refraction at 10 µm	2.34 to 2.42	2.40
Electrical resistivity [ohm·cm]	10^{12} to 10^{16}	10^{16}
Dielectric constant (45 MHz to 20 GHz)	5.6	5.70
Dielectric strength [V/cm]	10^6	10^6
Loss tangent (45 MHz to 20 GHz)	< 0.0001	-----
Saturated electron velocity	2.7	2.7

Composites

Generation I coatings used single-component, and despite enormous efforts to develop new coatings and coating systems only a few single-component films prevailed on the market and continue to be favorites. The commercially successful coatings included TiC, TiN, CrN, CrC, Al_2O_3, TiAlN, TiCN, DLC, W_2C, WC/C, MoS_2, diamond, soft metals and some polymers. Experiments were conducted with a large number of elements, including Zr, Hf, V, Nb, Cr, Mo, W, Al, and Si, with various chemical combinations. From the initial binary hard materials, titanium and chromium nitride and carbide have been improved by alloying these binary structures with metal and/or metalloid components.

Materials are composed of grains separated by grain boundaries. The size of grains in currently produced materials, which can be called the conventional materials, varies over a wide range from about 100 nm to several hundred millimeters, corresponding to monocrystals. However, no fundamental qualitative changes in properties of the conventional material can be expected over this size range of grain boundaries. Completely new properties are exhibited by nanocrystalline materials with a grain size of about 10 nm or less. (27) Under these conditions dislocations do not exist, because grain boundaries prevent their formation, and the boundary regions play a decisive role in the material deformation. A new deformation mechanism, called grain boundary sliding, replaces the dislocation activity which is the dominant deformation process in conventional materials.

From this complex research, it is now possible to tailor various structures, including multilayered, gradient, superlattice, nanostructured, and adaptive coatings with extreme tribological properties. The hardness of nanocomposite coatings correlates well with their structure. A decrease of the film crystallinity results in an increase of hardness. The material's resistance to plastic deformation can be controlled by the film hardness and its elastic modulus. (27) Relatively new vacuum deposition techniques now allow for the industrial application of these types of coatings.

Generation II coatings include multicomponent and multilayer coatings. Multicomponent coatings are made up of two or more constituents in the form of grains, particles or fibers. Multilayered coatings are composed of a periodically repeated structure of lamellae of two or more materials, with thicknesses up to a few tenths of a micrometer (if the thickness of each lamellae is in the nanometer range, these films are generally classified as superlattice).The advantage of combining several structures and compositions within one coating include:

1. Achievement of various individual physical properties (i.e. diffusion barrier + low friction)
2. Reduction of the mismatch in mechanical and chemical properties between the substrate and the coating (mainly to enhance adhesion)
3. Control of the residual strain and therefore the stress within the coatings
4. The ability to stop cracks during operation under severe conditions
5. Enhancement of hardness and/or toughness by allowing layers or phases to slide over each other when they deflect under load.

It was found that the system Steel/Ni/Au/Ag is most satisfactory for steel. The layers are deposited successively by electrolysis, the outer silver layer being the thickest (5μm). The coefficient of friction for such a system, determined on a Faville machine, under a load of 150 daN in the presence of demineralized water was $\mu \approx 0.11$. (56) This value remains constant for about three minutes. The range of applications of multilayers involves low sliding speed pairs and discontinuous running pairs which are inadequately lubricated or which operate in a hostile environment.

Short-fiber-reinforced high-temperature-resistant thermoplastic materials are now being used as sliding elements which were formerly composed of metallic materials only. Their applications can reach temperatures up to 220°C, pressures of more than 10 MPa and sliding velocities of about 3 m/s. (49)

Continuous-fiber-reinforced high-performance composites are another class of tribomaterials which can endure even higher pressures than short-fiber-reinforced thermoplastic materials, depending on the fiber orientation relative to the sliding direction. (49) The load limits, which finally determine the limits of their application, can be verified by finite element simulations.

Composite deposition plating is a further extension of aqueous solution electroplating or electroless coatings in that particles or fibers are suspended in the electrolyte, then occluded in the deposit. Oxides, carbides, silicides, refractory powder, metallic powder, and organic powder can be introduced into the electrolyte. The most widely used electrodeposited composites are cermet coatings, with Al_2O_3, ZrO_2, titania (TiO_2), and SiC added to increase strength, hardness, and wear resistance. The amount of ceramic particles incorporated in the coating depends on the current density and the bath loading, that is, the amount of particulate in the suspension. (31)

Polytetrafluoroethylene (PTFE), diamond, and SiC particles can also be incorporated into a nickel electroless plating for improved properties. Diamond and silicon carbide are used to enhance abrasion resistance; the surface hardness of these composites is reported to be 1300 HVN. Polytetrafluoroethylene is added to the electroless nickel bath to provide a composite coating with enhanced lubrication. Almost any particulate material can be deposited in a metallic matrix, provided the particles are sufficiently small to remain suspended in the bath and that the particles do not react chemically with the bath during electrodeposition. (31)

In a recent test, MoS_2 coatings with a sublayer of either thin dense chrome (TDC) or diamond-like-carbon (DLC) performed better than other multilayer coatings. Various multilayer coating combinations were created from four "hard" coatings and a top layer of four "soft" coatings. The four hard coatings selected were TDC, thin dense chrome with diamond particles (XADC®), titanium nitride (TiN) and DLC. The four soft coatings selected were two types of molybdenum disulfide (MoS_2), boron nitride (BN), and silicone. MoS_2 based soft lubricants showed low coefficient of friction and wear with all four hard coatings. The lowest coefficient of friction (0.08) was obtained when evaluating DLC + MoS_2. The solid lubrication system consisting of TDC + MoS_2 showed three times higher load carrying capacity compared to current gun lubricants (7788 vs. 3338 N). Both TDC + MoS_2 and DLC + MoS_2 have longer endurance life with lower frictional torque values than current gun lubricants. The TDC + MoS_2 based solid lubrication system showed a superior subscale performance for the weapon system. (53) The test concludes that solid lubricants have the potential to provide a much better performance than current gun lubricants in extreme environmental conditions, especially in sand, cold, and humid environments. The concept of solid lubrication system for weapons applications has been validated using subscale tests. Teflon was considered as an option but was not included in this test. In order to maintain a high rate of fire with fully automatic machine guns, oil must be applied in quantities that would also collect a large amount of sand. With the advent of these boutique coatings, automatic machine guns will no longer rely on oil and will be designed to shoot in bursts of ~100 rounds.

Generation III coatings can be sensitive to friction, high temperatures, and high pressures. There are three types of Generation III coatings: superlattice, gradient, and nanostructured:

- Superlattice coatings are nanometer-scale multilayers composed of two different alternating layers in the 5-50 nm range. (29) The major function of these structures is to significantly enhance hardness, fracture toughness, and adhesion of the coatings, thereby improving their wear resistance. According to the composition of the bilayer, superlattice coatings can be divided into five groups: (1) metal superlattices, (2) nitride superlattices, (3) carbide superlattices, (4) oxide superlattices and (5) nitride, carbide, or oxide/metal superlattices. Experiments show that metal superlattices exhibit a relatively low hardness. On the contrary, single-crystal nitride superlattice coatings are superhard materials with a hardness ranging from 45 to 55 GPa. (27) The overall hardness of the superlattice coating is greater than that of the material of each components of the bilayer. A difference in elastic modulus between the two layer materials is required to increase the hardness of the superlattice film. It is difficult to ensure the same thickness of all superlattice layers on all coated objects, particularly when they have a complex shape. Variations in hardness can also be caused by the interdiffusion of elements in neighboring layers at high service temperatures.
- A gradient in composition can be designed to provide a gradient in wear resistance or other properties. Grading the composition by a drastic control of the deposition process has been

achieved to combine a relatively hard TiAlN phase with a softer MoS_2 phase with an increase in the latter phase toward the top surface. (29) Another benefit of grading the composition is that it improves adhesion of DLC-based coatings that contain metal additions.

- Nanostructured coatings include nanocrystallized films (with grain sizes in the nanometer range) and nanocomposite films. Nanocomposites include structures that combine amorphous phases with crystallized ones. The most recent efforts to extend the use of nanometer-scale coatings have been largely devoted to improving their stability at high temperature to mainly avoid phase transformation, grain growth, and diffusion.

Generation IV coatings are adaptive coatings that have the ability to change their properties to meet the requirements of the operating conditions. Smart coatings imply a deep understanding of the film structure and composition dependence vs. temperature, contact pressure, and environment. The most recently developed cutting-tool coatings based on TiAlN with the addition of yttrium or chromium may produce a stable oxide during cutting at high temperature and enhance the wear resistance. No single material is known to be lubricious from ambient temperature to 800°C. Thus, the way to produce a lubricant coating that can operate over a broad temperature range is to combine low- and high-temperature lubricants into a composite or layered structure, such as CaF_2 and WS_2, which interact during friction to form $CaSO_4$.

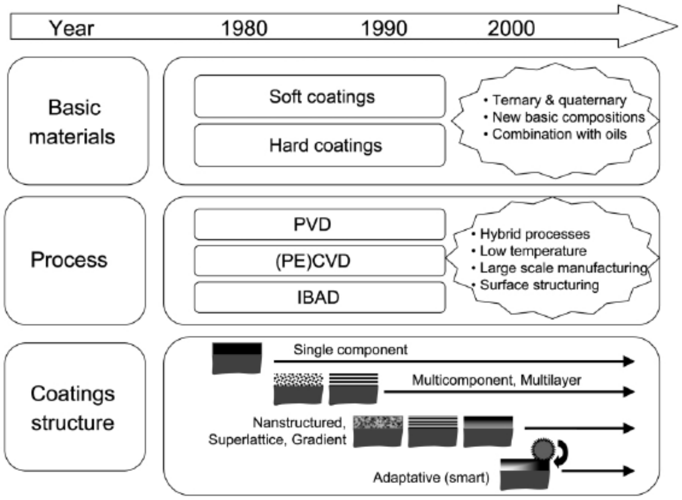


Figure 8.4. Historical development of composite coatings. (29)

Composite materials will find increased applications in mechanical system design. Not only do they support a load without undue distortion, deformation or fracture, but they can maintain low friction and wear over long periods without seizure. In addition, they provide the opportunity for the design of a low mass system which leads to lower dynamic loads in the system and to lower frictional losses. For example, although composites containing PTFE have low friction and high thermal stability which is particularly attractive for sliding applications, their poor mechanical strength, excessive viscoelastic deformation under load and high rate of wear usually necessitate some form of reinforcement. (34) The potential for redesigning entire components around a designer coating has been demonstrated with the fabrication of entire barrels using composite reinforced ceramics. (52)

Chapter 9: Coating Firearms

Firearm coatings were virtually non-existent prior to the dramatic evolution over the last two centuries. Firearms were first put into use around 1350 AD. The first protective finish "applied" to iron was rust, or what we currently call rust-bluing. By carefully controlling the process, a somewhat preservative rust layer can be built-up. For almost 3,000 years, rust bluing and scouring the iron bright, were the only finishes available for iron implements. Right up past the American Civil War, scouring rifle barrels bright with a wet application of campfire ashes was considered an appropriate method for cleaning and maintenance. (55) The first and oldest types of finishes are: browning, bluing, color case hardening, and Parkerizing. These processes result from a chemical reaction with the surface of the steel itself. The second type of finish adheres to the steel and seals it away from oxidation. These coatings include chrome, nickel, gold, epoxy, or even paint. The third type of finish combines multiple materials to create a rust resistant, hard, low friction surface. These coatings include: diamond like coatings, titanium nitride, tungsten carbide, titanium-aluminum-nitride, nickel-boride, and boron carbide. All of these types of coatings will be discussed in greater detail in the order listed in Appendix E, as follows.

I. Conversion Coatings

1.a. Browning

Originally, guns were rusted brown by various processes and the act became known as browning. The brown coating was caused by ferric oxide (red rust). The browning process caught on and by 1700 nearly all gunsmiths had perfected the process. (33) Eventually some gunsmith discovered that if he cleaned off the rust a little sooner, the finish would be black or blue, instead of brown. Due to tradition, after the blue finish almost completely supplanted the brown, the processes were still called browning although either a brown or blue finish could be meant. This process should not be confused with bluing, since it can take anywhere from four to fifteen days as opposed to the couple hours that some bluing processes take.

Browning treatments have long been applied to the production of a black finish on steel and, like temper films, this finish is oil-absorbent. There are several processes that can be used for browning, but salammoniac-brown is the fastest and most uniform. Salammoniac-browning requires swabbing the part with five passes of a 0.5% solution of salammoniac, or ammonium chloride. (56) Additional passes with it will produce an almost black finish. If the solution is boiled and the metal parts boiled in it, three passes will give a durable dull-black finish. Allow the solution to dry and then give the part a final cleaning. Dip the article in oil or coating with a thin film of tallow or linseed oil, followed by heating for 30 minutes at temperatures ranging from 200-400°C (392-752°F). (57)

Browning is slightly thicker than bluing, and provides more protection against scratches. The rust pits of a good browning solution or mixture are microscopic and very little different from those of popular blued finishes, so that the finished metal has a sheen similar to a good polish. (56) The introduction of sulfur into the oil darkens the film. The coating is only a temporary protective and is impregnated with a suitable oil. If the oil is constantly renewed the coating gives good protection under corrosive atmospheric conditions.

1.b. Black Oxide (Fe_2O_3, Bluing, Blackening)

Black oxide coatings, commonly called bluing in the firearms industry, are formed by a chemical reaction that produces a conversion coating in the form of rust and offers no protection from oxidation, rather, relying on a protective layer of oil. Some bluing methods have been around since the 1800s. Contrary to general opinion, black finishing steel by use of a single hot bath chemical solution is not very new – some processes have been used since 1910. The black oxidizing of steel at low temperatures was first patented in 1901. (56) World War II gave the system considerable momentum, and helped produce stable mixtures and standardized procedures. Unpolished steel takes a dull, black color, but polished steels, particularly the mild alloys used in rifles, come out a rather good blue-black. Only very limited corrosion protection, under mildly corrosive conditions, is obtained as a result of black oxide coating. There are six types of bluing techniques: rust-bluing, hot-water-bluing, cold-bluing, heat-bluing (AKA fire-bluing), carbonia bluing, and hot-dip-bluing (AKA hot-caustic-bluing).

Rust-bluing involves controlled rusting of the surface with chemical solutions and humid rooms. Back when rifles were rust-blued from the factory each rifle would be rubbed with the rusting solution and then stored in a steam room. The next day the resulting rust would be "carded" or buffed down to blued steel and given the chemical treatment again. This would be repeated for days or weeks until the parts were deemed "blued." Rust-bluing has the same effects and is very similar to browning, but is much more time intensive. The slow rusting process might take anywhere from four to 15 days or more. (33) The process offers more protection than fire-bluing but is labor- and time-intensive. The finish is a very attractive satin blue when the parts are properly polished and the blue applied. One advantage that rust-bluing has over hot-dip bluing is that it does not attack soft solder or epoxy.

Hot-water-bluing was developed in the late 1800s when manufacturers and gun makers started looking for a faster way of obtaining an attractive, durable, rust-inhibiting finish on their firearms. (33) Rust-bluing could take up to 14 days long, while a very satisfactory finish could be obtained using hot-water-bluing in only an hour or two. The hot-water-bluing formulas were jealously guarded by the professional gunsmiths of the day. It seemed that each gunsmith had developed his own formula. Most of the formulas were based on a solution consisting of sodium and potassium nitrates, potassium chlorate, and bichloride of mercury, mixed in distilled water. The hot-water-bluing method is the easiest to setup with the least expense, and is less dangerous than the hot-dip-bluing method that can ruin floor tile, take enamel off the kitchen stove, eat through leather shoes and wool clothes, and cause blindness if any of the hot caustic solution should splash in your eyes.

Cold-bluing is a finishing process that uses a chemical that reacts to the steel and forms a dark deposit on the surface. The majority of cold blues involve some variation of a sulfur reaction to the steel, and some variations use nitric or hydrochloric acid. Successive coats are applied until the desired finish is reached. The cold black oxide process routinely shows color variation from part to part and the black material frequently rubs off in your hands. Cold-bluing does not meet military or automotive specifications, and entails a lot of patience, time, and work. The results are often disappointing because it is one of the hardest types of blue to use properly. This is especially true if an attempt is made to blue the whole gun. This is fine for touching-up worn or scratched areas, but a whole rifle cannot be cold-blued successfully. While you could cold-blue a rifle, the finish would quickly wear off, and the rifle will smell of rotten eggs.

In heat-bluing the parts are placed in a furnace with the appropriate chemical mixtures and carefully brought up to the oxidation temperature of steel, around 316°C (600°F). (54) The parts are soaked in the furnace until the surface has entirely reacted to atmospheric oxygen. The resulting “fire-blue” is very striking. This was previously done by heating the parts with a propane torch or in a furnace to temperatures between 371-538°C (700-1000°F) and then quenching them in oil; varied by repeated dipping in oil and burning off the oil. (55) This method is not suitable for larger parts (those larger than screws) because it is very difficult to obtain an even finish. One area of the part will be of a different temperature than another resulting in a different shade of blue. Heat bluing does not offer much protection. Heat-bluing is not any more durable than the old browning method.

Carbonia-bluing was a method produced by Colt, Smith and Wesson, and some firearm manufacturers prior to World War II. This process required that the parts to be blued be suspended on rods inside a large metal container partially filled with a special chemical in powder form. The metal container was rotated and heated up to (700°F). As the special powder fell on the heated metal surfaces, it produced a deep, lustrous, mirror blue that is often considered to be the finest in the firearm industry. (33) However, the system is a complicated one that requires considerable expense to set up and it is more dangerous to use than most other methods.

Hot-dip-bluing was patented around the turn of the century, but has only been used on firearms for the last 50 years. (33) Hot-dip-bluing is considered the standard of the industry, but by the standards of current coatings and platings, it is hardly effective against corrosion. (55) It is cost effective, fast, efficient, and reasonably durable. Refinishing hot-dip blued firearms is faster and less expensive than re-plating. The particular chemical solution used by a factory or a re-finisher really doesn’t matter. Any hot-dip solution can be used on all carbon steels, including springs. Tossing a stainless part in the solution is a waste of time, as the part will come out looking dirty, not blued. On anything but stainless, all hot-dip methods produce a dark blue, almost black finish. While attractive, this finish will not cover pits or errors in polishing. If neglected, it will quickly rust.

Hot-dip-bluing begins with a dip in a boiling cleaning solution to remove oil, petroleum, wax, and fingerprints from the steel. Then, if necessary, the parts are polished or bead blasted. Next is an acid etching solution (pickling bath) to remove any oils or oxidation accumulated during the polishing. This also removes any remaining blue finish. For hot-dip-bluing, parts are typically submerged/dunked in a boiling alkaline solution of caustic salts heated to temperatures ranging from 132-141°C (270-285°F) for 20-30 minutes. (55) The salt bath is usually comprised of either lye and ammonium nitrate, or sodium hydroxide, potassium nitrate, or sodium nitrate. The reaction between the iron of the ferrous alloy and the hot oxide bath produces a magnetite (Fe_3O_4) on the actual surface of the part. The bluer will adjust the heat of the solution and the time of exposure depending on the alloys of steel involved, the particular chemicals, how fresh they are, and how pure the water is. When they reach the desired color, the parts go into a cold water bath to neutralize the bluing salts. A good finish can be achieved in less than a day, which is much faster than cold-bluing. Hot-dip-bluing has proved more durable than browning, rust-bluing, or fire-bluing.

All of the blacking processes attack lead and epoxy, and destroy soft solders. These processes devour aluminum alloys. It is possible to oxidize non-ferrous metals under suitable conditions to form black oxides. Robar, a gunsmithing company, offers a blackening process specifically for stainless steel. The chrome already in the stainless alloy is oxidized in a chemical treatment solution, resulting in a Chrome-sulfide surface. Since the surface is not plated, the dimensions of the parts are not changed. While not changing the heat-treatment or durability of the steel, the process does increase resistance to corrosion. The stainless steel blackening process is specific to the alloy being treated.

1.c. Color Case Hardening

Case hardening or surface hardening is the process of hardening the surface of a metal by infusing elements into the material's surface, forming a thin oxide layer of a harder alloy. The case hardening process must be regarded as primarily combating wear and erosion rather than conventional chemically induced corrosion.

The process starts by packing the bare frames in a case containing carbon-containing medium, usually bone meal, and heating them in ovens to 760°C (1,400°F) for 2 to 4 hours. (33) The temperature drives carbon from the bone meal into the surface of the iron or steel. To stop the heating, the frames are quenched in clean, soft water, agitated by bubbles, which fixes the carbon to the surface. The colors that result can mottled yet very attractive, due to the variations in the carbon-containing medium. Unfortunately, the hardness only penetrates 127 μm (0.005 inches) below the surface. (33) Longer soaking times in the oven, or higher temperatures, drive the carbon deeper into the surface. The color, however, rapidly diminishes as the carbon penetrates deeper. Nobody uses this process anymore. The heat-and-water-quench warps too many parts making the process too expensive.

Case hardening, as the name implies, is the process of providing a tough and hard outer case of carbon around a soft inner core of iron or mild steel. The depth of the case is usually very thin – one sixteenth inch or less – but this case is the finest of close-grained steel and highly resistant to wear, strain, and impact. It is also highly rust resistant.

Unfortunately, the only authentic way of reproducing case-hardening colors is with the use of cyanide – just about the deadliest poison known – and the methods are certainly not for the home gunsmith. (33) This work should be left strictly to the specialists who know what they are doing and are equipped to safely handle the work.

1.d. Carbonitriding (FeN, gas cyaniding, liquid cyaniding, nicarbing, nitrocarburizing, and Tenifer)

Nitrocarburization is the generic term for these various salt bath nitride processes. Other trade names for nitrocarburization include Tenifer, Melonite, Sursulf, Arcor, Tufftride, and Koline. One of the most popular processes of nitrocarburizing is done in a cyanide-cynate salt bath and is called Tenifer. Tenifer is used by Glock on its firearms. Tenifer is a trademark of Durferrit, a company located in Germany.

Nitrocarburization coatings are used mainly to increase the surface hardness, along with increased corrosion and wear resistance. The surface layer consists of ε-$Fe_{2-3}N$ and γ'-Fe_4N. (58) The nitrogen and carbon content decreases continuously from the edge towards the core, as a result of nitrogen diffusion. The corrosion resistance is also better for iron and conventional steel, but not for stainless steel. Most stainless steels need not be nitrided, since they have chromium to fight against corrosion and rust (this is why we call these metals stainless). Nitriding a stainless steel part will almost always lower the corrosion resistance of the stainless steel; the nitrogen will react with some of the chromium at the surface of stainless steel to form Chromium-nitride (CrN), which is not as corrosion resistant. The true nitrocarburization coatings have a dull-gray color surface, and are never black. In some applications, carbonitride coatings can also be polished to give a bright metal finish appearance. Firearm manufacturers can attain a black appearance with nitrocarburization by applying a phosphate or black oxide coating for aesthetics. These processes are simple, cost effective, and appropriate for parts made of various steels.

The bath is performed in a molten, nitrogen-bearing liquid containing either cyanides or cyanates heated to temperatures ranging from 550-580°C (1022-1076°F). (58) The parts are then quenched in oil, which does not warp parts since the carbonitriding bath temperature are relatively low. The first reaction in the carbonitriding process is carbon-nitride (CN) with oxygen to produce a nitro-carbon-dioxide byproduct plus nitrogen. The simultaneous second reaction takes place when nitrogen is in contact with Iron to form iron-nitride (FeN). The thicker the case, the greater the increase in wear resistance and hardness the part will have. Because the carbonitriding is affecting only the top layers of the steel, and not depositing an additional layer, it does not significantly alter the dimensions of the part.

Previous investigations have shown that a compound layer, ranging from 15 to 20 μm in thickness is formed during the nitrocarburizing process. This layer consists of iron nitrides. Post-oxidized samples contain iron oxide which fills the pores in about the first 5 μm. The coating creates oxygen in the surface layer down to the depth of approximately 6 μm. Finely dispersed particles of iron oxide fill the pores of the carbonitride layer in the depth range up to 5-10 μm. (58) In the same time a compact oxide layer is produced on the surface.

Obviously, gas-nitriding is a simpler process (but not necessarily cheaper) to form a tough wear resistant coating. In this case, pure nitrogen gas is chemically reacted with the metal such as iron by holding the metal in the nitrogen gas environment at high temperature allowing the chemical reaction to take place.

1.e. Phosphating (Parkerizing)

The process of phosphate coating, in use since the late 1800s, found itself refined around 1910 and trade-named Parkerizing. (55) Early developments included the use of zinc phosphate (Coslettizing), manganese dihydrogen phosphate (Parkerizing), and accelerators such as copper or nitrate (Bonderizing). Later, the trade name came into common usage to describe the general process. Parkerizing is a very durable non-reflective finish that changes the surface of steel to a semi-neutral phosphate to provide a considerable resistance to ordinary rust. Parkerization is more durable and resists rusting much better than bluing does. The Parkerizing will absorb oil and protect the metal. Even though it is more practical than bluing, the downside is that Parkerization is not very aesthetically pleasing. While aesthetics are not significant to the military, it is not very appealing to civilian hunters and sportsmen. The military began using this process with their Springfield 1903 service rifles. (33) Parkerizing was used by the military until about 1940, when similar but more modern finishes replaced it to a large extent. (56) Phosphating is also a widely used method of reducing wear on machine elements.

By immersion into an aqueous solution of a dihydrogen phosphate the surface of a metallic part becomes covered with an adherent phosphate layer. Depending on the bath composition the resulting layer is either crystalline or amorphous. (63) Phosphate coatings range in thickness from less than 3 to 50 µm (0.1 – 2 mils). (62) Coatings can be produced with a wide range of thicknesses, depending on the method of cleaning before treatment, composition of the phosphating solution, temperature, and duration of treatment. In phosphating, no electric current is used, and formation of the coating depends primarily on contact between the phosphating solution and the metal surface and on the temperature of the solution. Consequently, uniform coatings are produced on irregularly shaped articles, in recessed areas, and on threaded and flat surfaces, because of the chemical nature of the coating process.

The firearm is first dipped in a cleaning mild acid bath. Once clean, the parts are immersed in a boiling solution of phosphoric acid containing filings of iron and either zinc- or manganese- phosphate. (62) In the process, minute particles of the part's surface are dissolved and replaced by insoluble phosphates which give a gray, non-reflecting and rust-resisting finish. Depending on the particular steel and the precise solution, the surface reacts to form either manganese phosphate or zinc phosphate. The manganese phosphate is a heavier and more durable finish than the zinc. A dull, non-reflecting surface is produced by either, dead-black on mild or carbon steel, gray, green, or blue-black on high nickel alloys or tool steels. As the chemical solution eats into the surface of steel, the process is necessarily limited to exterior parts to prevent damaging the close tolerances of interior moving parts.

Because a rough surface is larger than a smooth one, and provides more area with which the phosphate can react, Parkerizing is best done to a surface that has been bead-blasted or brushed with a coarse wire wheel. After Parkerizing, a firearm is even rougher than it was going into the tanks as any previous polishing gets matted both when the steel is dipped in acid and during the Parkerizing process itself. A tightly fitted pistol may require re-lapping the slide and frame until they slide smoothly. Parkerizing does not require a lot of polishing time like bluing. The newly rough surface traps and holds oil, and an oiled Parkerized surface is very rust resistant. Rather than spend money polishing and bluing parts, manufacturers will Parkerize the parts to eliminate those costs.

Military guns with Parkerized finishes can be blued directly over the Parkerizing for a fairly decent hunting finish. (33) You can then improve this finish by gently polishing the resulting finish with oil. You will then have a tough, rust-resistant finish on your arm that will resemble the more conventionally blued guns. Just polishing Parkerized guns (without bluing) will also improve the firearm's appearance. Just make certain not to polish too hard because you might remove some of the original finish. Use soft wire wheel at about 600 rpm and touch the surface very lightly. Military standards prohibit Parkerizing on carburized or nitride surfaces. (31)

1.f. Anodizing

Anodizing was first used on an industrial scale in 1923. It is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. This process is not a useful treatment for iron or carbon steel because the iron oxide flakes off, constantly exposing the underlying metal to corrosion. Anodizing forms a hardened layer out of the surface layer of the metal, and increases corrosion resistance and wear resistance. The most widely used anodizing specification, MIL-A-8625, defines six types of aluminum anodization: (59)

Type I – Chromic acid anodizing, conventional coatings produced from chromic acid bath
Type IB – Chromic acid anodizing, low voltage process, 22 ±2V
Type IC – Non-chromic acid anodizing, for use as a non-chromate alternative for Type I and IB coatings
Type II – Sulfuric acid anodizing, conventional coatings produced from sulfuric acid bath
Type IIB – Thin sulfuric acid anodizing, for use as a non-chromate alternative for Type I and IB coatings
Type III – Hard Anodic Coatings

Types I, IB, and II anodic coatings are intended to improve surface corrosion protection under severe service conditions or as a base for paint systems. Anodic coatings can be colored with a large variety of dyes and pigments. Types I, IB, and II coatings provide better corrosion protection at higher cost than the chemical conversion systems.

Type IC and IIB coatings provide non-chromate alternatives to Type I and IB coatings where corrosion resistance, paint adhesion, and fatigue resistance is required. Please note that Type IC or IIB may not serve as suitable replacements when the effects of electrolyte entrapment is the primary concern.

Type III coatings, also referred to as hardcoats, is the most expensive type of anodization. It is generally twice the cost of H_2SO_4 anodize and 50% more than CrO_3 anodize. (62) Hardcoats are intended to provide wear and abrasion resistant surfaces with improved corrosion protection due to greater thickness and weight than the conventional anodic coatings. Sealing of Type III coatings is not recommended unless corrosion resistance is also a factor. Wear resistance is reduced by sealing. Anodic coatings form an excellent base for most types of dry film lubricants. Hard coatings may reduce fatigue strength. These factors should be considered in proposed use of parts subjected to cyclic loads. Thicknesses of the heavy Type III coating can be controlled to extremely close tolerances. Anodized coating can be obtained with tolerances of as little as ±2.5 µm (0.0001 in.).

The hardcoat anodize process produces a coating that is normally 50 µm (2 mils) thick, although other thicknesses can be specified. The coating is extremely hard. It is described as file hard (equal to about 60-70 HRC). The color of the class 1 coating ranges from gray to bronze to almost black, depending on the alloy coated, the coating thickness, and the electrolyte temperature. Hardcoat penetrates the base metal for one-half of its thickness and builds above the original base metal dimension for one-half of its thickness. Thus, for a thickness of 50 µm (2 mils) per side, the dimensional change would be 25 µm (1 mil) per side. Commercially available coating thickness tolerances are the greater of ±5 µm or ±10% of the total targeted thickness. (62)

The hardcoat is a naturally porous substance that can be used in many areas in which the bonding or impregnation of other materials to aluminum is needed. This coating bonds very well with paints and adhesives. Also, it can be impregnated with Teflon (polytetrafluoroethylene, or PTFE) and many dry film lubricants to impart lubricating properties to the coating.

Although almost all alloys can be coated, the 6000-series aluminum alloys produce the best hardcoat properties. Regardless of the other type of anodization, high-silicon die castings produce the lowest-quality coatings. Also, because the hardcoat process is sensitive to copper, alloys in the 2000 series should be avoided if possible. Alloys containing copper can be hardcoated, but only a relatively few commercial sources have the ability to coat these alloys with reliability. (62)

Because all of the anodic processes produce porous Al_2O_3 coatings, it is often desirable to seal the coating to close these pores and to eliminate the path between the aluminum and the environment. Sealing involves immersing the coating in hot water; this hydrates the Al_2O_3 and causes the coating to swell in order to close the pores. Conventional sealing is generally done at a minimum temperature of 95°C (200°F) for not less than 15 min. (62) However, because sealing softens the coating somewhat, hardcoat anodization is usually not sealed unless criteria other than hardness have the maximum importance in the finished coating.

Under atmospheric weathering, the number of pits developed in the base metal decreases exponentially with increasing coating thickness. The pits may form at minute discontinuities or voids in the coating, some of which result from large second-phase particles in the microstructure. After the 8½-year exposure, the pits were of pinpoint size and had penetrated less than 50 µm (2.0 mils). Specimens with coatings at least 22 µm (0.9 mil) thick were practically free of pitting. (62)

Sulfuric acid is the most widely used solution to produce Type II anodized coating. Coatings of moderate thickness 1.8 µm to 25 µm (0.00007 to 0.001in.) are known as Type II, as named by MIL-A-8625, while coatings thicker than 25 µm (0.001in.) are known as Type III, or hardcoat. Very thin coatings similar to those produced by chromic anodizing are known as Type IIB. Thick coatings require more process control, and are produced in a refrigerated tank near the freezing point of water with higher voltages than the thinner coatings. Hard anodizing can be made between 25 and 150 µm (0.001 to 0.006 in.) thick. Anodizing thickness increases wear resistance, corrosion resistance, ability to retain lubricants, and electrical and thermal insulation. In typical commercial aluminum anodization processes, the aluminum oxide is grown down into the surface and out from the surface by equal amounts. So anodizing will increase the part dimensions on each surface by half of the oxide thickness.

Before being anodized, wrought alloys are cleaned in either a hot soak cleaner or in a solvent bath and may be etched or brightened in a mix of acids. The anodized aluminum layer is grown by passing a direct current through an electrolytic solution, with the aluminum parts serving as the anode (the positive electrode). The current releases hydrogen at the cathode (the negative electrode) and oxygen at the surface of the aluminum anode, creating a build-up of aluminum oxide. Alternating current and pulsed current is also possible but rarely used. The voltage required by various solutions may range from 1 to 300 V DC, although most fall in the range of 15 to 21 V. Higher voltages are typically required for thicker coatings formed in sulfuric and organic acid. The anodizing current varies with the area of aluminum being anodized, and typically ranges from 0.3 to 3 amperes of current per square decimeter (20 to 200 mA/in^2). The film thickness can range from under 0.5 micrometers for bright decorative work up to 150 micrometers for architectural applications. The anodized surface is porous, and often filled with colored dyes and/or corrosion inhibitors before sealing. Because the dye is only superficial, the underlying oxide may continue to provide corrosion protection even if minor wear and scratches may break through the dyed layer.

Depending on the dye used near the end of the process, you can have aluminum anodized a whole series of colors, including the ever-popular black. Multi- color anodizing has also been accomplished by dying the part with the lighter color first and then masking the off the light color to dye it with a darker shade. There have been successful attempts at achieving a camouflage pattern on AR15 receivers. When hard-anodizing aluminum, it is very difficult to obtain uniform coloring. (60) Since aluminum parts contain various different alloys, they may accept coloring differently. Aluminum parts in the same lot may experience slight variations during the heat treatment process, which can also cause color variation. Even identical parts colored at the same time in the same vat may have color variations depending on their location within the vat. To make parts match, parts must be anodized together and then matched by hand. This is an additional time consuming and costly task. Over time and under use, however, anodizing will fade. An aluminum frame being re-anodized must have all of the steel parts removed, or they will contaminate the chemical solutions.

II. Metalic Coatings

2.a. Gold Plating

Gold plating offers no durability and is flashy, expensive, and very soft. Since it is highly electropositive, it offers little electrochemical protection to the base metal. The resistance of gold to chemical attack and tarnish makes it a particularly desirable metal for a corrosive environment. In very expensive custom firearms, gold can be inlaid into the surface of the steel. As inlaid wire gold is slightly more durable. The most frequent use for gold plating is on small parts of a presentation handgun, to accentuate the bluing of the frame, slide, barrel, cylinder, or other larger parts.

2.b. Nickel Plating

Near the middle of the 19th century, nickel began showing up as a protective finish. First available in mirror-bright, and later in brushed or bead-blasted, nickel finishes did offer protection from corrosion. Because some shooters desire a shiny finish, nickel is available from refinishing shops. Even properly done, electrolytic nickel can peel and crack away from the underlying steel. Some solvents may cause the nickel finish to flake or crack.

Electrolytic nickel plating is a complicated and costly process, involving electricity, expensive chemicals, and the expensive disposal of those chemicals when exhausted. A firearm that isn't plated properly will easily chip or flake. Firearms manufacturers gradually phased out nickel, replacing the finish with stainless steel.

Military standards specify that nickel plating shall be used for the following applications only: (31)

1. Where temperatures do not exceed 538°C (1,000°F) and other coatings would not be suitable
2. To minimize the effects of crevice corrosion with unplated corrosion-resisting steel or stainless steel in contact with other stainless steel.
3. As an undercoat for other functional coatings.
4. To restore dimensions by rebuilding worn surfaces.
5. For resistance to sand erosion.

2.c. Electroless Nickel

Electroless nickel plating is used to deposit nickel without the use of an electric current; thus it is sometimes called autocatalytic plating. Electroless nickel is a definite improvement over the nickel plating process. It offers a matte finish with a slight gold or yellow tinge to it instead of the old bright nickel. Electroless nickel starts off as a heated solution containing nickel, and chemically deposits a very uniform coating. Most electroless nickel plating is done by exposing a catalytic surface to a solution consisting of nickel salt, a reducing agent (sodium hypophosphite, to provide anions for the chemical reaction), and an organic acid to control the reaction rates, pH of the solution, and the concentration of the nickel ions to prevent deposition of nickel phosphate. (31) When the solution is driven through the proper temperature ranges, the nickel precipitates onto the firearm. Electroless nickel does not build up the slightly thicker deposits on corners and edges that electrically-driven plating processes such as hard chrome can. Properly applied electroless nickel plating will not peel away from the underlying steel, even if the part is bent through 180°.

Electroless plating baths have been developed for copper, nickel, silver, gold, and a number of other metals, but the systems with the most importance for corrosion and wear applications are the nickel-phosphorus and nickel-boron systems. The part acts as a catalyst for the reduction of the nickel ions by the reducing agent. The reducing agent causes the metal ion reduction and the nickel coating on the part continues to act as a catalyst as the plating process continues, unlike in electroplating where the ions pick up electrons from the cathode. When the process takes place using a hypophosphite-reducing agent, the finished nickel coating is not pure nickel, but contains phosphorus inclusions. Phosphorus content can be as high as 13%. When the process takes place using a borohydride compound reducing agent, the finished product is a nickel-boron alloy. The boron content can be as high as 5%. (31) Nickel-boron coatings have excellent resistance to wear and abrasion, but because they are not completely amorphous they have reduced resistance to corrosive environments. Furthermore, there are much more costly than nickel-phosphorus coatings. (31) When electroless nickel is used for corrosion protection or wear resistance, the minimum thickness shall be 38 μm (0.0015 in.) and the maximum thickness shall not exceed 76 μm (0.003 in.).

As deposited, the microhardness of electroless nickel-phosphorus coating is about 500 to 600 HVN (48-50 HRC), equivalent to many hardened steels. After precipitation hardening, hardness values as high as 1100 HVN are reported, which is equivalent to commercial hard-chromium coatings. Because of their high hardness, electroless nickel coatings have excellent wear and abrasion resistance in both the as deposited and hardened condition. (31)

Electroless nickel coatings can be easily soldered and are used in electronic applications to facilitate soldering of light metals such as aluminum. Electroless nickel is often used as a barrier coating; to be effective, the deposit must be free of pores and defects. In the as-deposited amorphous state, the coating corrosion resistance is excellent, and in many environments is superior to that of pure nickel or chromium alloys. However, after heat treatment the corrosion resistance can deteriorate. (31)

2.d. Electroless Nickel and Teflon (NP3)

NP3 is a surface treatment for steel and metal alloys that combines sub-micron particles of PTFE (polytetrafluoroethylene), otherwise known as Teflon, with electroless nickel. A company called Robar developed a process that combines electroless nickel with Teflon, which Robar calls NP3. The coating combines sub-micron particles of Teflon throughout the plating. If the nickel wears, fresh Teflon-bearing surface is exposed. The plating is extremely even, and only 5.08 μm (0.0002 in.) thick. (55) The finish is a silver-gray and shows the texture of the base metal. If you have the surface of your handgun sandblasted, you will end up with a dark gray finish. The Teflon trapped in the nickel results in a very low coefficient of friction. Oil is not required for two contacting NP3 coated surfaces. Although, oiling parts reduces the cleaning time of your firearm, which only requires a simple wipe-clean operation. NP3 is black in color and has a surface finish that is reflective and slippery.

The application of NP3 is auto-catalytic, that is, not requiring any form of electricity. This process is preferable to standard electrolytic plating as all active surfaces are evenly plated. With the PTFE evenly distributed and locked into the nickel-phosphorus matrix, NP3 is a true composite. If wear occurs, fresh particles of PTFE are exposed to keep the opposing surfaces lubricated throughout the life of the coating. NP3 has a micro hardness of 48-51 Rockwell as plated (nickel matrix). NP3 also has a lifetime warranty against peeling and flaking, since its adhesion is generally between 30 to 60 kpsi (compared to chrome's adhesion between 12 to 15 kpsi).

2.e. Chromium Plating (Hard Chrome)

Invented around the middle of the 19th century, but not perfected until the early 1900s, hard chrome is an electrochemical deposition of chromium on the surface of ferrous alloys. Using the same metal as decorative chrome, hard chrome was developed to plate the cutting edges of milling and drilling tools, affording them longer life in industrial applications. Hard chromium coatings are used for hydraulic pistons and cylinders, piston rings, aircraft engine parts, and plastic molds, where resistance to wear, heat abrasion, and/or corrosion are required. (31) When hard chroming had grown common enough in the mid- to late 1970s, firearm owners started treating their handguns. If military applications require the firearm's color to be subdued, use special purpose paint or use Robar's Stainless Steel Blackening once the firearm is plated to hide the reflective chrome.

Hard chrome is a bright silver-colored plating with a thickness of less than 25.4 μm (0.001 in.), commonly 10.2 μm (0.0004 in.), is very stark. Chromate conversion coatings are formed by a chemical or an electrochemical treatment of metals or metallic coatings in solutions containing hexavalent chromium (Cr^{6+}) and, usually, other components. The process results in the formation of an amorphous protective coating composed of the substrate, complex chromium compounds, and other components of the processing bath. Any flaw left behind while preparing the surface will be very apparent. The bond is so strong that a blow hard enough to dent the underlying steel will not cause the chrome to separate. When properly done, hard chrome will not crack, chip, or flake. To repair worn chrome plating requires stripping the whole rifle in an acid bath and re-plating it. Chromium processes are widely used to finish aluminum, zinc, steel, magnesium, cadmium, copper, tin, nickel, silver, and other substrates. (62)

In many regards hard chrome comes very close to being an ideal firearms finish. Although it is not the ultimate in corrosion resistance, (steel will rust through, though very slowly), it is very popular with competitors whose firearms see a lot of use. The high resistance to oxidation is normally attributed to the formation of an insoluble oxide which renders the metal passive. In the passive state chromium is cathodic to the above basis-metals, so that porosity in this case is again a limiting factor. (57) Porous coatings rapidly show rust spots. An important advantage of copper or nickel undercoats is that they may be far more readily polished than steel. Hard chrome also has a very low coefficient of friction, and two chromed surfaces sliding on each other rub less than two steel pieces do. The harder surface and decreased friction greatly increase the service life of any moving parts. Despite the cost and the looks, hard chrome is one of the most protective finishes you can apply to a rifle.

Hard chrome tends to form cracks, which allows combustion gases to wash through and erode the substrate material. This leaves a pit in the substrate with horizontal extensions that cause separation between the coating and the substrate. The erosion traversed along the interfacial boundary, essentially debonding the substrate from the coating. Many materials in the eroded region have been identified and include sulfur, oxygen, and talc, which are from the propellant additives. (67) Sulfur, which penetrates deeply into the eroded pits, comes from the black powder igniters and potassium sulfide flash suppressants used in the charges. The chemical reactions between the propellant products and the substrate gun steel in this interfacial region are primarily caused by the temperature of the substrate. If the substrate material is separated from the coating by a gap, then one of the heat transport mechanisms (conduction across the interface) is interrupted.

The disposal of spent solutions and rinse waters requires waste treatment. Hexavalent chromium must be reduced to Cr^{3+} before neutralizing and precipitation. Sodium pyrosulfite ($Na_2S_2O_5$) is usually used as the reducing agent in smaller operations, while for larger plants, sulfur dioxide (SO_2) is preferred for economic reasons. Wastewater treatment sludges from chromating operations are considered hazardous waste. As a result, the use and disposal of chromium and chromium compounds have received much regulatory attention because of the toxicity of chromium and indications that it is a cancer-causing agent. Due to worker health and safety concerns, alternatives to chromate conversion coatings are being sought. Firing trials are cited where barrels coated with chromium using metal-organic chemical vapor deposition (MOCVD) showed improved erosion resistance, compared to those coated with electrodeposited chromium. (52) Unfortunately, MOCVD chrome plating is still in the trials phase and there are currently no drop-in substitutes to chromate conversion coatings that adequately match their corrosion resistance, adhesion, and wear resistance. (62)

2.f. Black Chrome

Back in the 1980s, black chrome was thought to be the next, great leap forward in firearms finishes. With a black chrome finish, it was thought, shooters could have the durability of hard chrome and the black color of bluing. Unfortunately, black chrome is not very durable. It does not reach into the internal spaces of a handgun, so the magazine well of a pistol may not be fully blackened. While the jet-black finish is quite attractive, for the same durability, at a lower cost, and the ability to patch-repair the finish, you are better off with a baked-on epoxy.

2.g. Thin Dense Chrome (TDC)

Thin dense chrome (TDC) was first introduced in 1957. (68) The TDC plating process is an alternative to standard chrome plating, which may develop small cracks. Unlike chrome plating, TDC is so thin it does not build up enough internal stress to cause cracking and therefore has good corrosion resistance. Compared to standard hard chrome processes, TDC offers better adhesion, corrosion resistance, and surface hardness.

It uniformly deposits a dense, high-chromium, non-magnetic alloy on the surface of any metal without measurably changing the thickness of the base metal. The plating can be applied in thickness ranges from 0.635 to 12.7 μm (0.000025 to 0.0005 in.) and are uniform to within ±0.625 μm (0.000025 in.). (68) The electro-deposition takes place in a special fluoride bath heated to approximately 140°F, and is applicable to all ferrous and nonferrous metals without causing distortion. The plating exhibits no build-up on corners or sharp edges.

2.h. Thin Dense Chrome with Diamond Particles (XADC®)

In 1997, the Armoloy Corporation created a metal coating harder than thin dense chrome called XADC. It is based on technology developed by the Soviets during the cold war era. This diamond-chrome coating eclipses the normal life expectancy of metal surfaces subjected to extreme wear, abrasion, and corrosive stress. XADC will adhere and perform well on all major ferrous and nonferrous metals with the exception of aluminum, magnesium, and titanium. XADC offers good durability, lubricity, adhesion, and resistance to abrasion. XADC outperformed standard hard chrome, electroless nickel, and titanium nitride in wear tests. (68)

XADC coating incorporates perfectly spherical and extremely dense "Ultradiamond" composite particulate in an evenly dispersed form, to achieve hardness measurements exceeding 98 R_C. In addition, the coefficient of friction is 20% lower than that of the TDC coating. XADC will not fracture from the substrate unless the metal substrate itself fractures or fatigues. XADC withstands temperatures from -240°C to 870°C (-400°F to 1600°F). At temperatures above 1200°F, XADC will react with certain materials such as carbon monoxide, sulfur vapor and phosphorus. Temperatures above 1800°F are not recommended. Tests have shown that XADC provides corrosion resistance exceeding that of 440C stainless steel.

2.i. Low Temperature Iron Titanate (LTIT)

In 1997 Low Temperature Iron Titanate (LTIT) was made by Adiabatics, Inc., with the support of the US Army Tank Automotive Research & Development Engineering Center. This bore coating is a ceramic composite consisting primarily of iron oxide, iron titanate, and partially stabilized zirconia. (69) This coating is tailorable by the level of metal powder to iron oxide / iron titanate powder is in the coating mixture. The iron oxide has previously been shown to provide an excellent wear surface over a wide range of temperatures. Iron titanate being softer yet comprised of iron oxide and titanium dioxide has been shown to yield a coating that has a significantly lower friction coefficient yet not the low wear rate of iron oxide alone. (69) This coating is not currently commercially available, and the deposition method is still under development for commercial application.

III. Polymer Coatings

3.a. Paint

Paint is any liquid, liquefiable, or mastic composition which after application to a substrate in a thin layer is converted to a solid film. The broad category of paint includes various paints, varnishes, and enamels that have long been used as protective coatings for metals. These coatings may be used for their esthetics or to help shield a more protective coating, but offer poor protection for the metal substrate.

Liquid-applied organic coatings have four basic components: a resin, a solvent, pigments, and other miscellaneous compounds. The resins, often called binders, are identified by their generic type. The pigments are added for such functions as rust inhibition, decreased permeability, to provide color, or to increase resistance to ultraviolet light or weathering conditions. Miscellaneous compounds added include dryers, flow-control and floss-control agents, and suspension agents. Although the resin or organic binder of the coating material is most influential in determining the resistance and properties of the paint, the type and amount of pigments, solvents, and additives will dramatically influence the application properties and protective capability of the coating system. (62)

Paints are generally too thick to be used on many moving parts with close tolerances. Esthetic coatings that do not meet the desired performance characteristics of this experiment, but these coatings perform well as exterior coatings to subdue or camouflage a firearm. There are several popular consumer products used for home refinishing, such as Duracoat by Houts Enterprises. Artistically inclined individuals have used these types of coatings to applying a multi-colored camouflaged pattern. These types of coatings are usually protected with two coats of non-glare polyeurethane finish, and can be easily reapplied to worn areas.

Varnishes normally consist of a resin dissolved with a drying oil, a thinner or solvent, and sometimes pigment. Varnish finishes are usually glossy, but may be designed to produce satin or semi-gloss sheens. They are not heat resistant enough to be used on firearms, and their gummy nature makes them unsuitable for internal moving parts.

Enamels have a tendency to crack or shatter when the substrate is stressed or bent. Enamels are divided into two main classes, organic and vitreous. Organic coatings are employed for their resistance to wear and corrosion. Vitreous coatings are employed for their resistance to heat and corrosion. Vitreous enamel is the colorful result of fusing powdered glass to a substrate by firing, usually between 750° and 850°C. Historically, enamels have been primarily used as a decorative coating for pottery, statues, and jewelry. However, enamels have been used as protective coating for signs, exterior household appliances, interior oven walls, and cooking pots.

Military standards prohibit applying any paint-type coatings to "functional, working, or wearing surfaces; to lubricated surfaces; to adjustable screw threads; to lubrication or drain holes; to bearing or sliding surfaces; to areas where they could be rubbed or scraped onto surfaces that must be clean and bare to function properly; or to any other surface where the application of the coating may cause malfunction of the part or system." (61)

3.b. Phenolic Resin

Phenolic resin coatings have a base of phenolic resin with molybdenum disulfide suspended in it. There are several popular consumer products used for home refinishing, such as KG Gun Kote by KG Industries and Moly Resin by John Norrel Arms. The resin is sprayed (from an aerosol can) onto the metal that has been heated to 180ºF and then baked in an oven for half an hour at 300ºF. This creates a tough coat on the metal that is similar in appearance to parkerized metal. A material identical to Gun Kote is often used by the Navy and Marines for refinishing their M16 rifles. (27)

3.c. Nylon

Nylon, one of the most common polymers, was discovered in 1935 by Wallace Carothers at DuPont. Nylon is the generic name for a family of thermoplastic polyamide resins. All these resins are related, but not identical, in chemical composition. By definition, a nylon is any long-chain synthetic polymeric amide which has recurring amide groups as an integral part of the main polymer chain and can be formed into filaments in which the structural elements are oriented in the direction of the axis. It can be reinforced and filled with fiberglass, graphite, molybdenum disulfide, and other materials to improve its friction and other properties. Nylon parts can operate continuously at 121°C(250°F), and for short periods up to 204°C (400°F) under light loads. Nylon is a thermoplastic material – it melts on heating and re-solidifies on cooling. Unlike most other thermoplastics, however, nylon has some degree of crystallinity, so that it has a relatively sharp melting point. It does not soften gradually when approaching its melting point, but it remains rigid, although with decreasing stiffness. Rapid cooling from the melt causes the formation of the amorphous form, whereas slow cooling produces high crystallinity. Articles with high crystallinity have superior hardness, stiffness, and dimensional stability, whereas articles that are highly amorphous are more flexible, have better impact strength, and are more transparent. The average coefficient of friction of Nylon ranges from 0.15 to 0.33 without any lubricant.

Fiberglass, molybdenum disulfide (MoS_2), graphite, and other fillers are added to overcome some of the deficiencies of unfilled nylon. Fiberglass is the most common addition for improving mechanical properties. Molybdenum disulfide is also used as filler in nylon to improve its wear, abrasion resistance, and frictional characteristics. Flexural strength, modulus, and heat resistance are also improved. The presence of MoS_2 promotes solidification and crystallite formation during molding of nylon.

Nylon powders can be precipitated from solution and subsequently pressed and sintered by a process somewhat similar to powder metallurgy. Sintered nylon parts can be impregnated with oil to maintain up to 25% of fluids by weight and provides a coefficient of friction of 0.01. Accelerated wear tests show the superiority of sintered nylon over injection molded nylon in friction and wear. Sintered nylon is used in cams, slides, rollers, bearings, and other parts subject to wear in business machines, automotive equipment, aircraft instruments, and textile machinery.

Sintered nylon was originally conceived as a practical means for reducing the dimensional instabilities found in injection-molded polyamides. Because of its higher crystallinity as compared with injection-molded nylon, sintered nylon has superior frictional and wear qualities and higher compressive strength, although its tensile strength, elongation, and impact strength are lower. Precipitation from high-temperature solution gives a powder that has a relatively high percentage of crystallinity, usually about 80%. Whereas injection molded nylons have an average crystallinity of about 43%.

3.d. Polytetrafluoroethylene (PTFE, Teflon)

Teflon is made from poly(tetrafluoroethylene) (PTFE), which is a synthetic fluoropolymer. Teflon was patented in 1941 and later sold to the DuPont company. Teflon films produced from aqueous dispersions were developed at the US Naval Research Laboratory as dry-film lubricants and protective coatings for weapons, ammunition cartridges, aircraft parts, and submarine parts. (18) It was not until the 1970s that Teflon started appearing on handguns. The process has improved greatly in the years since. Teflon can be applied to both stainless and carbon steel, but it should not be applied to internal moving parts. Teflon forms a thicker layer than typical metal plating, and this can cause problems with tightly fitted parts. Teflon will not be rubbed off by sliding wear, as bluing does. Since Teflon is applied with an airbrush, different colors can be used. Once baked on, the finish protects while it hides.

Teflon is a fluorocarbon, which are essentially hydrocarbons in which all or nearly all of the hydrogen has been replaced by fluorine. Fluorocarbons are thermoplastics. Their most noteworthy characteristics for applications involving friction and wear are their very low coefficients of friction and good resistance to heat. They can be used from ~232°C (450°F) to about 260°C (500°F). (18) According to DuPont its melting point is 327°C (620.6°F), but its properties degrade above 260°C (500°F).

PTFE's coefficient of friction is 0.1 or less, which is the lowest of any known solid material. (62) A value of 0.04 is usually quoted for its coefficient against steel, and a value as low as 0.016 has been reported for very high loads. PTFE also has a resistance to van der Waals forces, which means that it is the only known surface to which a gecko cannot stick. The low friction of PTFE has been attributed to its low adhesion to the mating surface, the low shear stress needed to overcome adhesion at the interface, and to its ability to transfer on the bare surfaces resulting in PTFE versus PTFE contact. (39)

In actual practice, thin films of PTFE are transferred to surfaces sliding against it until the other surfaces are covered with it, so that the true condition is that of PTFE sliding against PTFE. At slow speeds (or high temperatures), the low friction of Teflon is associated with the formation of a thin, highly oriented transfer film of Teflon between 100 and 400 Å thick. The high friction at high speeds (or low temperatures) is associated with the transfer of relatively large fragments of Teflon. Teflon undergoes a phase transition at room temperature; below room temperature its friction can be about one-half of the value above room temperature. The molecular structure of PTFE prevents bonds from forming across the interface of a contacting surface, and shearing takes place along the surface. Another explanation is that the low friction is related to the intrinsically low adhesion between the PTFE molecular chains or transfer films together with a relatively high bulk shear strength due to interlocking between rigid chains in the bulk of the plastic. (18) Another mechanism of the reduction in friction is the formation of a PTFE-transfer film on the surface of the counterpart. (49)

Considering the coefficient of friction of high load composites, PTFE is usually more effective as a solid lubricant addition than MoS_2 provided the temperatures remain at less than about 250°C. This is probably due to the fact that the coefficient of friction decreases with increasing temperature for PTFE as a consequence of the reduction in shear strength; the friction also decreases with increasing load. This is probably due to the third body film being generated on the harder substrate by the sliding process. (34)

The use of a phosphate treatment on steel substrates is also reported to improve the wear life of sintered Teflon films. Porous, hard anodized coatings on aluminum have been impregnated with Teflon to combine the lubricity of the fluorocarbon with the hardness and abrasion resistance of the anodized coating. Materials are available that are essentially porous metal compacts impregnated with fluorocarbon resin. These materials provide a film of the fluorocarbon at the surface. One of their obvious advantages is that the metal body provides a hard substrate with good thermal conductivity for dissipating frictional heat. Also, the pores provide means for storing the fluorocarbon, so that additional lubricant is available after the surface layers have been worn away. (18)

Adding glass fiber, bronze, and carbon filler to PTFE were found effective in reducing the wear rate, reducing the cold flow, increasing the load-bearing capacity of the PTFE composite. At the same time, wear rates are reduced by factors of several thousand, while the filled composites retain the same low friction as the unfilled resins. As a result, filled fluorocarbons are superior in friction and wear to any other plastic bearing material within their operating range. Glass fiber is the most universally used PTFE filler; it has the least effect on chemical and electrical properties, and it has the lowest coefficient of friction and best wear performance under various loads and speeds. (47) Graphite and molybdenum disulfide help to reduce the initial wear and starting friction, in addition to improving the mechanical properties. (18) PTFE + 10 vol% bronze + 10 vol % CF exhibits an excellent wear resistance. (49) Bronze and bronze/graphite are particularly good filler material at cryogenic temperatures. Lead and lead oxide improve wear resistance at elevated temperatures, and ceramics such as ZrO_2 or aluminum silicate which improve the cold flow and high temperature deformation under load. (39) The addition of bronze improves significantly the tribological properties of the composite because of its outstanding thermal conductivity.

A Teflon finish can be used in applications where other finishes will not work. A revolver with an aluminum frame, for example, cannot be otherwise plated. Solutions to plate the aluminum will attack the steel pivot pins of the hammer and trigger, as well as the steel barrel and cylinder. Solutions to plate the steel will dissolve the aluminum frame. Before Teflon, plating a gun like this required prying the steel parts out and reinstalling them later.

Brownells sells their Telfon/Moly Oven Cure Gun Finish in a variety of colors. It comes in an aerosol can and is sprayed on after degreasing and abrasive-blasting the part, then baked in a regular kitchen oven at 177°C (350°F) for 30 minutes.

3.e. Epoxy (Polyepoxide, Roguard)

Epoxy or polyepoxide is a thermosetting epoxide polymer that cures (polymerizes and crosslinks) when mixed with a catalyzing agent or "hardener". Epoxies provide the needed durability that paints do not provide. A reaction between two or more chemicals, epoxy forms a tough and lasting coating. The epoxy finish for a handgun doesn’t fade, and is very scratch- and chip-resistant. Epoxy coatings only come in one color, black. The commercial applications will go on in a layer only 25.4 µm (0.001 in.) thick, so you do not lose any markings that are on the slide, frame, or receiver. (55) They are not as hard or abrasion resistant as metallic coatings, but they are more wear resistant than bluing or Parkerizing.

One of the popular epoxy finishes that has shown the best results is Roguard, from Robar. Roguard is a molybdenum-disulfide based polymer finish which is sprayed on a Phosphate base and then baked to cure. It is specifically designed to provide lubricity and corrosion protection. Roguard has a lifetime warranty against peeling and corrosion. Other epoxy finishes are Enduracoat by Accurate Plating, and Tech-Kote by Spradlins. Do-it-yourself epoxy finishes are available, but there are two drawbacks to baking on your own finish: the smell and the need to have an oven large enough to hold long parts, such as the barrel.

IV. Ceramic Coatings

4.a.i. Nickel Boride (Ni_2B, Ni_3B)

Nickel Boride has been used in aerospace technology, engine parts, hydrodynamic propulsion systems and military rocket sled testing. The well bonded and wear-resistant coating has a low friction coefficient that eliminates the need for lubrication, decreases galling, and significantly increases hardness and firearm lifespan. The mil-spec parts are dipped in baths through which the alloy/ceramic Ni_3B coating is autocatalytically and uniformly deposited on surfaces. This creates a considerably smoother surface texture and resistance to corrosive environments. Key wear areas are polished to improve function and further reduce friction, decreasing heat. Cleaning and maintenance requirements are significantly reduced. UCT Coatings has introduced Ni_3B coatings, which it calls EXO Technology, into its “Fail Zero” line of bolt carrier assemblies, hammers, and upper receivers.

4.a.ii. Titanium Diboride (TiB_2)

Titanium diboride (TiB_2) is an extremely hard ceramic compound composed of titanium and boron that has excellent corrosion resistance at high temperatures and very good wear resistance. It does not occur naturally in the earth. Many TiB_2 applications are inhibited by economic factors, particularly the costs of densifying a high melting point material. Current use of this material appears to be limited to specialized applications in such areas as impact resistant armor, cutting tools, crucibles and wear resistant coatings. It is also used as an inoculant to refine the grain size when casting aluminum alloys.

Thin films of TiB_2 have a wide range of potential industrial applications due to the wear and corrosion resistance properties that TiB_2 can provide to a cheap and/or tough substrate. The electroplating of TiB_2 layers possess two main advantages compared with plasma (PVD, CVD) methods: the growing rate of the layer is 200 times higher (up to 5 $\mu m \cdot s^{-1}$) and the inconveniences of covering complex shaped products are dramatically reduced.

Due to the small dimension across the TiB_2 nanocolumns, nucleation and glide of dislocations is inhibited during hardness indentation measurements while the high cohesive strength of the thin boron-rich tissue phase prevents grain boundary sliding. Together, these two effects explain the observed superhardness of boron-rich TiB_2 layers. (69)

4.b.i. Boron Carbide (B_4C)

Boron carbide (B_4C) is an extremely hard ceramic material. It is the fifth hardest material known behind boron nitride, diamond, ultrahard fullerite, and aggregated diamond nanorods. While it is exceptionally hard and has good wear resistance, it is very poor at corrosion prevention. Boron carbide is now produced industrially by the carbo-thermal reduction of B_2O_3 (boron oxide) in an electric arc furnace.

B_4C films are characterized by high hardness and stress resulting in excellent wear resistance, however, they show relatively high friction coefficients of 0.3-0.4. After annealing at 800°C, reduced friction coefficients of 0.03-0.05 due to oxidation of B_4C can be obtained. The low-friction mechanism is based on the reaction of the B_2O_3 with ambient humidity to form a thin boric acid (H_2BO_4) film. The low friction coefficients of boric acid are associated with its layered triclinic crystal structure. The layers consist of closely packed and strongly bonded boron, oxygen, and hydrogen atoms, but the layers are widely separated and attracted by van der Waals forces only. During sliding, these atomic layers can align themselves parallel to the direction of relative motion and slide easily over one another. Above ~170°C, boric acid tends to decompose, thus losing its layered crystal structure and hence its lubricity. The use of boric acid as a low-friction coating is also limited to reasonably humid conditions, precluding its use in dry environments. (69)

4.b.ii. Silicon Carbide (SiC)

Silicon Carbide (SiC) is one of the important refractory materials being used as a structural ceramic in advanced propulsion systems. The high hardness, and sufficient toughness, give an excellent abrasion resistance. Depending on the environmental conditions, SiC may be a promising material for a sliding surface since it combines high hardness and chemical inertness with high thermal conductivity, which is important at high sliding velocities. (63) Wear rates during testing were relatively low in some environments and showed that wear was almost independent of sliding velocity.

The friction coefficient of SiC riders sliding on the precipitation-hardened nickel-base-alloy Inconell 750 at a velocity of 9 m/s (1770 fpm) decreased steadily from 0.4 at 25°C to 0.2 at 930°C. (34) The coefficient of friction of SiC in unlubricated sliding contact ranged from 0.5 to 0.8. (64) Experiments using SiC in unlubricated sliding contact showed that tribo-oxidation and surface fracture were identified as the dominating deterioration mechanisms. (64) The tribochemical instability has a potential to disturb the otherwise favorable SiC/SiC applications. Since the compound is metastable in air, surface oxidation and the formation of silicon-based wear debris will dominate the wear behavior of silicon carbide sliding unlubricated on itself, or against another hard surface, in the presence of oxygen. Under sliding conditions that create SiO_2 tribo-oxidation products, the friction and wear remain at a level reasonable for unlubricated systems. If the access of air into the sliding interface is restricted and if the surface temperature due to frictional heating is high enough, reactions producing SiO wear debris may take place, leading to increased wear and friction. (64) If the access of air into the sliding interface is restricted and access of air into the sliding interface is restricted and if the surface temperature due to frictional heating is high enough, reactions producing SiO wear debris may take place, leading to increased wear and friction.

4.b.iii. Tungsten Carbide (WC)

Philco-Ford publishes the report "Process Development and Characterization of Chemical Vapor Deposited Tungsten for Gun Barrel Applications." A 20-month program was conducted to develop improved chemical vapor deposition (CVD) processes for applying tungsten to the bores of gun barrels, and further, to characterize the physical and mechanical properties of the CVD tungsten as deposited. Conventional and high strain-rate tensile and compression tests were conducted on CVD tungsten as deposited on 4150 steel at temperatures of -65°F, ambient, and 200°F. Density, thermal expansion, and thermal conductance measurements were also made. Barrel materials of CG-27, L-605, 718, and Pyromet X-15 were also investigated. Based on test firings, acceptable CVD tungsten adherence was demonstrated on 4150, but the other four alloys revealed only marginal quality. Fourteen MG3 test barrels of the five materials (chambered in .220 Swift) were fabricated and delivered to the USAF.

4.c.i. Boron Nitride (h-BN, c-BN)

Boron nitride (BN) is a binary chemical compound, consisting of equal numbers of boron and nitrogen atoms. Cubic boron nitride has the second highest hardness next to diamond, high thermal conductivity, and high chemical and thermal stability. The major disadvantage of c-BN coatings is high internal residual stress. (73) Boron nitrides exists as various polymorphic forms, one of which is analogous to diamond and one analogous to graphite. The graphite-like polymorph is a useful lubricant and the diamond-like polymorph is one of the hardest materials known. Although BN has better thermal stability than MoS_2 or graphite, its use is rather limited because it is difficult to bond it to substrates. (39) It is also chemically inert and thermally inert with iron and iron-based alloys, unlike CVD diamond.

Hexagonal boron nitride (h-BN) is a common solid-lubricant due to its easily activated hexagonal shear systems with possible application temperatures up to 770°C (1418°F). (42) h-BN is the graphite-like polymorph of boron nitride. The hexagonal polymorph is composed of layers of hexagonal sheets, analogous to graphite. Hexagonal BN is a lubricant at both low and high temperatures (up to 900°C). Thin films of boron nitride can be obtained by chemical vapor deposition from boron trichloride and nitrogen precursors. Industrial production is based on two reactions: melted boric acid with ammonia, and boric acid or alkaline borates with urea, guanidine, melamin, or other suitable organic nitrogen compounds in nitrogen atmosphere. The combustion of boron powder in nitrogen plasma at 5,500°C yields ultrafine boron nitride, which is used in lubricants and toners. The h-BN compound can be included in ceramics, alloys, resins, plastics, rubbers and other materials, giving them self-lubricating properties. The lack of self-lubricating properties remains largely unexplained.

Cubic boron nitride (c-BN) is insoluble in iron, nickel, and related alloys at high temperatures, whereas diamond is soluble in these metals to give carbides. Polycrystalline c-BN abrasives are therefore used for machining steel, whereas diamond abrasives are preferred for aluminum alloys, ceramics, and stone. Low-pressure deposition of thin films of cubic boron nitride is possible using ion beam deposition, plasma enhanced chemical vapor deposition, pulsed laser deposition, reactive sputtering, and other physical vapor deposition techniques are used as well. Commercial products are known under names "Borazon" (by Diamond Innovations), and "Elbor" or "Cubonite" (by Russian vendors). The c-BN film has a higher wear resistance compared to amorphous and hexagonal BN films. (73)

Boron nitride is competing with diamond and silicon carbide in most applications, including friction-reducing coatings. As for diamond a wide variety of synthesis methods are being used, and boron nitride can be grown in many phases. The cubic phase chemically and thermally inert and is the most desirable phase for applications, because c-BN is second only to diamond in hardness. Many researchers believe that c-BN films offer great opportunities for wear parts, cutting tool inserts, rotary tools, and dies. The c-BN films are especially valuable for protective coatings on surfaces that come into contact with iron-based materials, where diamond cannot be used because of its high chemical wear due to its aggressive reaction with iron.

Transmission metal composites of boron nitride help tailor their properties for a specific application. CrBN is a popular nanocomposite since the addition of Cr adds corrosion resistance to an extremely hard material. It can be classified as a nanocomposite since the small grains (2-5 nm) of cubic CrN are embedded in a large fraction of predominantly amorphous BN matrix. Within the amorphous BN matrix, a hexagonal lattice can only be identified for a few atomic layers. Consequently, these sub-5-nm crystalline h-BN domains do not support shearing in a macroscopic tribological contact due to their small lateral extension and random orientation. The coefficient of friction for all of the various proportions of CrBN was ~0.6±0.15, independent of their chemical composition and microstructure. (42)

4.c.ii. Carbon Nitride (C_3N_4)

Since Liu and Cohen predicted that a carbon nitride, β-C_3N_4, may posses extremely high hardness comparable to or greater than that of diamond, many attempts have been made to synthesize this hypothetical material by means of a variety of techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD) and high-temperature and hire-pressure methods. (77) In β-C_3N_4 the octet rule is satisfied in this structure, and no antibonding states are occupied. The unit cell is hexagonal and contains two formula units (14 atoms) with local order such that C atoms occupy slightly distorted tetrahedral sites while N atoms sit in nearly planar triply coordinated sites. The atomic coordination suggests sp^3 hybrids on the C atoms and sp2 hybrids on the N atoms. (77) The prediction of hardness does not guarantee usefulness in engineering applications, since other factors such as chemical reactivity and fracture toughness are important for applications.

The calculated lattice constant, bulk modulus, and electronic band structure of β-Si_3N_4 are in good agreement with experimental results. (78) This gives support for the predicted properties of β-C_3N_4. The bulk modulus of β-Si_3N_4 is found to be comparable to diamond, and its moderately large cohesive energy suggests that the prototype structure may be metastable. β-C_3N_4 is a more suitable coating than β-Si_3N_4, since Si results in ionic Si-N bonds compared with a covalent C-N bond. (78) The original study of C_3N_4 was motivated by an empirical model for the bulk modulus of tetrahedral solids which indicates that short bond lengths and low iconicity are favorable for achieving large bulk moduli. Since the C-N bond satisfies these conditions, tetrahedral C-N solids were suggested as candidates for new low compressibility solids.

A flurry of attempts to produce the elusive C_3N_4 material that is theoretically harder than diamond has been reported. Most of the films deposited are, in fact, amorphous CN_x, with $x \approx 0.1\text{-}0.3$. Primarily due to a large variation in their microstructure and chemical stoichiometry, amorphous CN_x films produced by various research groups exhibit large variations in mechanical properties and tribological performance. Reported friction values range from 0.05 to >0.5 in air, and friction tends to increase as the film's nitrogen content is increased. (79) Noteworthy, however, is the extreme surface smoothing of the coating that takes place during sliding wear with RMS surface roughness of <0.5nm, and this smoothing has a large impact on applications that involve sliding contacts. Normally most hard materials are brittle, but CN_x films are very elastic which seems to be a contradiction. Recent evidence shows that CN_x may exhibit a fullerene-like structure, which would give an elastic behavior consistent with a resilient material. Carbon nitride, thus, deforms elastically due to bending of the structural units. (79) The wear rates of carbon nitride coated disks can be 10 times lower than those of disks coated with a commercial DLC film of the same thickness. (80)

X-ray powder diffraction patterns were simulated for five structures proposed for C_3N_4 – i.e. β-, α-, defect zincblend-type and cubic C_3N_4. No work has yet presented unambiguous evidence for the crystallization of carbon nitrides with the proposed structures. Identification of carbon nitrides has been more or less ambiguous. Crystal-structure images were taken with transmission electron microscopes in some cases. The crystals deposited were always small in amount and, in many cases, composed of small crystallites embedded in amorphous phases. (81)

4.c.iii. Chromium Nitride (CrN)

The hardness and excellent wear properties of chromium nitride (CrN) coatings by IBAD and other physical vapor deposition techniques are well documented. Using highly sensitive surface analysis techniques, researchers have found that nitrogen tends to segregate at the surface of a metal undergoing anodic dissolution, so that the small amount of nitrogen commonly added to steels can have a significant effect on the corrosion behavior. The primary kinetic barrier to corrosion in these steels is still a Cr_2O_3-based passive film, but the presence of N enhances some secondary barriers: namely, surface segregation of Cr and Mo underneath the passive film. (90) A low nitrogen content (less than in pure Cr_2N) leads to poor corrosion behavior. The pure chromium nitride phases Cr_2N and CrN resisted against the attack approximately two times as long as the chromium films. They were comparable to a classical electroplated chromium film more than six times as thick. (84) Chromium Nitride (CrN) also has a superior oxidation resistance compared to TiN. (91)

Proper introduction of both Ti and Al elements into the CrN structure can improve further the structural integrity as well as the mechanical and tribological properties of the CrN-based multicomponent coatings. The wear rate can be three times lower than that of pure CrN coatings. (92) Similar to TiN, chromium nitride (CrN) has been successfully applied to the molding dies, wear components, and cutting tools. CrN is known to be superior to TiN in corrosion and wear resistance, friction behavior, and toughness. In comparison with TiN-based coatings (e.g. TiAlN), better tribological properties and toughness of CrN-based multicomponent coatings (e.g. CrAlN) could be expected. Recently, CrAlN coatings have been reported exhibiting even higher oxidation resistance than TiAlN, as both the chromium and aluminum could form protective oxides which suppressed oxygen diffusion. Similarly, a better corrosion resistance of CrAlN coatings could also be expected than that of TiAlN coatings could also be expected than that of TiAlN coatings. TiAlN coatings exhibit a strong (111) crystalline orientation, while the CrAlN coatings showed a random orientation. CrAlN coatings showed an evidently better corrosion resistance than the TiAlN coatings. (38)

Bodycote Diamond Black, Inc. is the maker of Diamond Black, which is a thin ceramic film with nano-crystalline structure applied in vacuum chambers via physical vapor deposition. Diamond Black is a trade name for a sputter deposited thin film coating of boron carbide. It is composed of chromium nitride, tungsten carbide, and carbon, effectively giving the surface a 3-8μm layer of industrial-grade diamond. Diamond Black is chip, crack, and peel resistant. The boron coating is impervious to most harsh chemicals, acids, and bases. It virtually eliminates corrosion and maintains its lubrication longer. Bodycote has recently partnered with IonBond, another leader in the field of physical vapor deposition.

Hard metal nitride coatings produced by ion beam assisted deposition (IBAD) are being considered as replacements for electroplated hard chromium (EHC) in a number of Army systems, especially as environmental considerations make the once-common use of EHC in a number of Army systems, especially as environmental considerations make the once-common use of EHC more expensive and hazardous.

4.c.iV. Titanium Nitride (TiN)

Titanium nitride (TiN) is an extremely hard ceramic material used to harden and protect cutting and sliding surfaces. TiN features high hardness and low wear. These coatings have a golden color, which is not ideal for an exterior finish for a tactical firearm, but exterior finishes can be painted. Since TiN is more durable than gold plating, it has been used for quite some time as a good and inexpensive decorative coating for artificial jewelry, wrist watch cases, and other various small metallic objects. Since TiN is neutral with respect to the human pH balance, featuring total corrosion resistance in human saliva and does not exhibit any cryotoxic effects in body fluids. (15) Thanks to these properties it is used for coating working surfaces of surgical and dentistry instruments. Since the maximum barrel temperature of an M4 carbine and M16 rifle is 871°C (1,600°F), TiN is unacceptable in this application because of its inadequate oxidation resistance at 540°C. (83) TiN produced by means of physical vapor deposition (PVD) technique is good for wear protection, but exhibits poor corrosion protection. (84)

Unlubricated tribological tests on films produced by these techniques tend to result in coefficients of friction in the range 0.3-0.9. TiN coatings deposited by pulsed magnetron sputtering (PMS) resulted in structural densification. PMS deposited TiN coatings compared to deposition by conventional sputtering has demonstrated significantly enhanced tribological properties, such as higher hardness, lower wear rates, lower surface roughness, better coating to substrate adhesion, and lower coefficient of friction (values as low as 0.09 to 0.12 have been recorded in unlubricated tests against tool steel). (85) While the enhancement of tribological performance of the films produced by pulsed processing may well be attributable to the structural and topographical modifications arising from the use of this deposition process, the exact mechanisms by which these modifications occur are not fully understood. Reduction in friction coefficient was also observed in sliding tests on TiN coatings formed by plasma assisted chemical vapor deposition (PACVD) containing residual chlorine. (86)

Two techniques to improve tribological properties in TiN coatings are ion implantation and the use of a thin titanium interlayer. Ion implantation of the surface layer of TiN coatings with N and Al atoms caused the hardness to increase and the coefficient of friction to decrease. Al + N implanted plates show the highest wear resistance increase (200%). The Al-implanted plates show a moderate improvement of 130%. (87) To enhance the adhesion it is common to use a thin layer of titanium or in some cases chromium as an interlayer. The reason for using these metals is process related to a large degree in that it is convenient to build a nitride and a metallic interlayer using the same metal. Titanium does have good properties in terms of governing adhesion. (88)

4.c.v. Titanium Aluminum Nitride (TiAlN)

Titanium aluminum nitride (TiAlN) is an extremely hard, wear resistant, and corrosion resistant coating. The micro-pores in the 5 μm thick coating also act as a trap for oils so it technically is considered self-lubricating as the silicon in the oils will remain in the small voids. TiAlN coatings are generally a matte dark-charcoal in color, compared to the gold color of TiN. High ionization sputtered TiAlN improves resistance to coating flaking and chipping as well as abrasive wear resistance. (89) The higher the aluminum content, the better the oxidation resistance and resistance to high-temperature wear. The aluminum in the coating material reacts with oxygen in the air and forms a passive Al_2O_3 layer, which prevents the film from further intensive oxidation.

TiAlN may not be suitable for all firearm applications due to its poor oxidation resistance at higher temperatures, but CrAlN may be suitable alternative. Since the maximum barrel temperature of an M4 and M16 is 871°C (1600°F), TiAlN is unacceptable in this application because of its inadequate oxidation resistance at 540°C. (83) It is concluded that for sliding materials with dominating severe adhesive wear, as for example for the couple TiAlN/stainless steel, the protective function of the TiAlN coating is not sufficient. (89) CrAlN coatings showed an evidently better corrosion resistance than TiAlN coatings. (38) TiAlN-based coatings, typically deposited as 2-5 μm thick films with hardness ranging between 3000-3300 HV, are thermally stable between 800-900°C and have the coefficient of friction against steel counterparts between 0.35-0.4.

4.c.vi. Titanium Carbon Nitride (TiCN)

Titanium carbon nitride (TiCN) is very similar to TiN, but is harder and gray/black in appearance instead of gold. Please see the description for TiN for more information.

4.d.i. Chrome Oxide (Cr_2O_3)

Chrome oxide (Cr_2O_3) is one of the principal oxides of chromium. It adopts the corundum structure, consisting of cubic close packed oxides with 2/3 of the octahedral holes occupied by chromium.

4.d.ii. Keronite Plasma Electrolytic Oxidation (Keronite, PEO)

Keronite Ltd. are the makers of the Keronite process, which uses plasma electrolytic oxidation to convert the surface of light metals such as aluminum, magnesium, and titanium into extremely hard, dense oxide ceramic with outstanding corrosion and wear resistance. This allows steel parts to be replaced by aluminum, magnesium, or titanium. The chemical solutions are environmentally acceptable as well. No chromium or other heavy metals, ammonia, or acids are present, and no hazardous waste is generated.

The chemically inert Keronite layer grows both above and below the surface of the component being treated, much like anodization. Self-regulating, this ceramic layer closely follows the contours of the component. Its thickness can be controlled and predicted with accuracy, making it suitable for high precision parts, complex geometries and cavities or parts with vulnerable edges. As a ceramic, Keronite has excellent thermal properties. Its relatively low stiffness gives excellent strain tolerance and compliance. This means that Keronite remains flexible and performs well in extreme temperatures and yet it is tough and resistant to crack propagation.

Keronite has been used to improve automobile efficiency by replacing steel pistons with aluminum pistons, which reduced piston temperature by 30°C (54°F). (65) Components treated using the Keronite process can often be reprocessed and repaired rather than replaced, and initial tests by a leading automotive manufacturer indicate that treated parts present no problems when it comes to recycling. Steel firearm parts can be replaced with lighter Keronite coated aluminum and titanium parts for added efficiency.

4.e.i. Molybdenum Disulfide (MoS_2)

The first practical application of a solid lubricant was the rubbing-in of molybdenum disulphide powder on metal surfaces; a homogenous solid lubricant film is generated by polishing. The lubricating film is significantly smoother than the original metal surface. During the contact of two sliding components, the load is distributed over a larger contact area and the contact pressure is reduced. (34) The MoS_2 film has a very high load carrying capacity and protects the metal surface from wear under extremely high loads. Furthermore, this solid film provides the metal surface with a very low friction. When sliding MoS_2 coatings, a low shear transfer film is rapidly built up on the counterface which can result in ultra-low coefficients of friction down to 0.002. (66) Such dry films cannot be replaced without substantial effort.

The crystal structure of molybdenum disulfide (MoS_2) is laminary, similar to graphite. MoS_2, on the other hand, has very weak van der Waals forces between the sulfur bonds and is not dependent upon adsorbed vapors for its lubricating properties. It consists essentially of planes of molybdenum atoms alternating with planes of sulfur atoms. The molybdenum and sulfur are covalently bonded within each layer, but adjacent layers are held to one another with relatively weak van der Wall forces. As a result, the adjacent planes of sulfur atoms can slide readily over one another, and this has been thought to be responsible for the low frictional resistance provided by MoS_2. (18) This weak bonding between layers of MoS_2 results in low shear strength, and hence low friction in the sliding direction. This implies that the basal plane of the crystals in polycrystalline films lies parallel to the sliding direction for good lubrication. (39) Therefore, the MoS_2 film orientation should affect the coefficient of friction. At the same time, there is an immense resistance to penetration in the direction normal to the crystalline lamellae.

MoS_2 coatings can be divided into two types. Type I films are columnar and tend to be more porous than type II films, and the former enhances the formation of MoO_3 in humid air, which results in an increase in friction coefficient and a decrease in coating endurance compared to type II MoS_2. Type I films lubricate, as the columnar plates tend to detach near to the interface with the substrate due to their inherent porosity, and reorient in lubricating particles; this occurs after a few sliding runs and results in a buffer layer a few tens of nanometers thick. Type II coatings are denser than type I and the basal plane orientation develops in and below the wear track, due to stress-induced crystallization. These microstructures can be deposited by adjusting the deposition conditions (pressure, deposition rate) or by the incorporation of co-sputtered or multilayer dopants. (39)

MoS_2 shows good friction performance in vacuum and under dry running conditions, but degrades quickly in moist and oxidizing environments. It is well known that humidity or oxygen has an inverse effect on the friction properties of MoS_2. This is attributed to the formation of oxides in the contact zone. MoS_2 is a dichalcogenide with weak van der Waals forces between the sulfur bonds and is not dependent upon adsorbed vapors for its lubricating properties. It is subject to oxidation above 573K (572°F) and its nature is such that high humidity conditions deleteriously affects its lubricating characteristics. While not confirmed, it has been reported that MoS_2 films sputtered at certain parameters are not as grossly affected by high humidity conditions as is the natural product.

The efficiency of MoS_2 as a lubricant is degraded significantly due to oxidation. The oxidation product of MoS_2 is molybdenum oxide (MoO_3) which is considered abrasive to most alloys and has been reported to increase friction and reduce wear life. (39) Inorganic resins (for example, sodium silicate) are more thermally stable than organic resin binders under oxidizing conditions. These binders provide some form of oxidation protection to the MoS_2 by excluding air from the particles.

MoS_2 is often used in composites to improve its wear properties. Most bonded coatings use organic (thermoplastic and thermo-setting) resins to adhere the lubricant strongly to the substrate. Cellulose or acrylic lacquers can be used up to about 65°C. Phenolics can withstand service temperatures up to 200°C, whereas epoxy resins are thermally stable up to about 300°C. (39) Inorganic binders such as sodium silicates are more thermally stable then organic binders under oxidizing conditions. MoS_2 /metal composite coatings provide good wear and friction properties. MoS_2 /metal composites have hardness that ranges from 1,000-2,000 HV compared to 400 HV for MoS_2. MosS2-based metallic composites retain these desirable properties in humid atmospheres and are suitable for terrestrial applications.

These composites are deposited using physical vapor deposition (PVD) by co-depositing small amounts of titanium in the MoS_2 matrix. This process creates titanium in solution with the MoS_2 structure, which is ideal for excellent wear and friction properties. When the titanium content is greater than 20%, the formation of multilayers can be observed, reducing the wear and friction properties. Excellent results in terms of tribological properties have been reported for other metallic (such as Mo, Cr, Zr, Au, and W), non-metallic (such as C and N_2), and ceramic components (such as Ti-C, Ti-Au, and Ti-N). (39)

PVD has become the most common way of depositing MoS_2 coatings. Most of the early work involving the use of PVD methods was carried out by RF sputtering, and this method is still very much the usual method by which MoS_2 coatings are deposited. Compared to previous methods for the deposition of MoS_2, RF sputtering produces coatings with low friction characteristics and enhanced adhesion. (39)

4.e.ii. Tungsten Disulfide (WS_2)

Tungsten disulfide (WS_2) is limited in usefulness to about 650°C in air, where it oxidizes appreciably. (39) WS_2 is available in two forms, layered (platelets) WS_2 (2H) and inorganic fullerene-like WS_2 nanoparticles (IF). IF nanoparticles impregnated into the pores improve the tribological properties of powder materials in comparison to a reference sample or the sample impregnated with 2H solid lubricant particles. The shape of the IF nanoparticles is preserved during the friction tests under high loads. Impregnation of the IF nanoparticles increases the load bearing capacity of powder materials in comparison to a porous matrix impregnated with oil or commercially available layered WS_2 (2H) particles. (88)

An interconnected system of pores renders the impregnation of the solid lubricant nanoparticles throughout the entire metal piece. IF nanoparticles are gradually furnished to the contact surface, which is their main advantage over 2H particles. The main friction mechanism of powdered materials is sliding/rolling of IF nanoparticles in the interface.

V. Carbon Coatings

5.a. Graphite (C)

Graphite is an allotropic form of carbon. It is a transition element and is insoluble in all common solvents. Graphite is a lamellar compound which lubricates because of weak van der Waals forces at the slip planes. The carbon atoms in graphite are covalently bonded and situated at the corners of regular hexagons. The basal planes of the hexagons are parallel but slightly offset laterally. However, as is well known, graphite depends on an intercalation of gases, liquids, or other substances between its layers. It is not, therefore, useful as a lubricant in an environment where these intercalated or adsorbed materials cannot be maintained. Therefore, its efficiency is curtailed by its high shear strength when dry.

In air, graphite's limiting factor is its high oxidation rate. Small particles begin to oxidize at an appreciable rate at about 450°C, which is its maximum use temperature. (39) Graphite has an upper operating temperature range of 823-933K (1022-1220°F) at atmospheric pressure unless stabilized against oxidation with adjuvants. (89) Graphite is one of the few laminar solids that can provide excellent lubricity beyond 450°C in the form of gaseous oxidation products.

5.b. Graphite Fluoride $(CF_x)_n$

Graphite fluoride $(CF_x)_n$, also referred to as carbon monofluoride (when x = 1), is a relatively new solid lubricant that can be loosely described as a layer lattice intercalation compound of graphite. It is prepared by the direct reaction of graphite with fluorine gas at controlled temperature and pressure. It is grey to pure white, depending on its stoichiometry. The subscript x in $(CF_x)_n$ can vary from about 0.3 to 1.1. Early research of the lubricating properties of $(CF_x)_n$ applied thin lubricating films of $(CF_x)_n$ and of MoS_2 were burnished on 440C and 301 stainless steel disks and evaluated in pin on disk experiments. The $(CF_x)_n$ films were the more durable ones over the entire temperature range shown. Friction coefficients were for the most part well below 0.1 up to the failure temperatures of the coatings. Failure temperature was 400°C for MoS_2 and 480°C for $(CF_x)_n$. (34)

5.c. Diamond-Like Carbon (DLC, CVD Diamond)

Carbon coatings are often a mixture of graphite and diamond bonds, hence such coatings are often referred to as Diamond-Like Carbon (DLC). Diamond's extreme hardness, high abrasion resistance, good fatigue strength, high thermal conductivity, good radiation and temperature resistance, chemical and thermal inertness, high corrosion resistance, and environmental compatibility make it excellent for tribological applications. Modern diamond belongs to one of four distinct categories: natural diamond, high-pressure synthetic diamond, CVD diamond, and diamond like carbon (DLC). Natural diamond and high-pressure synthetic diamond have limited applications because of the crystals' small size and high cost. The major drawback of CVD diamond, which restrict its use as a tribological coating, are its low bending strength and its very high deposition temperature. DLC has two disadvantages: low deposition rate and high internal residual stress. Unlike diamond it cannot be obtained as thick monolithic shapes, at least with the present technology. CVD diamond and DLC may be limited by their pronounced reactivity with iron and iron-based alloys. (93)

DLC coatings constitute a class of artificial metastable materials with a wide range of composition, properties, and performance. DLC is the term commonly accepted for carbon-based coatings which have mechanical, optical, electrical, and chemical properties similar to natural diamond, but which do not have a dominant crystalline lattice structure. DLC can be harder than natural diamond and have a coefficient of friction less than that of Teflon. In dry sliding the friction of diamond and diamond-like hard carbon coatings can be extremely low with a coefficient of friction less than 0.01 and a wear resistance more than one order of magnitude better than for any other hard coating. (91) It has been demonstrated that DLC coatings improve the wear life of coated metal surfaces. (71) Diamond and diamond-like carbon coatings also provide an excellent wear resistance of about one order of magnitude lower wear than for any other wear-resistant coatings. (66) The standard DLC coatings are stable up to about 300°C (572°F) in air and the addition of silicon to DLC (~30%) increases the temperature stability to about 600°C (1112 °F). The required DLC coatings being rather thin (5 μm) no post fabrication grinding of coated component is necessary. DLC coating is an environmentally acceptable process and thus is an improved alternative to the currently used hexavalent chrome plating process for steel. (71)

Diamond-like carbon (DLC) is used in the engines of most modern supersport motorcycles, Formula 1 racecars, and NASCAR vehicles. DLC has been used on aluminum pistons to increase the horsepower of engines by 1-2%. Pistons with DLC have been tested in a motorcycle engine and compared with standard aluminum pistons. DLC coatings also added wear resistance to the piston skirt, and also reduced the friction between piston and liner. This ultimately leads to a higher power output from the engine. (76) Diamond-like coatings are currently being tested for use in coating both the interior and exterior of firearm barrels.

Table 9.1 Classification of carbon films. (75)

	Carbon films													
Designation	**1 Plasma-polymer films**	**2 Amorphous carbon films (diamond-like-carbon films / DLC)**							**3 Crystalline carbon films**					
									Diamond films					Graphite films
Thin film / thick film	Thin film	Thin film							Thin film			Thick film (free standing)		Thin film
Doping, additional elements		hydrogen-free			hydrogenated				undoped		doped	undoped	doped	undoped
				modified			modified							
				with metal			with metal	with non-metal						
Crystal size on the growth side	./.	(amorphous)							1 to 500 nm, nano-crystalline	0.5 to 10 µm, mikro-crystalline	0.1 to 5 µm	(5 µm to) 80 to 500 µm	80 to 500 µm	
Predominating C-C-bond type	sp^2 or sp^3, linear bond	sp^2	sp^3	sp^2	sp^2 or sp^3	sp^3	sp^2	sp^2	sp^3	sp^3	sp^3	sp^3	sp^3	sp^2
Film No.	**1**	**2.1**	**2.2**	**2.3**	**2.4**	**2.5**	**2.6**	**2.7**	**3.1**	**3.2**	**3.3**	**3.4**	**3.5**	**3.6**
Designation	**Plasma-polymer film**	**Hydrogen-free amorphous carbon film**	**Tetrahedral hydrogen-free amorphous carbon film**	**Metal-containing hydrogen-free amorphous carbon film**	**Hydrogenated amorphous carbon film**	**Tetrahedral hydrogenated amorphous carbon film**	**Metal-containing hydrogenated amorphous carbon film**	**Modified hydrogenated amorphous carbon film**	**nano-crystalline CVD diamond film**	**micro-crystalline CVD diamond film**	**doped CVD diamond film**	**CVD diamond**	**doped CVD diamond**	**graphite film**
Recom-mended abbreviation	./.	a-C	ta-C	a-C:Me	a-C:H	ta-C:H	a-C:H:Me (Me = W, Ti, ...)	a-C:H:X (X = Si, O, N, F, B, ...)	./.	./.	./.	./.	./.	./.

DLC can be considered a metastable carbon produced as a thin film with a broad range of structures (primarily amorphous with variable sp^2/sp^3 bonding ratio) and composition (variable hydrogen concentration). DLC is any of seven forms of amorphous carbon materials that display some of the unique properties of natural diamond (see Table 9.1). (19) DLC films are classified into two closely related categories based on their hydrogen content: (1) amorphous, hydrogen-free DLC (a-DLC or a-C) and amorphous, hydrogenated DLC (a-C:H, H-DLC, or a-C:H). Amorphous DLC, the most common type of DLC, consists of a mixture of sp^2 (graphite) carbon, a moderate amount of sp^3 (diamond), and a variable and appreciable amount of hydrogen (up to ~50 at.%). The a-C:H films generally contain 30 at.% hydrogen and the amount of sp^3 bonding is typically 70%. Higher hydrogen content results in low adhesion to other counterpart materials yielding low friction coefficients. The non-hydrogenated films can be divided into amorphous C showing a high amount of sp^2 hybridization and tetragonal amorphous C (ta-C) with a predominance of sp^3 hybridization of up to 85%. (39) The a-C films are hydrogen-free, usually containing less than 1 at.% hydrogen. The a-C films were bonded predominantly by sp^3 bonds. The a-C films were harder, showing about 5,600 HK microhardness while the hydrogenated a-C:H films had about 2,200 HK microhardness. Generally, a-C:H films have a smooth appearance with only a few inhomogeneous particles on the surface. The a-C coatings had a greater number of irregularities on the coating surface, predominantly particles smaller than 1 μm. (92)

Both a-C:H and a-C have low friction in dry sliding conditions (0.15 to 0.22), which can further be decreased by 10-40% under boundary lubrication. When sliding against different metallic or ceramic counterparts, the friction coefficient ranges from 0.1 to 0.02. The lowest friction (0.10) is attributed to the a-C:H)Ti) film in dry tests against steel. Thin diamond-like carbon coatings have turned out to provide excellent wear properties in dry sliding conditions, particularly a-C films. As a general trend, the hydrogen-free a-C coatings proved to be more wear resistant compared to hydrogenated a-C:H films, both in dry and lubricated conditions. On the other hand, the counterparts sliding against a-C films suffered from more severe wear compared to counterparts sliding against the a-C:H films. (92)

A tribologically beneficial transfer layer is formed on the counterface when a steel or ceramic surface slides against a DLC coating providing a low friction coefficient and reducing wear. (91) In the aqueous environment the layer formation was inhibited and the pins showed increased wear. The beneficial effect of tribolayers with DLC films is clearly shown, since the a-C:H(Ti) coating provided a lower friction coefficient in dry conditions. (92) The friction behavior of DLC is controlled by an interfacial transfer layer formed during sliding. This transfer layer of low shear strength (sp^2-type) is formed from the top layer of the DLC coating and is responsible for the low friction coefficients.

The two types of diamond-like carbon films also behave differently in different environments. The friction coefficient of a-C:H films in ambient air increases with air pressure, particularly as the relative humidity increases. For a-C:H films, water is an aggressive media that significantly increases wear. In a recent experiment a-C:H coatings prepared by the ion beam technique performed successfully in water-lubricated tests; suggesting that the aqueous conditions is dependent on the composition and structure of the a-C:H coating and that the hydrogenated structure of a-C:H film produced by rf-plasma technique is vulnerable in the water environment. (92)

When the coatings are exposed to water lubrication, the water is a very aggressive medium for the a-C:H coatings and causes catastrophic failure of the coating. The a-C:H (Ti) film, with a titanium-alloyed surface layer, endures the test even though the water lubrication increases the wear of the coating. Since titanium alloying of the a-C:H coating improves the performance of the coating in the water, it is suggested that the hydrogenated structure itself is vulnerable in a water environment. Conversely, the a-C coating performed well with water lubrication, since no measurable wear could be detected even after 21 hours of sliding in the pin-on-disc test. (88) Components coated with a-C coatings can be used in lubricated conditions to further reduce friction and control wear.

DLC is typically produced by processes in which high energy carbon atoms (e.g. in plasmas, in sputter deposition and in ion beam deposition) are rapidly cooled or quenched on relatively cold surfaces.

These coatings can be deposited using chemical vapor deposition (CVD), physical vapor deposition (PVD), ion beam assisted deposition (IBAD), plasma-enhanced chemical vapor deposition (PECVD), magnetron sputtering, and other novel methods such as plasma source ion implantation (PSII). The CVD method is often a high temperature process, above 300°C. Therefore this process is unfavorable for steel components as they become annealed at elevated temperatures. The PVD process works at low temperature, less than 250°C and is therefore suitable for coating steel components. (70) Amongst these techniques, PECVD is the most promising for depositing good quality films on large areas at high deposition rates. (71) The basic reaction in the chemical vapor deposition involves the decomposition of a hydrocarbon, such as methane, as follows:

$$CH_4 \rightarrow \text{(Activation)} \rightarrow \text{C(diamond)} + 2H_2$$

The carbon species must be activated, since low pressure graphite is thermodynamically stable and, without activation, only graphite would be formed. Activation is obtained by two basic methods: high temperature and plasma, both of which require a great deal of energy. Several CVD processes based on these two methods are presently in use. The four most important activation methods at this time are:

1. High-frequency, plasma glow discharge using the microwave and radiofrequency processes
2. Plasma arcing using the direct-current arc and radiofrequency arc processes
3. Thermal CVD using the hot-filament process
4. Combustion synthesis using an oxyacetylene torch

Generally, DLC films do not adhere well to steel due to the presence of native oxides on the surface. Delamination may lead to a major breakdown and therefore the quality of the adhesion must be very high. Prior to DLC film deposition, in-situ sputter etching the substrates using argon plasma is required with the addition of an intermediate bonding layer to yield consistently well adherent DLC films. (71) Elements belonging to groups IVb, Vb, and VIb are all capable of forming hard carbides with high melting points, indicating the formation of strong covalent bonds and therefore can be used as bonding intermediate layers between steel and DLC. (72) By applying different metallic interface layers (e.g. Cr, Mo, Si, Cu), the adhesion has been improved considerably. (74) Generally the combination of Cu and a metal belonging to one of the IVb (Ti, Zr, Hf), Vb (V, Nb, Ta), or VIb (Cr, Mo, W) groups of elements was observed to give good adhesion. These elements are all capable of forming hard carbides with high melting points, indicating the formation of strong covalent bonds, and may therefore be suitable elements for improving adhesion. (74) Cu/Cr appeared to give the best adhesion.

The properties of a-C:H coating have been in many cases improved with different alloying agents. Elements like silicon, nitrogen, and metallic species (Ta, W, Ti, Nb) have been used to enhance mechanical properties to control the stress state, enhance adhesion properties of the a-C:H coatings, increase the thermal stability and stabilize the friction behavior in humid atmospheres. Alloying improves mechanical, stress, adhesion, and thermal properties. It also improves the resistance of a-C:H in aqueous environments. The a-C coating, which consists of carbon atoms mainly bonded by sp^3 bonds and has therefore high hardness and high internal stresses. (92)

The addition of metal (like W or Ti) or non-metal (like F or Si) atoms into the carbon matrix cause changes in chemical and mechanical properties of a-C:H coatings. The hardness depends on the amount of hydrogen, the coating process, and if the carbon matrix is doped with other elements. Typical values for hardness are 7 to 40 GPa. The modulus of elasticity is in the range of 25 to 400 GPa. The coating thickness is usually between 2 to 5 µm. (70)

5.d. Tungsten Diamond-Like Coatings (W-DLC, Nitron)

Tungsten Diamond Like Carbon (W-DLC) is another excellent chemical vapor deposition coating for ferrous alloys and stainless steels. The total thickness of the coating is approximately 1 to 3 µm. It is usually applied with plasma assisted vapor deposition. One advantage is the temperature for the coating application is approximately 300°F, compared to 900°F for Ti coatings. Neither should affect common firearm steels, but lower temperatures are preferable. The cost of W-DLC is less than that of TiAlN (higher temperature) and performs similarly, if not better. The W-DLC coating are black (not charcoal), but it can made in many colors depending on the process. In this manner titanium aluminum nitride and W-DLC are similar.

The corrosion resistance is enhanced with W-DLC due to the 3 µm electroless nickel interlayer that is typically added. It is demonstrably better than conventional TiAlN due to the undercoat of electroless nickel even though it is very thin. Suffice it to say that the Sigarms P226 is the US Navy SEALs standard sidearm and it wears the electroless Nickel topped with W-DLC (called "Nitron" by Sigarms).

Chapter 10: Sample Preparation

Contamination is an important factor in determining such solid surface properties as adhesion. Sample preparation is so important that most coaters will spend the same amount of time preparing parts as actually coating them. If the preparation is poor, then the time spent coating will be in vain since poor preparation leads to poor adhesion. To ensure the best possible adhesion, the following standards were followed during sample preparation:

- *ISO 8502 Preparation of Steel Substrates Before Application of Paints and Related Products – Tests for the Assessment of Surface Cleanliness*
- *ISO 8503 Preparation of Steel Substrates Before Application of Paints and Related Products – Surface Roughness Characteristics of Blast-Cleaned Steel Substrates*
- *ASTM E3 Standard Guide for Preparation of Metallographic Specimens*

Thin contaminant layers, such as adsorbed gases, water vapor, and hydrocarbons of atomic dimensions (approximately 2 nm thick), are unavoidably present on every surface of any solid that has been exposed to air. (19) These contaminant layers are unavoidably present on every surface of any solid matter that has been exposed to air (see Figure 10.1). In fact, these contaminants can penetrate a perfectly clean surface that is exposed to air within fractions of a second. In other words, the simplest and most common occurrence recognized with real surfaces is that nearly all surfaces contain adsorbates, either physically adsorbed or chemically adsorbed material that has formed through interaction with the environment. Sometimes oxide layers of various depths are present beneath the surface contaminants. Knowledge of the contaminant and the oxide layers is of great interest to materials researchers trying to improve material properties. Because contaminants are weakly bound to the surface, physically rather than chemically, they can be removed by bombarding them with rare gas ions (e.g., argon ions) or by heating to say 700°C. (19)

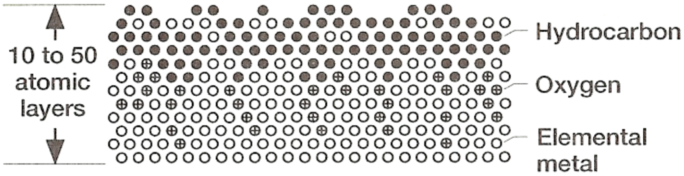


Figure 10.1 Schematic model of metal exposed to air, showing contaminant layer. (19)

In environments containing oxygen, such as air, a thin (about 1-10 nm thick) oxide layer is formed very quickly on most metal surfaces. Some oxide layers, like copper oxide, are sheared more easily than the metal, while others, such as aluminum oxide, form a very hard layer. (66) Regardless of hardness, practically all published work agrees that extremely small amounts of oxygen or other contaminants can greatly reduce the adhesion between metals. However, there are situations where modest amounts of oxide produce a relatively small decrease in adhesion. Conversely, when the surfaces are clean, very strong adhesive bond forces are created that are near the cohesive energy of the substrate.(34) The bond energy is slightly less than the cohesive energy because of lattice disregistry at the interface, which generates misfit dislocations.

Four possible surface events influence to a greater of lesser extent adhesion, friction, and wear: (1) reconstruction, (2) segregation, (3) chemisorptions, and (4) compound formation (see Figure 10.2). These surface events cause a marked reduction in strength and often to embrittlement. Reconstruction occurs when the outermost layers of atoms of the solid surface undergo a change in structure, appreciably changing the coefficient of friction of the solid. Segregation of alloy species can also occur at the surface. When this process is irreversible, the alloying elements remain on the surface. In each case, segregation has been shown to significantly affect adhesion, friction, and wear. Chemisorption impacts the adhesive properties of materials. For example, minor modification on the hydrocarbon structure can produce marked differences in measured adhesive forces. The last surface event is that of compound formation. When clean metal surfaces are brought into solid state contact, adhesive transfer from one surface to another always occurs. The compound formation produces strong interfacial bonds at the contacting surfaces and influences the adhesive behavior. (34)

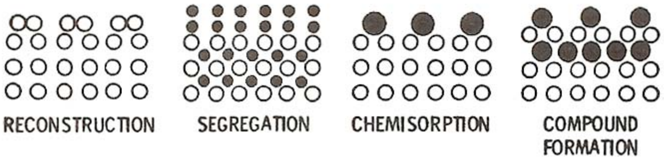


Figure 10.2 Possible surface events. (34)

For example, minor nuances in the molecular composition of chemisorbed species can produce significant differences in adhesive behavior (see Table 10.1). Such bulk properties as cohesive energy, d-valence bond character, lattice radius ratio for alloys, and the presence or absence of crystallinity have all been shown to be related to friction and wear performance. Some of these properties such as cohesive energy can be shown to relate to surface behavior via adhesion and friction results. (34)

Table 10.1 Effect of various hydrocarbons on adhesion of clean iron. (34)

Hydrocarbon Chemisorbed to Iron	Adhesive Force [Dynes]
Clean F_e	>400
Ethane C2H6	280
Ethylene H2C = CH2	170
Acetylene HC ≡ CH	80
Vinyl Chloride H2C = CHCl	30
Ethylene Oxide H2C – O – CH2	<10

*Load 20 dynes, 10^{-10} torr, 20°C, both surfaces (001) planes

Chapter 11: Tribology

To achieve a holistic understanding of the complete tribological process taking place and to understand the interactions, it is useful to analyze separately the tribological changes of four different types: the macro-, micro-, and nano-scale mechanical effects, the chemical effects and the material transfer taking place. The macro-mechanical tribological mechanisms describe the friction and wear phenomena by considering the stress and strain distribution in the whole contact, the total elastic and plastic deformations they result in, and the total wear particle formation process and its dynamics. The micro-mechanical tribological mechanisms describe the stress and strain formation at an asperity-to-asperity level, the crack generation and propagation, material liberation, and particle formation. The tribo-chemical reactions taking place at the surface during sliding contact, and also during the periods between repeated contacts, change the composition of the outermost surface layer and its mechanical properties. This has a considerable influence on both friction and wear because they are determined to a great extent by the properties of the surface.

In contacts between two surfaces of which one or both are coated, four main parameters can be defined which control the tribological contact behavior: (1) the coating-to-substrate hardness relationship, (2) the thickness of the coating, (3) the surface roughness, and (4) the size and hardness of any debris in the contact which may originate from external sources or be produced by the surface wear interactions themselves. For further understanding of tribology, adhesion, hardness, friction, wear, and corrosion will be examined individually in greater detail.

Adhesion

Adherence of coatings to the substrate or of layers of a multi-layer coating to one another, described by the force necessary to detach the coating from the substrate or layers from each other, reflects the character of the dominating bond. Aside from surface purity, the adherence of a coating is affected by: residual stresses, degree of surface development (higher roughness – better adherence), and differences in the ductility of surface and substrate materials.

Theoretically, the best adherence can only be achieved when the distance between the coating and the substrate is comparable to lattice parameters, i.e. when the crystalline structure of the coating is an extension of that of the substrate. Such an extension of structure is possible when lattice parameters of the substrate and the coating differ by not more than -2.4 to 12.5%. An adherence approaching the optimum can be achieved with very thorough cleaning of the substrate before depositing the coating. If the substrate is very well cleaned mechanically and, in particular, chemically, the adherence of a coating may approach a value equal to that of the tensile strength of the weaker of the two materials.

The stresses generated by direct loading from the barrel internal pressure, and the difference in thermal expansion of coating and substrate at the interface itself. Once cracks in the coating have reached the substrate the exposed gun steel begins to erode.The differences in hardness between the metallic interlayers influence the practical adhesion more than differences in E-modulus. Furthermore, in order to optimize adhesion, the hardness of the interlayer should be close to the hardness of the substrate. In order to improve adhesion there are mainly three things to aim for: (88)

- Low energy in the interface; which is related to the microstructural match, rather than miss-match, between substrate and coating.
- The creation of strong and stable chemical bonds between substrate and coating.
- A low stress in the interface; which improves the ability to sustain externally imposed shear stresses in the interface/ Detrimental gradients can, for example, arise from differences in thermal expansion of substrate and coating.

Several techniques are used for improving adhesion. These can be divided into three different categories: (i) pretreatment – cleaning of the substrate prior to insertion in the deposition chamber, (ii) in situ treatment – pre-heating and sputter cleaning of the substrate, and (iii) interlayer deposition – a thin layer of a material, usually a metal, deposited between the substrate and the coating. The idea of pre-treatment and in situ treatment is to remove contaminations, such as grease, oxides, etc., from the substrate surface to increase surface reactivity that facilitates the formation of strong chemical bonds. The purposes of applying an interlayer are to minimize stresses in the interface and/or to dissolve contaminations. (88)

Hardness

Hardness is a complex property related to the extent to which solids resist both elastic and plastic deformation by concentrated forces, acting on a small surface area. Hardness is a conventionally defined characteristic, allowing the comparison of the resistance of different materials to surface damage. It is at the same time the most frequently measured surface property. For materials with defects, hardness can be limited by many factors including point defects, dislocations, and macroscopic defects. On the microscopic level, for ideal systems, hardness is determined by the bulk modulus, which in turn depends on the nature of the chemical bonding. It is the strength and compressibility of the bond that plays the primary role in a solid's ability to resist deformation. The largest bulk moduli are found in covalently bonded materials. Diamond, which has the largest bulk modulus (4.43 Mbar), is also the hardest known solid. A theory of the bulk moduli of covalent solids is therefore useful for suggesting schemes to increase hardness.

With inorganic materials, such as metals and ceramics, however, the position is different, for although their elastic moduli are generally large, metals and ceramics deform elastically over a relatively small range, predominantly outside the elastic range. Consequently, considerable plastic or permanent deformation often occurs. For this reason the hardness of metals and ceramics is bound up primarily with their plastic strength properties and only to a secondary extent with their elastic properties. In ceramics the fracture properties may be as important as the plastic properties, particularly at high loads. Thus, hardness is another way of determining the plastic yield strength of a material, namely the amount of plastic deformation, produced mainly in compression, by a known force. (19)

It is obviously advantageous if the substrate under the hard coating is as hard as possible, to avoid fracture of the brittle coating by deformation, to improve the load support and to decrease the real area of contact. Increasing the hardness of the substrate to inhibit deflections and plowing resulting from counterpart loads. Hard coatings are thus particularly useful in abrasive environments. Low friction can be achieved with hard coatings if a low shear strength microfilm is formed on the top of the coating. Thus the shear takes place within the microfilm and the load is well supported by the hard coating. (66)

All of the traditional firearm coatings lie on the low end of the hardness scale (see Figure 11.1). Three materials covered in the coating section are not shown in Figure 10.2, but are as follows: tungsten carbide's hardness is 2,300 kg/mm^2, c-BN has a hardness of 5,500 kg/mm^2, and diamond has been reported to have hardness values ranging from 6,000 to 12,000 kg/mm^2. (19) The diamond crystal is the hardest known material, although theoretical works suggest that the hypothetical compound β–C_3N_4 should be as hard as or even harder than diamond. This fact makes it difficult to measure diamond's hardness, since only another diamond can be used as an indenter, and may help to explain the wide variations in reported values of diamond hardness. The very low coefficient of friction of polished diamond and diamond-like coatings are further explained by the extreme smoothness of the surface excluding effects such as interlocking and asperity plowing, as well as of the hard coating reducing the plowing component of friction. (66)

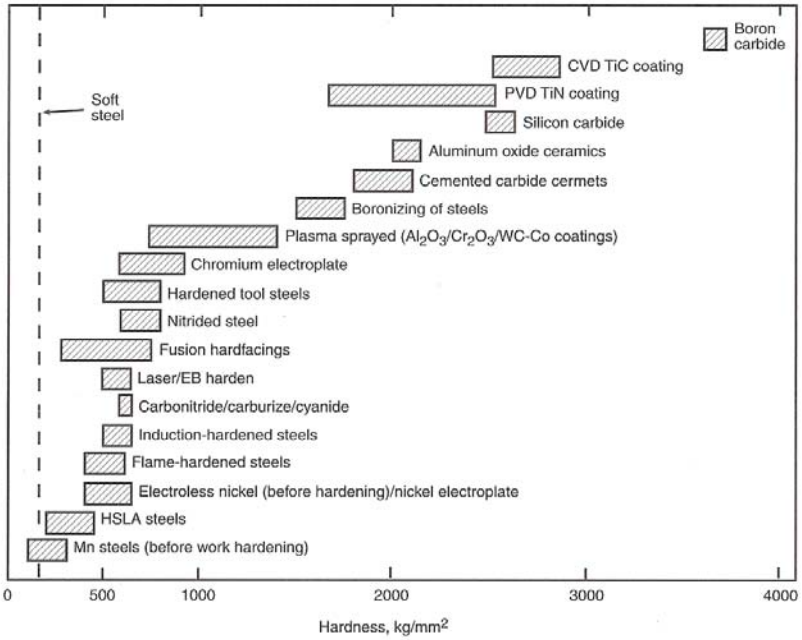


Figure 11.1 Range of hardness levels for various materials and surface treatments.

Coating hardness is not only specific to the type material, but also depends on the deposition technique used (see Table 11.2). Modern coating practices allow hardness values that were previously unachievable. Not only are the hardness value higher, but the coatings are now thinner than ever. This advent has brought about new coating concepts such as multilayered, gradient, and adaptive coatings. Ion beam assisted deposition (IBAD) has shown the ability to reproducibly tailor the adhesion, stress, and stoichiometry of protective metallurgical coatings for maximum tribological performance in specific applications of interest to the Army. (90) In plasma-deposition vapor deposited thin films, the material's microstructure can be designed during growth or post-deposition annealing treatments. (103) The microstructure can be designed by choice of the deposition technique chosen, understanding the growth process taking place on a film surface, either by sequential deposition of layers or by taking advantage of newly discovered self-organization processes including segregation effects of the elements.

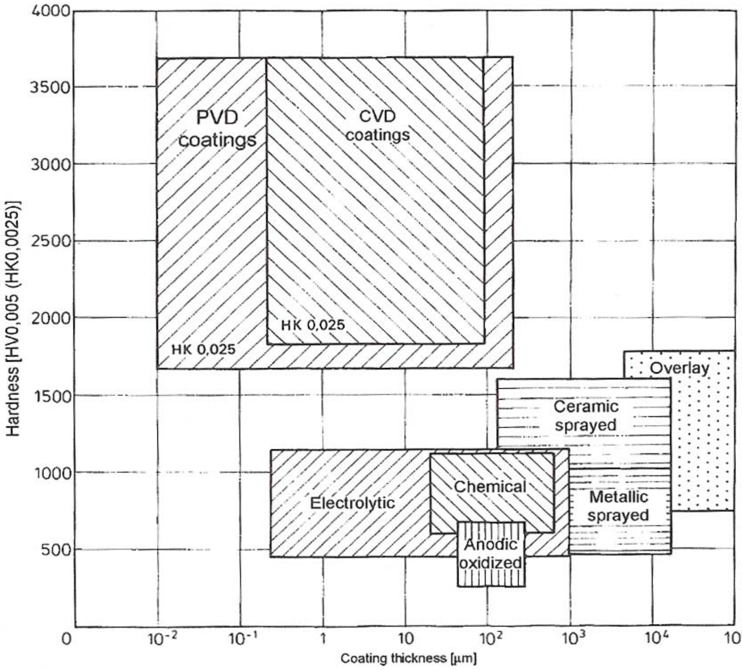


Figure 11.2 Coating hardness with respect to thickness and deposition method. (15)

The wear processes that are usually mitigated by the use of hard surfaces are low-stress abrasion, wear in systems involving relative sliding of conforming solids, fretting wear, galling, and to some extent, solid-particle erosion. A range of hardnesses are used for many of the surface engineering processes used to control wear. All of the treatments shown in this figure have hardness values greater than ordinary constructional steel or low-carbon steel. The surface-hardening processes that rely on martensitic transformation all have comparable hardness, and the diffusion treatments that produce harder surfaces are nitriding, boronizing (boriding), and chromizing. The hardest metal coating is chromium plate, although hardened electroless nickel plate can attain values just under that of chromium. The surfaces that exceed the hardness of chromium are the cermets or ceramics, or surfaces that are modified so that they are cermets or ceramics. These include nitrides, carbides, borides, and similar compounds. The popular solid ceramics used for wear applications – aluminum oxide, silicon carbide, and silicon nitride. (31)

Friction

The increased understanding of the origin of friction at the atomic scale and even why friction exists has resulted in an examination of the relationship between the commonly used laws of friction at a macro scale and the molecular frictional behavior on a nano scale. The energy loss process due to friction has been divided into different phases. First, mechanical energy is introduced into the contact zone by the formation of the real area of contact. Second, transformation of mechanical energy takes place mainly by plastic deformation, plowing, and adhesion. Third, the dissipation phenomena include the effects of thermal dissipation, storage, or emission.

The classical model for sliding friction assumes that the friction force arises from two contributing sources. First, an adhesion force is developed at the real area of contact between the surfaces (the asperity junction). Second, a deformation force is needed to plow or cut the asperities of the harder surface through the softer. The resultant friction force is the sum of the two contributing sources: friction due to adhesion and friction due to deformation and/or fracture. The adhesion arises from the attractive forces between the surfaces in contact. This model serves as a starting point for understanding how thin surface films can reduce friction and provide lubrication. There have been suggestions that friction arises from atomic lattice vibrations occurring when atoms close to one surface are set into motion by the sliding action of atoms in the opposing surface. (91) Thus, some of the mechanical energy needed to slide one surface over the other would be converted to sound energy, which is then eventually transformed into heat.

Heat generation at friction results from the deformation of material in the actual contact area. Some processes transform mechanical energy into heat, which can proceed via plastic deformation, hysteresis, dispersion, and viscous flow. Another source of heat can be attributed to origination and breakdown of adhesion bonds. Often it is believed that the temperature effect on friction coefficient with hardness and shear strength was found for some polymers. (93) Such correlation is valid only when temperature produces no effect on adhesion.

Friction and wear are not intrinsic material properties and a tribological system consists of three components: the interacting solids, an interfacial medium and the environment. Friction and wear are influenced by many processes, conditions, and parameters. No simple property behavior relations exist. There are two main non-interacting components of friction, namely, adhesion and deformation. (93) The observable friction and wear are determined by interaction characteristics rather than by any intrinsic properties of single components. There are three basic phenomena involved in the friction of unlubricated solids: (34)

1. The area of real contact between the sliding surfaces.
2. The type of interfacial bond that is formed at the contact interface.
3. The way in which the material in and around the contacting regions is sheared and ruptured during sliding.

When two surfaces are brought into contact, the surface forces of attraction and repulsion act between the atoms and molecules of two approaching surfaces. Due to these forces the bonds formed between the contacting surfaces are followed by junctions developed on the real contact spots. Formation and rupture of the junctions control the adhesion component of friction. For the majority of polymers, the Van der Waals and hydrogen bonds are typical. A component of frictional force is from the force required to break interfacial bonds. In general, the formation, growth, and fracture of interfacial junctions are influenced by the nature of the surfaces, surface chemistry, and stresses in the surface layers (loading conditions). If the interfacial bonding is stronger than cohesive bonding of the weaker material, then this material is fractured and the polymer transfer takes place. Otherwise fracture occurs at the interface. (93)

Friction is also a function of relative humidity. The adverse effects of humidity are further illustrated by the friction and wear of steel specimens lubricated with MoS_2 powder. As the relative humidity increased from 15 to 70%, the coefficient of friction increased from 0.05 to 0.38 and the wear in a 6-hr period increased by 200%. Drying the MoS_2 films due to frictional heating can cause a gradual reduction in the coefficient of friction. The decrease in friction observed with increasing the sliding velocity or contact pressure is also probably associated with increased dryness caused by frictional heating. (18)

The surface roughness is an important parameter influencing the contact stresses, especially at the coating/substrate interface. Roughness factor may be defined as the ratio of true to apparent surface area and values may be as high as 100 for coarse materials, while even electropolishing yields a value as high as 2.5. This was first shown in hard coatings with thicknesses less than 15µm on softer substrates, the maximum von Mises stresses both in the coating and in the substrate will be located just at their interface. This points out the importance of analyzing the stresses at the coating/substrate interface and comparing them with the coating adhesion strength. (66)

Metallic adhesion plays a central role in the area if friction and wear of rubbing tribological pairs. There are, however, few quantitative theoretical calculations regarding this phenomenon. In the study of metallic adhesion in a real world contact, we must consider the surface topography, and the mechanical properties of a solid, that is ductile or brittle, the nature of the deformation which may be elastic or plastic, and, in addition, the effects of surface films and adsorbates on the binding forces and on the mechanical properties of the interface.

Tribochemical films created during friction are not just a consequence of reactions between environment and surfaces. They imply the mechanical behavior effects at the interface when colloidal products are sheared. This initial wear-in deformation may also be accompanied by changes in friction characteristics.

There are several basic modes of lubrication (see Figure 11.3). In all modes, contact surfaces are separated by a lubricating medium, which may be a solid, a semisolid, or a pressurized liquid or gaseous film. Fluid film lubrication is the most desirable form of lubrication, since during normal operation the films are thick enough to completely separate the load carrying surfaces. Thus, friction is at a practical minimum, being due only to shearing of the liquid lubricant films. With the lubricant film thickness stepping down, lubricating state will undergo following changes: hydrodynamic lubrication → elasto-hydrodynamic lubrication → thin film lubrication → boundary lubrication → dry friction. In TFL, because the lubricant film is confined in a narrow gap separating the solid surfaces in relative motion of tribo systems, the molecules of lubricant film tend to be structurally ordered in friction shear process, due to the load and surface energy. Then lubrication film at the sub-micro or nano scales will comprise three types of film with different structures and properties (i.e. the adsorbed film, the ordered film, and the fluid film. (94)

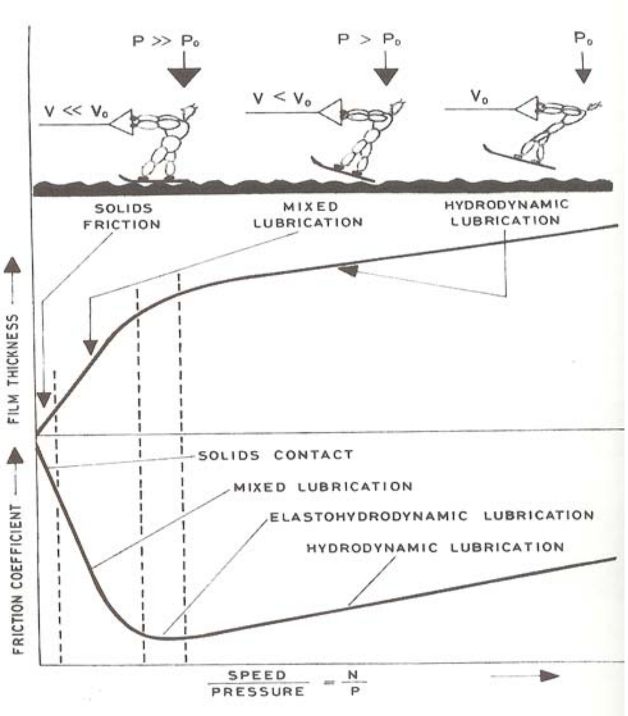


Figure11.3 Various lubrication regimes explained by oil film thickness and friction coefficient.

Hydrodynamic lubrication is a system in which the shape and relative motion of the sliding surfaces cause the formation of a fluid film having sufficient pressure to separate the surfaces. *Hydrostatic lubrication* is a system in which the lubricant is supplied under sufficient external pressure to separate the opposing surfaces by a fluid film.

Elastohydrodynamic lubrication (EHL) is a system in which the friction and film thickness between the two bodies in relative motion are determined by the elastic properties of the bodies in combination with the viscous properties of the lubricant at the prevailing pressure, temperature, and rate of shear. The recognition and basic understanding of elastohydrodynamic lubrication (EHL) was one of the major developments in tribology in the 20th century. Perhaps because of the prior work in the field of full film lubrication, tools were ready for application to this new mode of lubrication and advances and understanding came fairly swiftly. The definition of EHL is taken to be, "the study of situations in which elastic deformation of the surrounding solids plays a significant role in the hydrodynamic lubrication process." (34) Film thicknesses of EHL are typically of the order of 0.1 - 1μm.

Dry-film (solid-film) lubrication (DFL)is a system in which a coating of solid lubricant separates the opposing surfaces and the lubricant itself wears away.

Thin Film Lubrication (TFL) is ascribed to a lubrication regime where the liquid film thickness is of the order of nanometers or molecules. In thin-film lubrication, the lubricant usually is not bonded to the surfaces and it does not separate opposing surfaces. Lubricant viscosity affects friction and wear. (101) TFL is a distinctive lubrication state, bridging the gap between EHL and BL, which has its own distinctive lubrication traits. Two main influence factors of thin film lubrication (TFL) are the solid surface effects and the molecular properties of the lubricant, whose combination effects result in alignment of liquid molecules near the solid surfaces and subsequently lubricant, whose combination effects result in alignment of liquid molecules near the solid surfaces and subsequently lubrication with ordered film emerged.

Boundary lubrication (BL) is a mode in which friction and wear are affected by properties of the lubricant. In boundary lubrication, each surface is covered by a chemically bonded fluid or semisolid film, which may or may not separate opposing surfaces, and viscosity of the lubricant is not a factor affecting friction and wear. Thicknesses of boundary lubrication (BL) are usually of the order of several nanometer.

Friction is generally of secondary importance, so long as it is low enough to avoid excessive drag and frictional heating. Unfortunately, there is no general relation between wear and the coefficient of friction of a material and wear tests are necessary.

Wear

Wear is the primary basis for design and material selection, since it determines how long a part can operate before needing replacement. Wear is studied in great detail to mitigate its occurrence and to increase the products lifespan. The wear phenomenon occurs in a series of steps. Firstly, mechanical energy is introduced into the contact zone by the formation of the real area of contact. Secondly, a transformation of mechanical energy takes place mainly by the effect of plastic deformation, plowing, and adhesion. Thirdly, the dissipation phenomena include the effects of thermal dissipation, storage, or emission. (34) Wear can be classified by the type of motion that is causing material displacement (see Figure 11.4), but it is more commonly categorized by the type of interaction that is occurring between the two mating surfaces, also called wear phenomenon.

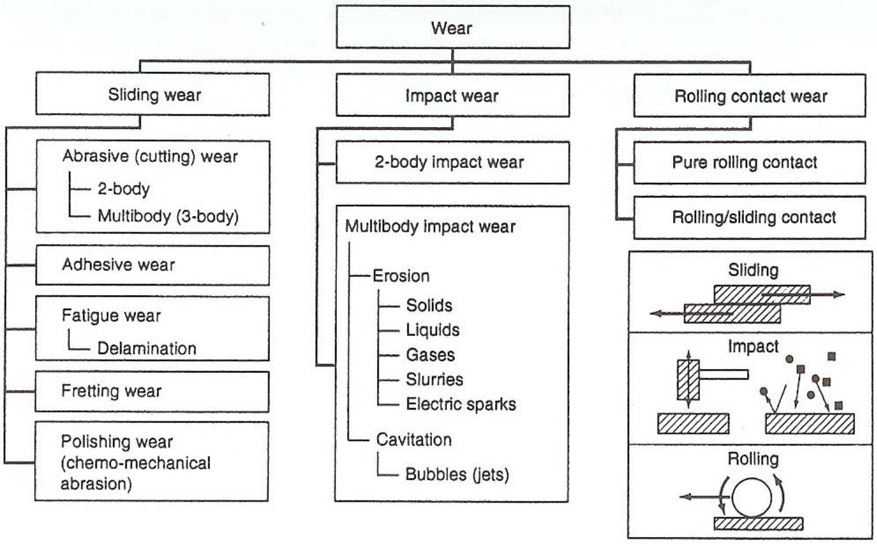


Figure 11.4 Major categories of wear classified by the type of relative motion encountered.

Wear may be divided into four broad classes: abrasion, adhesion, surface fatigue, and erosion (tribochemical processes). The manner in which the various mechanisms of wear interact is very sensitive to the specific operating conditions and, therefore, unless a single wear process dominates, the surface changes and the complex interactions make wear prediction extremely difficult. To discuss the importance of materials on the wear behavior, the chain of events which leads to the generation of wear particles must be considered. The initiation of wear particles and their removal from a tribological system is caused by two types of interactions. The first of these are stress interactions which are due to the combined action of load and forces and frictional forces and these lead to wear processes described broadly as surface fatigue and abrasion. The second area is that in which the intermolecular forces between the interacting solids or between the solid bodies and the environmental atmosphere, lead to wear processes which could be described as tribochemical reactions and adhesion. (34)

Abrasive wear causes friction and wear by displacing material from one of two surfaces in relative motion. It may be caused by hard protuberances (asperities) on the second contact surface (two-body conditions) or by hard particles between the surfaces (three-body conditions) or embedded in one of them. The hard asperities and hard particles plow (groove) or cut one of the rubbing surfaces. In the simplest model of the abrasive wear processes, the wear volume is related to the slope of the penetrating abrasive particle and to the hardness of the abraded material. More complex abrasion models have been formulated; one being related to a critical strain at which crack growth is initiated. Another model considers the detailed processes of micro-cutting, plowing, and cracking. Some of the factors which are now being considered are flow pressure, hardness, capacity of work-hardening, ductility, homogeneity of strain distribution, crystal anisotropy and mechanical instability. All of these factors influence the abrasive wear mechanism. (34) Abrasion is a common wear phenomenon in many mechanical engineering systems that is of great economical importance. Approximately 50% of the wear encountered in industry is caused by abrasion mechanisms. (19)

Since the majority of the wear phenomenon is due to the abrasive wear, it is important to understand the role of hardness. Generally, a greater degree of hardness results in less wear (see Figure 11.5), but surface roughness and wear particle size and hardness also come into play. In addition, in an abrasive wear process in which there is repeated sliding causing transfer of material, vibration of the rubbing component is seen as a natural an unavoidable phenomenon. The model is also used to explain those situations in which the harder solid has a greater degree of wear than the softer material. Seizure of metals is also explained on the basis of this model. Seizure is a special case of the growth of transfer particles in the sliding interface. (34)

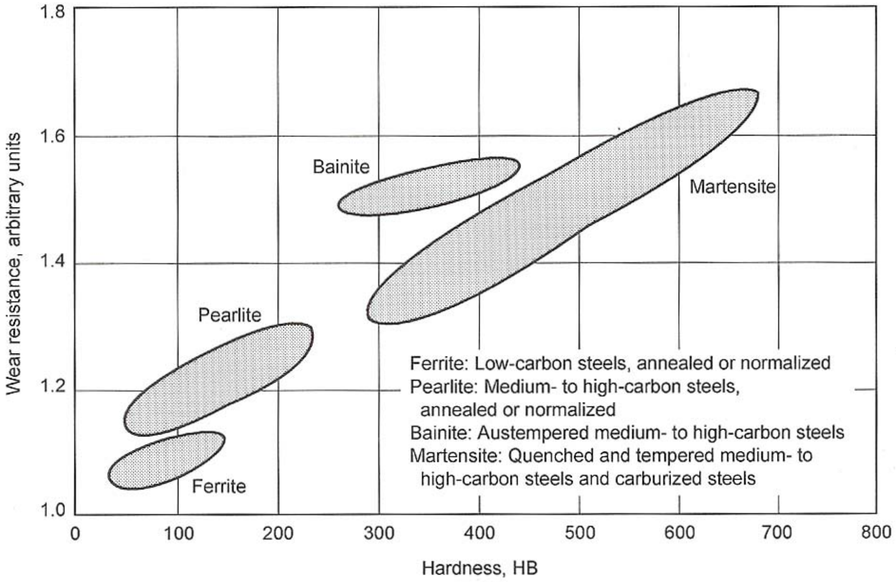


Figure11.5 Effect of structure and hardness on abrasion resistance.

Adhesive wear processes are initiated by the interfacial adhesive junctions which form when solid materials are in contact on an atomic scale. It is obvious that a number of properties of the contacting solids influence the adhesive wear mechanism. Since adhesive wear is influenced by surface contaminants and the effect of environment, it is very difficult to relate adhesive wear processes with elementary bulk properties of materials. In vacuum, where exterior influences are eliminated, the following parameters have been seen to influence adhesive wear processes in metal/metal pairs: 2) electronic structure of the contacting surfaces, 2) crystal structure, 3) crystal orientation. (34)

In *tribochemical wear*, the environmental and the dynamic interactions between the material components and the environment determine the wear process. The chemical reactions on the surfaces are strongly influenced by the high local pressures and the flash temperatures, which can be over 1000°C, at spots where asperities collide. (38) Tribochemical wear of steel occurs by a process of oxidation, deformation and fracture to produce layers which are compacted into grooves in the metal surface. Oxidative surfaces become smoother with time as the troughs become filled with oxide. Then oxidative wear occurs by the fracture of plate-like debris. These interactions are cyclic processes which include the following sequence: 1) material surfaces react with the environment and reaction products are formed on the surfaces, 2) as a result of crack formation and abrasion in the contact area, an attrition of the reaction products produces “fresh” reactive surface and stage 1 repeats.

Wear particles are formed in the real area of contact. The geometric interference between the asperities of the two surfaces is such that there is a high probability of an oblique contact and thus it is possible for fracture to occur in the interior of either of the bulk materials even if the shear strength at the interface is weaker than in the bulk. When the system is in sliding contact, a shearing fracture occurs near the contact portion and a small fragment is produced, transferred and adhered to the opposite surface. This small transfer piece is known as a “transfer element.” Because of the unsymmetric contact, shearing may occur in the harder material rather than in the softer. As the transfer elements move between the two surfaces, there will be a time when there will be a merger of two transfer elements into a "transfer particle" which will then adhere to one of the surfaces. In a repetitious process, the transfer particle gradually grows until it reaches such a size that it is removed from the surface by impingement against an asperity on the opposite surface. It is this particle that is called the "wear particle." (34) Dust generation increases with friction force and wear volume. The generated dust column is about 1/200 to 1/300 of the wear volume without lubricant. (95)

In dry friction conditions, detached and trapped wear particles (third body) circulate constantly within the contact region. Shear and fracture are two basic mechanisms for the nucleation of a wear particle and a wear scar. (99) The trapped wear particles separate the rubbing surfaces, and prevent intimate contact between the first bodies. Particle embedding, entrapping, hiding, and crushing represent typical contact condition involving the influence of debris. (66) Abrasion displays scratches, gouges, and scoring marks on the worn surface, and the debris produced by abrasion frequently takes on the appearance of fine cutting chips. The damage caused by abrasion can be generally called plowing, and it should be noted these scratches, gouges, and scoring are always accompanied by adhesion. (93)

Wear protective layers are formed from agglomeration and compaction of the fine wear debris particles entrapped within the sliding surfaces. At higher temperatures, compaction and sintering enable smooth, heavily deformed and compact glazed surfaces to develop on, and from, the particulate layers. The frictional behavior becomes similar to that of an elastic solid material and the wear rates become very low. The formation of wear protective layers is not controlled by oxidation but is closely related to the adhesion between the debris particles within the wear surfaces, which has been observed over temperatures from 20-600°C (68-1112°F) for like-on-like specimen combinations. (96) Substrate hardness may also affect establishment of the wear-protective layer since the rubbing surfaces become closer as the substrate hardness decreases, thereby increasing the removal probability of wear debris particles; this may make it more difficult to establish the wear-protective layer.

The particle's effect on the contacting surface will depend on its size and hardness. Hard and soft wear particles affect the friction and wear behavior of contact pairs differently. (88) Hard particles are more disruptive, while soft particles may mold themselves into the low points of the contacting surface and reduce friction as a transfer layer. Hardness and its affects vary on a broad spectrum, and these affects are also related to particle size. The size of wear debris particles tend to increase with increasing load. (96) Also, the critical particle size needed to establish a stable wear-protective layer decreases with increasing load, while the rubbing surfaces become closer; both effects increase the removal probability of debris particles from the rubbing surfaces. An optimum mean particle diameter can be calculated for a given theoretical surface and environment, but there is a more complex interdependence between particle size, its hardness, and the anti-wear characteristics of the suspension. Thus, under light loads particle size has no effect, while under heavy loads larger grain sizes result in increased wear. The interdependence between the above factors is further complicated by classifying the suspension by the mean particle size, as various distributions of particle diameter may exist for the same mean size. (63)

As the films wear, the lubricant is gradually sluffed off. This "sluff-off" or wear debris must have someplace to go or else it expedites destruction of the film. Therefore, wherever possible the component design should incorporate recessed areas in the contact zone. The wear microstructure includes the transfer layers which are so important to the wear process. Discarding the large torn particles leaves a collection of very fine particles (of the order of 50 Å) that are layered into the surface. These particles are a mixture of materials from both sliding surfaces and appear to be sintered into continuous layers. These layers can de-bond and be emitted as flakes. It is assumed that the large flakes come from a detachment mechanism of the transfer layer by fracture at the boundary with the substrate.

Corrosion

In the most general sense, corrosion is a process of gradual destruction of all materials, existing in all environments, as the result of chemical or electrochemical effect of the environment on these materials. All environments – air, gases, water, soil, particularly in the presence of oxygen, moisture and chemical compounds of sulfur, acids, alkalis, electric field and other factors – spontaneously act destructively (with very few exceptions) on all structural materials, i.e., metals and their alloys, concrete, rocks, ceramic, wood, plastics, etc.

The potential available to promote the electrochemical corrosion reaction between dissimilar metals is suggested by the galvanic series, which lists a number of common metals and alloys arranged according to their tendency to corrode when in galvanic contact (see Appendix F). Metals close to one another on the table generally do not have a strong effect on each other, but the farther apart any two metals are separated, the stronger the corroding effect on the one higher in the list. It is possible for certain metals to reverse their positions in some environments, but the galvanic order is maintained in natural waters and the atmosphere. (103) The area relationship between the anode and cathode may also strongly affect the corrosion rate; a high ratio of cathode area to anode area produces more rapid corrosion. In the reverse case, the cathode polarizes, and the corrosion rate soon drops to a negligible level. (103) Uniform corrosion can be prevented or reduced by proper materials selection, the use of coatings or inhibitors, or cathodic protection. These corrosion prevention methods can be used individually or in combination.

Surface roughness significantly affects corrosion resistance. The lower the roughness, the higher the resistance. A rise in surface roughness intensifies corrosion processes by the development of real surface of contact of the element subjected to corrosion, creation of possibilities for accumulation on the surface of contaminants and moisture and, in consequence, chemical and electrochemical heterogeneity of the surface, conductive to the formation of corrosion sources.

There are only a few metals that will be stable in our water-based environment. Most metals will revert to their native mineral, ore-like states. Most metals are found as oxides and sulfides, which are the most atomically stable forms. Iron is more stable as an oxide than as a metal. In the corrosion process iron oxidizes in the presence of water, yielding Fe2+ ions. The Fe2+ ions, meanwhile, react with hydroxide ions in the water to make Fe(OH)2, or “green rust,” which reacts with oxygen in air to form Fe(OH)3 – what we commonly recognize as rust.

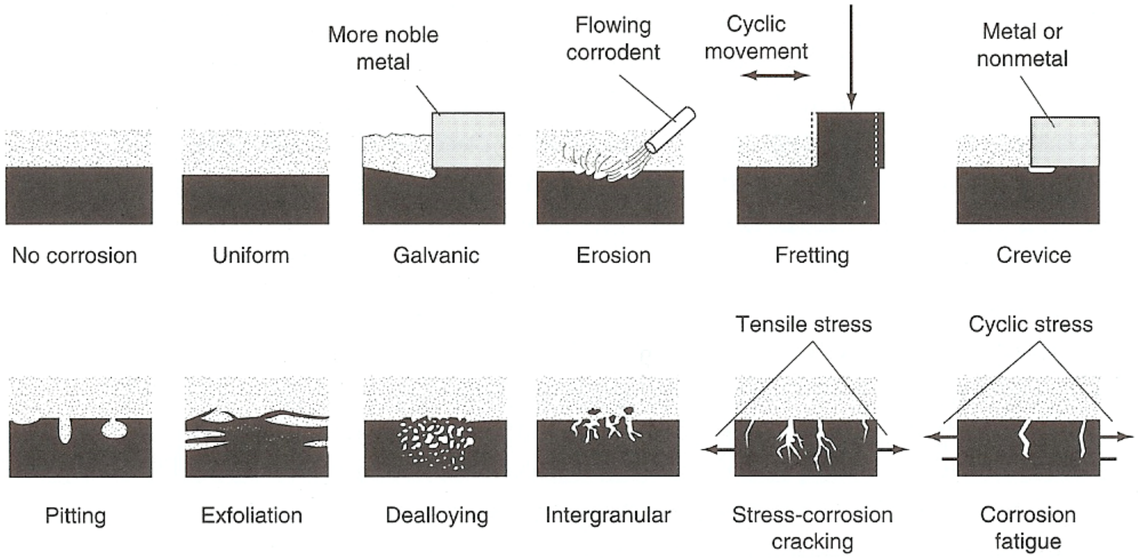


Figure 11.6 Schematics of the common forms of corrosion

Cavitation is a form of *erosion*-corrosion that is caused by the formation and collapse of vapor bubbles in a liquid against a metal surface. The appearance of cavitation is similar to pitting except that surfaces in the pits are usually much rougher. The affected region is free of deposits and accumulated corrosion products if cavitation has been recent. (103)

Fretting corrosion is a combined wear and corrosion process in which material is removed from contacting surfaces when motion between the surfaces is restricted to very small amplitude oscillations (often, the relative movement is barely discernible). Usually, the condition exists in machine components that are considered fixed and not expected to wear. Pressed-on wheels can often fret at the shaft/wheel hole interface. Fretting corrosion can be controlled by lubricating the faying surfaces, restricting the degree of movement, shot peening, or surface hardening. (103)

Pitting is a type of localized cell corrosion. Pitting develops when the anodic or corroding area is small in relation to the cathodic or protected area. For example, pitting can occur where large areas of the surface are covered by mill scale, applied coatings, or deposits of various kinds and where breaks exist in the continuity of the protective coating. Pitting may also develop on bare, clean metal surfaces because of irregularities in the physical or chemical structure of the metal. Localized, dissimilar soil conditions at the surface of steel can also create conditions that promote pitting. (103) Despite their good resistance to general corrosion, stainless steels are more susceptible to pitting than many other metals. High-alloy stainless steels containing chromium, nickel, and molybdenum are also more resistant to pitting but are not immune under all service conditions. (103)

Corrosion fatigue, or *stress-corrosion cracking*, is a term used to describe the phenomenon of cracking, including both initiation and propagation, in materials under the combined actions of a fluctuating or cyclic stress and a corrosive environment. Corrosion fatigue depends strongly on the interactions among the mechanical, metallurgical, and environmental variables (see Table 11.1). (103)

Table 11.1 Mechanical, metallurgical, and environmental influences on corrosion fatigue. (103)

Variable	Type
Mechanical	Maximum stress or stress-intensity factor, σ_{max} or K_{max} Cyclic stress or stress-intensity range, $\Delta\sigma$ or ΔK Stress ratio, R Cyclic loading frequency Cyclic load waveform (constant-amplitude loading) Load interactions in variable-amplitude loading State of stress Residual stress Crack size and shape, and their relation to component size and geometry
Metallurgical	Alloy composition Distribution of alloying elements and impurities Microstructure and crystal structure Heat treatment Mechanical working Preferred orientation of grains and grain boundaries (texture) Mechanical properties (strength, fracture toughness, etc.)
Environmental	Temperature Types of environments: gaseous, liquid, liquid metal, etc. Partial pressure of damaging species in gaseous environments Concentration of damaging species in aqueous or other liquid environments Electrical potential pH Viscosity of the environment Coatings, inhibitors, etc.

Often, severe tribological conditions such as high applied pressure, high temperatures, and corrosive environment pose extreme requirements for the coating. The oxidation resistance of a coating is usually deduced from the depth of oxygen diffusion into the film when the films are heated in oxygen or air. Films with a pronounced columnar morphology oxidize more than seven times faster than films with a dense and fine-grained morphology. (91) Pores negatively affect tightness of coatings, substantially reducing their corrosion resistance. This is true especially of coatings which are cathodic relative to the substrate metal and does not apply almost at all to anodic coatings. Porous coatings which are not tight do not assure total insulation from the surrounding corrosive environment, and do not totally inhibit the diffusion of aggressive agents through the coating which leads to the formation of local corrosion sources, sub-coating corrosion of the substrate, and blistering of the coating. (15)

The chemical composition of the superficial layer also has a decisive influence on the extent of corrosive wear of steel; alloying additions in the form of sulfur and phosphorous enhance, while chromium, nickel, manganese, copper, molybdenum and aluminum retard the rate of atmospheric corrosion.

Chapter 12: Coating Design

The ideal coating would be one which, when applied to the metal surface, is entirely impervious and resistant to the corroding medium, is firmly adhered to the basis-metal, and at the same time possesses a surface that is as hard, frictionless, and durable. The ideal functional requirements for a next-generation bore coating are a melting point higher than the gun steel, high elevated temperature strength, high fracture and impact toughness, an elastic modulus equivalent to or lower than the gun steel, high chemical inertness, a compatible coefficient of thermal expansion with the substrate, a low thermal conductivity and specific heat, and phase stability.

In some cases, a thin film or bonded solid lubricant coating is used as an overlay on the self-lubricating composite material to reduce the coefficient of friction. The thin film can be any material, such as soft metal, polymer, ceramic, or a modified surface layer of the diamond, that has low shear strength or low surface energy. The hard substrate reduces both the real area of contact and the plowing contribution of the counterpart material; a thin film or a thin surface layer reduces the shear strength and surface energy in the real area of contact. The low coefficient of friction can be attributed to the combination of the low shear strength and the low surface energy of the thin film or the thin surface layer and the small real area of contact resulting from the high elastic modulus and hardness of the substrate. This assures the minimum friction coefficient obtainable by enrichment of the composite surface with lubricant while providing long life due to the sintering and infiltration. Where coatings are appropriate, similar compositions can be prepared by plasma spraying. (34)

Precise patterning of coatings to improve tribological properties is a rather new concept that will probably progress in the near future. In the past decade, various surface texturing technology, such as laser, plasma, wire-electric, lithography and anisotropic etching of silicon wafers, and other micro-processing techniques, have been applied to surface engineering in the microelectronic industry. In the case of flat parallel sliding surfaces, a texture involving flat and smooth lands interrupted by local depressions can reduce wear, reduce friction, reduce the apparent contact area, and improve load bearing capacity. The elimination of wear debris from the interface reduces the plowing and deformation components of friction. Pore depths that yield to positive tribological improvements (>10 μm) are larger than film thickness (<5 μm). Another important effect of the surface depressions is to act as reservoirs for lubricants, capable of feeding the lubricant directly between the two contracting surfaces. Thus, the friction is reduced and the lifetime of the contact is increased. (73) The coefficient of friction is also reduced by reducing the apparent contact area by tailoring the pattern, size, and density of the surface texturing. It was found that a friction reduction of 30% and even more is feasible with textured surfaces. (107) The improvement to load bearing capacity caused by these "microgutters" is typically attributed to local hydrodynamic effects. Analytical solutions indicate that the effect of the ratio between the depth and diameter of a depression is more significant than the area fraction covered by depression. Only a handful of surface texture geometries have been attempted thus far, and have proven successful in reducing the coefficient of friction with unlubricated TiN coatings and lubricated DLC coatings, but at the sacrifice of increasing wear. (73) Coating patterning probably will be a major axis of development in coatings technology in the next decade.

In order to design a coating as a component of a complete system, the designer must be able to model the system using computer assisted design (CAD). Unfortunately, the various topics that tribology covers are not understood individually let alone as a whole. Valiant attempts are under way to unify thinking in tribology. However, a number of philosophical divisions remain, and these persist in the papers and books being published. Ultimately, the divisions can be traced to the divisions in academic institutions. The four major ones are: (108)

1. *Solid Mechanics:* focus is on the mathematics of contact stresses and surface temperatures due to sliding. Workers with this emphasis publish some very detailed models for the friction and wear rates of selected mechanical devices that are based on very simple physical tribological mechanisms.
2. *Fluid Mechanics:* focus is on the mathematics of liquid lubricant behavior for various shapes of sliding surfaces. Work in this area is the most advanced of all efforts to model events in the sliding interface for cases of thick films relative to the roughness of surfaces. Some work is also done on the influence of temperature, solid surface roughness, and fluid rheology on fluid film thickness and viscous drag. However, efforts to extend the methods of fluid mechanics to boundary lubrication are not progressing very well.
3. *Material Science:* focus is on the atomic and microscale mechanisms whereby solid surface degradation or alteration occurs during sliding. Work in this area is usually presented in the form of micrographs, as well as energy spectra for electrons and x-rays from worn surfaces. Virtually all materials, in most states, have been found. Second, material scientists (engineers, physicists) rarely have a broad perspective of practical tribology.
4. *Chemistry*: focus is on the reactivity between lubricants and solid surfaces. Work on this progresses largely by orderly chemical alteration of bulk lubricants and testing of the lubricants with bench testers. The major deficiency in this branch of tribology is the paucity of work on the chemistry in the contacting and sliding conjunction region.

Not only is there a disconnect between the major fields of study that comprise tribology, but there is also a lack of understanding for some of the most basic phenomenon that tribology seeks to understand. At the atomic level, current gaps in our understanding include the influence of atomic and molecular order, the origin of frictional anisotropy, and the role of discreet chemical reactions in the process of atomic-scale wear, the location of the slip plane(s) during sliding, the nature and real area of contact, the amount of strain at the interface and throughout the deformed volume, the energy density (temperature) and energy-density distribution in the contact, heat dissipation pathways and rates in abrasive interactions, equilibrium versus non-equilibrium interfacial composition, morphological changes occurring in the surface and subsurface regions, and tribochemical reactivity. (98) In order to begin understanding these phenomena, improvements are needed in two major areas. The first involves improving the reproducibility and reliability of tribological data coming from different laboratories/tribometers. Another area entails improving the capabilities of tribometers to allow dynamic characterization over the entire range of size scales. Once these two areas of measurement have been improved upon, engineering data base utilities need to be created for selecting engineering materials, manufacturing processes, or standardized components. An intelligent (knowledge-based) data base system must assist the user in setting up property requirements, establishing preferences for properties (range of allowable materials), and eliminating those materials and properties deemed to be unimportant or undesirable.

As a function of time the tribological process causes changes in both the geometry and the material composition and results in energy related output effects: friction, wear, velocity, temperature, sound, and dynamic behavior that can be very difficult to model. Dynamic problems with modeling: (108)

1. The real contact area cannot be measured and continually changes.
2. The surface temperatures change the material properties, strain, chemical reactivity of lubricant, and oxidation rates.
3. It is difficult to calculate heat flow, and temperature distributions.

To begin modeling tribological activity between two surfaces, it is imperative that we can measure or precisely estimate the contact area. A great number of methods have been attempted to measure real area of contact but all methods have shortcomings. Five methods and limitations are listed: (108)

1. Two large model surfaces with asperities greater than 1 inch in radius, one covered with in k which transfers to the other at points of contact. Acceptable simulation of microscopic asperities has not yet been achieved.
2. Electrical resistance method. This method is limited by surface oxides.
3. Adhesion and separation of sticky surfaces. In this method two clean metal surfaces in a vacuum are touched together with a small force and then pulled apart. The force to separate was thought to be $W = 3YA$. This method is limited by elastic recovery when load is removed and by fracture of bonds that may extend beyond the contact region.
4. Optical method, interference, phase contrast, total internal reflectance, etc. With these methods it is difficult to resolve the thickness of the wedge of air outside of real contact area down to atomic units, which is the separation required to prevent adhesion.
5. Acoustic transmission through the contact region between two bodies.

Another dynamic system that will be difficult to model is the erosion caused by the propellant. Historically, the propellant adiabatic flame temperature was used as an indicator of the erosivity of a propellant. Unfortunately, flame temperature is not the only factor influencing the erosion process, which includes mechanical abrasion, pyrolysis, melting, and spalling. Attempts to model erosion using first principles have been and are currently being made, although it is believed that significant additional work is still required to understand the fundamental physics involved. (41)

While these dynamic systems may be difficult to model, there are fundamental equations in place for modeling stress, strain, and deformation. Three modes of failure are each associated with a different type of stress, which can be tailored with the material property (see Table 12.1). The maximum von Mises stress is recognized as a key parameter for controlling the initiation of micro-crack and the wear caused by plastic yield. The stress strongly depends on the friction coefficient and, in general, the maximum stress appears below the surface when the friction coefficient is smaller than 0.3 and on the surface when the friction coefficient is smaller than 0.3 and on the surface when the friction coefficient is larger than 0.3. (102) Tailoring elastic moduli will not decrease von Mises stress in the interlayer, since no force corresponds to it. The maximum tensile stress occurs on the surface and appears just behind the trailing edge of contact. The stress sensitizes to the friction coefficient, coating thickness, and the ratio of elastic modulus of the coating to the substrate. It has been recognized also that the maximum tensile stress in concerned with the formation of tensile cracks under sliding contact. The maximum shearing stress is usually recognized as a key parameter for controlling the spalling of the coating from the interface between the coating and the substrate. The maximum shearing stress appears at the interface and is controlled by the relative coating thickness (ratio of coating thickness to the half contact width). In order to decrease the maximum shearing stress on the interface between the coating and the substrate under sliding contact, one of the methods is to design a softer interlayer.

Table 12.1. Association of material properties to failure.

Failure	**Associated Stress**	**Associated Material Property**
Plastic yield & micro-cracks	Von Mises stress	Friction coefficient
Cracks	Max tensile stress	Ratio of elastic moduli
Spalling	Max shear stress	Coating thickness and ratio of elastic moduli

Gradient coatings appear to be promising for designing coatings that minimize these stresses and their associated modes of failure, along with alloy coatings. Each layer can impart a specific property, such as the ability to act as a thermal barrier or diffusion barrier, or to impart abrasion resistance. Early models predicted that high-yield strength materials could be fabricated by alternating thin layers of high-shear-modulus material with thin layers of low shear modulus. (66)

To this day, we have not learned to design in the same manner that we approach mechanical design. Experiments were conducted for automotive engine applications with a number of proprietary composite coatings, all of which resulted in high friction and shear stresses resulting in edge chipping and large fractures. (35) Today, to this end, we still use traditional methods or develop a surface layer with various properties which is later tested in different conditions, first in the laboratory, next in the industry, to finally determine its range of applications. It is only in very rare cases that the opposite order is practiced.

A final general recommendation entails the need to forge closer links between the theoretical and experimental efforts. It is clear that any serious efforts to compare the results of experiment with the predictions of theory, or to relate tribological properties of the components, will rely on being able to accurately calculate and measure properties of the contact, an effort complicated by the dynamic dependence of real contacts. Knowledgeable, mathematical design of surface layer properties for strictly determined needs, along with their practical verification, constitutes a very important, although very difficult and, as yet, quite distant problem to be solved by surface engineering.

Many of the component failures occurring in service can be avoided or delayed by better incorporation of tribological principles into engineering design. Knowledge-based computer systems offer great potential for effecting tribology knowledge transfer and promoting improved design practice. Unfortunately, because there is a lack of straight-forward criteria regarding tribological design, the practical application of tribology fundamentals often requires a level of specialist insight that all but the most experienced of design engineers are unlikely to possess. It may be difficult to determine and model the exact mechanisms for a given tribological problem. For example, wear problems cannot directly be related to the occurrence of particular wear mechanisms such as adhesive, abrasive, fatigue, and chemical wear, which relate only to the physical and chemical processes occurring during the process of wear. (111)

The rapid increase in computer power over the last decade presents great opportunities. However, qualitatively new algorithms and modeling approaches are needed to span the complex nature of tribological processes, which occur over a wide range of length and time scales. Molecular dynamics (MD) simulations have been one of the primary approaches used to investigate tribological phenomena on the atomic scale. While this approach provides full information about the role of each atom and the ability to perform ideally controlled "experiments", it is limited to length scales of micrometers and smaller, and time scales of microseconds and less. Addressing the issue of length scales might involve linking atomic-scales analyses to continuum models through simultaneous or hierarchical hybrid approaches. (98)

Significant improvements are also needed in computer assisted engineering (CAE) models, which will allow incorporation of tribological effects in the design at the outset. (98) At the continuum level, currently available contact mechanics models are not capable of accurately predicting contact areas for rough surfaces. In many situations it would be desirable to anticipate the friction and wear properties of a specific interfacial contact based upon the composition, atomic/molecular structure, and topography of the individual materials. When asperities come into contact and elastically or plastically deform until the real area of contact is sufficient to carry the load. A bond may then occur between the two surfaces that is stronger than the intrinsic strength of the weaker of the two materials in contact. When relative motion between the two surfaces occurs, the weaker of the two materials fails, and material is transferred to the contacting surface. Modeling this dynamic system is incredibly complicated. Undoubtedly, quantitative predictions of friction and wear characteristics will rely upon an understanding of contact mechanics and energy dissipation as well, yet there still remain the need to understand and classify material pairs, for example, as low friction or low wear. (98) Unfortunately, for the time being, surface engineering is still designed with experience and handicraft.

In the future, tribological materials will be designed at the atomic scale by groups of tribologists, materials scientists, physicists, and chemists. Elemental properties will be taken into account such as material phases, microstructure, lattice structure, and forces from interatomic bonds. Lattice structures will be designed to prevent diffusion, prevent grain boundary sliding, and eliminate defects and vacancies. Considering that the theoretical strength of a solid is solely a function of the strength of the interatomic bonds between atoms, the theoretical maximum yield strength could be tailored specifically to a designed lattice structure. In practice, however, the strength of inherently strong solids never meets these theoretical expectations because of the presence of crystal imperfections, microscopic defects, and cracks. (103)

Chapter 13: Conclusion

The goal of this project is to lengthen a firearm's lifecycle while increasing performance and reliability through use of advanced coating techniques. This research identifies the Achilles' heel of the second highest selling assault rifle on the market. There are over 10 million AR15 and AR15 variants in circulation around the world. The average life of tooling with hard coatings is 2-5 times longer than that of uncoated tools, which makes it an economically viable solution despite the 50-100% increase in coating cost. (15) Firearms would have longer lifecycles, less down time for maintenance, and would be more reliable (a potentially lifesaving and priceless feature). These assault rifles in their current configuration suffer from catastrophic malfunctions such as failure to fire and failure to extract, which are potentially life threatening. The critical parts of these firearms include: the receivers, barrel, barrel extension, bolt carrier, bolt, and the extractor. All of the AR15 critical parts examined during this research were manufactured by Colt Defense, since they are the largest Department of Defense supplier of AR15 variants.

All critical parts except for the receiver were made primarily of iron with varying amounts of other alloys. The Bolt Carrier and the Barrel Extension were both similar to 90XX series steel except for the presence in the hundredths of a percent of boron, phosphorous, and sulfur. The bolt was almost an exact match for 40XX series steel, but the bolt contained copper. Compared to the bolt carrier and barrel extension, the bolt has the addition of nickel to change its microstructure from ferrite to austenite. This makes the bolt more ductile and tougher. The addition of nickel is common to maraging steels to improve their toughness. Unlike the other steel components, molybdenum and copper are missing from the extractor since a high strength to weight ratio is not critical for this small part, unlike the bolt carrier and barrel extension. Table 13.1 summarizes the materials and coatings used to make the critical parts.

Table 13.1 Critical parts materials and coatings.

Part	Material	Typical Coating
Receivers	·7075-T6 Aluminum	·Anodized Type III Hardcoat
Barrel	·ORD/AISI/SAE 4150 ·ORD/AISI/SAE 4150 Resulfurized ·4140 Chrome-Moly Steel ·Chrome-Moly-Vanadium Steel	·Manganese Phosphate ·Hard Chrome Bore and Chamber
Barrel-Extension	·90XX Series Steel	·Parkerized Exterior ·Hard Chrome Interior
Bolt	·40XX Series Steel	·Parkerized ·Hard Chrome
Bolt Carrier	·90XX Series Steel	·Parkerized ·Originally Chrome Plated
Extractor	·40XX Series Steel	·Parkerized

Etching revealed that the bolt, bolt carrier, and barrel extension received a surface treatment, which can be seen as the faint ring around the sectioned parts (see Figures 6.4, 6.5, and 6.6). This is interesting since these three parts are in direct contact with the cartridge as it undergoes combustion, and are the most highly stressed parts in this system. Nitrides, carbides, and borides are the hardest surface treatment operations, and their added cost would be justified for critical parts subjected to high temperatures and pressures.

A hardness and microhardness test of each critical part shows that the aluminum receivers are the softest, followed by the barrel, extractor, bolt, bolt carrier, and barrel extension (see Figure 6.9). The three hardest parts also show increased hardness around the outer edges, confirming that these parts had received surface treatment as indicated by the outlines revealed by etching. The barrel extension and bolt carrier were expected to have a more similar hardness profile since these parts had the same elemental composition, but they appear to have different microstructures or may have received different surface treatments.

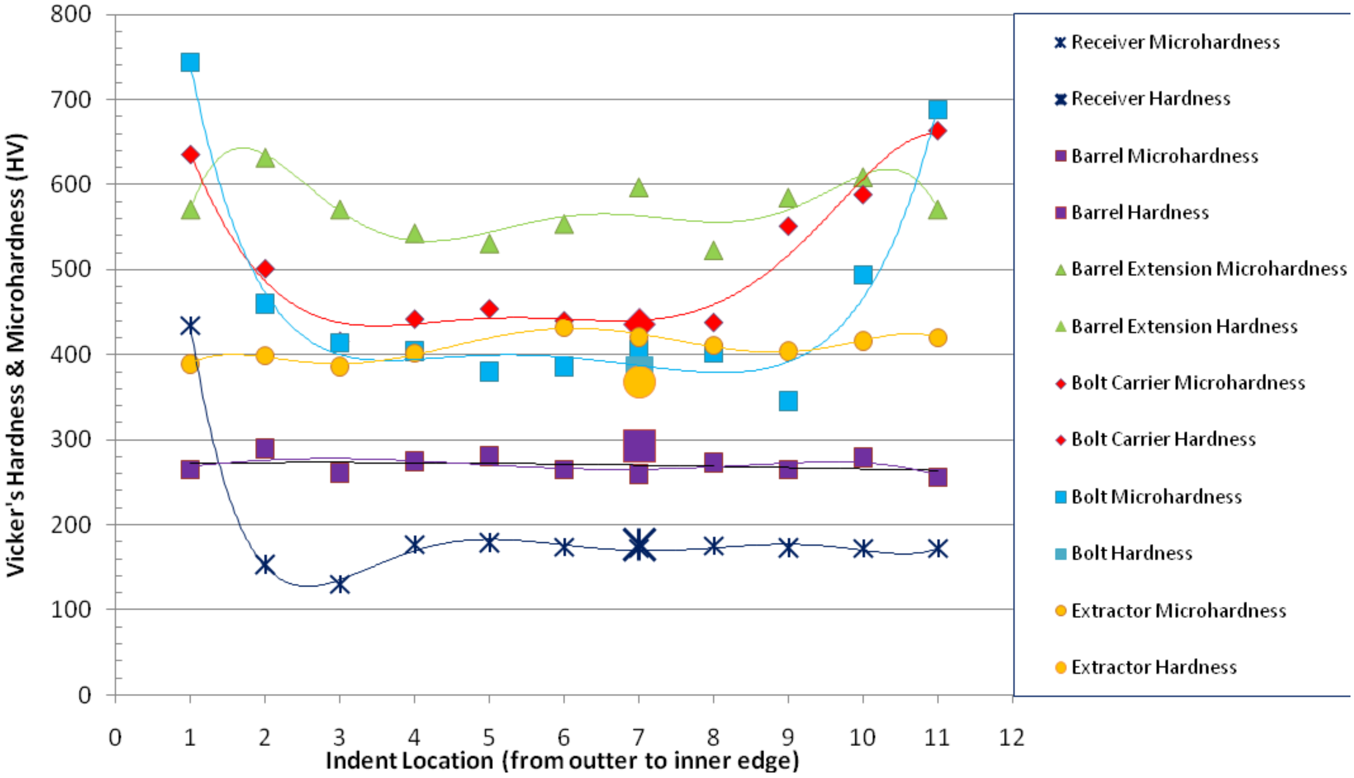


Figure 13.1 M16A2/M4 Critical Part Hardness Compared to Microhardness

Due to numerous catastrophic fractures of the M16 rifle bolt under firing conditions at an unspecified United States Army installation, a failure analysis of the M16 rifle bolt was conducted at the United States Military Academy. The analysis used (1) fractured bolts to gather metallurgical evidence, (2) new bolts to conduct a controlled experiment, and (3) geometric finite element analysis to analyze stress locations. The highest stress concentrations were present in the locking lugs which were immediately adjacent to the extractor (see Figure 6.5). The base metal exposed due to the wear makes this area susceptible to corrosion pitting. It was discovered that the fracture initiated at a localized corrosion pit and propagated by fatigue. The fractures of the M16 bolt are a result of the cumulative effect of high stress concentrations at the fillet radius and the additional stress concentration imposed by the presence of localized pitting at the surface. The primary cause for failure was coating wear. One possible countermeasure to prevent wear is to case harden the material. Disparities between microhardness profiles near the fillet region and 10 mm away from this region revealed that the bolt may not have been uniformly case hardened. The softer, less carburized region near the fillet contributes to the formation of a wear area after firing just 1800 rounds. (17)

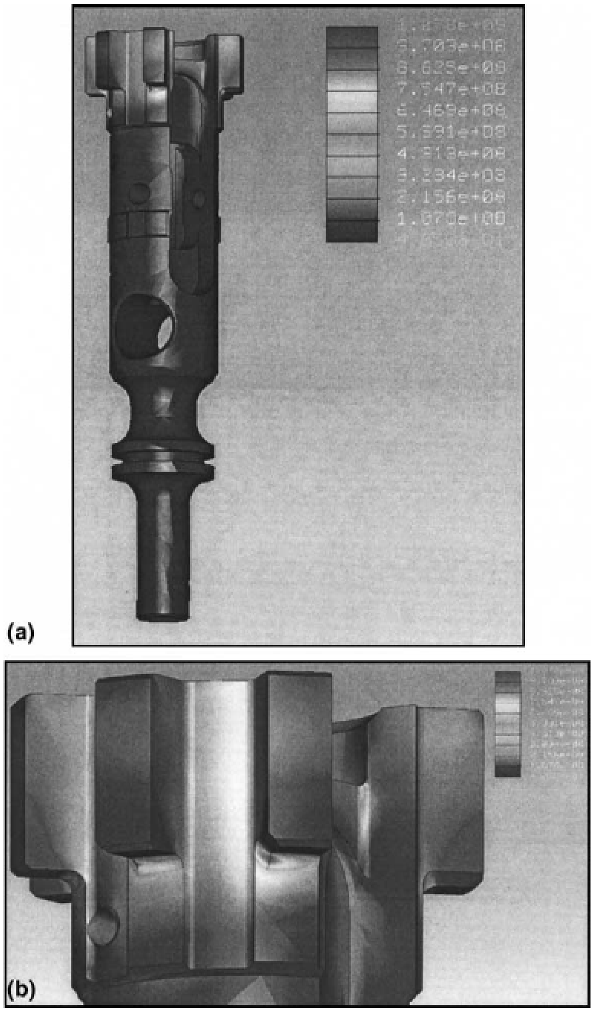


Fig. 13.2 (a) Model of von-Mises stress distribution in M16 bolt (stress values in Pa). (b) Model of von-Mises stress distribution in fillet region of locking lugs adjacent to extractor (stress values in Pa). (17)

When looking at the failure modes of firearm coatings, corrosion is the greatest cause for unserviceability. Chamber erosion gauges do not accurately determine the serviceability of the firearm, but Go, No-Go, and Field gauges can be used to check if the firearm is safe for firing, although accuracy is not guaranteed.

The fast development of a large variety of different advanced surface modification and coating deposition techniques during the last few decades offers remarkable possibilities to improve the functional reliability and lifetime of firearms, components, and other surfaces in sliding contact. Oil lubricants are overused and misused in today's military. Other, more economically and environmentally friendly alternatives exist.

Cleaner, Lubricant, and Protectant (CLP) is one of two lubricants authorized by the military for use on the M16 and other variants (the other being for cold weather climates). CLP is also used to clean all areas, internal and external, of powder fouling, corrosion, and dirt. CLP creates a thin film of Teflon after repeated use, which hot water and solvent will strip away. Poor training in the military has resulted in the frequent use of solvents for cleaning firearms. CLP and other oil lubricant traps sand, dirt, and dust particles in the firearm, which increases the likelihood of a jam.

Each tribological property was discussed individually in chapter 11, but the interconnection of these properties has not yet been emphasized. Adhesion is an important property in high temperature and high pressure environments. Without proper adhesion, firearm coatings would delaminate from the substrate reducing the hardness, wear resistance, and corrosion resistance. Surface hardness is important in regards to wear resistance, especially in a high pressure environment. Unfortunately, a rise in hardness is often connected with a rise in brittleness. The hardness of crystalline bodies depends on the limit of elasticity under compressive loading and on the modulus of elasticity. Friction control is extremely important to reduce wear resistance and increase reliability. Wear resistance helps increase reliability, durability, and helps prevent corrosion. When looking at the failure modes of firearm coatings, corrosion is the greatest cause for unserviceability. Corrosion causes a loss of mechanical strength or ductility for the overall metal component.

Coatings have been used on firearms for centuries to combat corrosion. Antiquated coatings, that have been the standard for firearm coatings for centuries, are beginning to be replaced by more modern coating materials and techniques. One such coating is black oxide coatings, commonly called bluing in the firearms industry, which have been used for over the past 200 years. Bluing is formed by a chemical reaction that produces a conversion coating in the form of rust and offers no protection from oxidation, rather, relying on a protective layer of oil. The process of phosphate coating, in use since the late 1800s, found itself refined by the military around 1910 and trade-named Parkerizing. (55) Parkerization is a very durable non-reflective finish that changes the surface of steel to a semi-neutral phosphate to provide a considerable resistance to rust. Chromium plating was perfected in the early 1900s, but has only been used in firearms since the mid to late 1970s. While electroless nickel and chrome plating have seen increased use over recent years, bluing and Parkerization are still the industry standard. Parkerization is more durable and resists rusting much better than bluing does, but the downside is that it is not very aesthetically pleasing to civilian hunters and sportsmen. Anodizing has also become an industry standard for aluminum parts, and has been further enhanced by incorporating PTFE to reduce friction. Anodizing is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts.

- Electroless nickel and chrome plating have proven to be economically, tribologically, and environmentally viable solutions. Of the plating techniques these are the two hardest. Although areas can be masked to prevent coating, electrodeposits are unable to achieve uniform deposition. Chrome is very hard, has a low coefficient of friction, and comes very close to being an ideal firearm finish, but it is not the ultimate in corrosion resistance.

- Polymers and solid lubricants, such as PTFE and MoS_2, can be potentially used in firearm coatings as a composite. Solid lubricants generally provide low coefficients of friction, and their wear rates can be low, depending on their binder. Friction is attributed to adhesion in the contact zone, and deformation of the contacting surfaces. Polymers have low to no van der Waals force and deform easily, thereby easily creating a transfer layer and minimizing friction.

- Ceramics are gaining increasing use in industry due to their wear properties, frictional characteristics, high hardness, corrosion resistance, high elastic moduli, and their high temperature capabilities. There are over 600 ternary compounds known involving carbon and nitrogen with transition metals belonging to groups IVb, Vb, and VIb of the periodic table. The most commonly used ceramics include: nickel boride (Ni_2B, Ni_3B), titanium diboride (TiB_2), boron carbide (B_4C), silicon carbide (SiC), tungsten carbide (WC), Boron Nitride (h-BN, c-BN), chromium nitride (CrN), titanium nitride (TiN), titanium aluminum nitride (TiAlN), and tungsten disulfide (WS_2). To date, titanium based coatings have defined the benchmark of ceramic coatings. Ceramics can be made self-lubricating by incorporating lubricating components into their basic structure or by surface diffusion of the solid lubricant material into the surface layer of the ceramic.

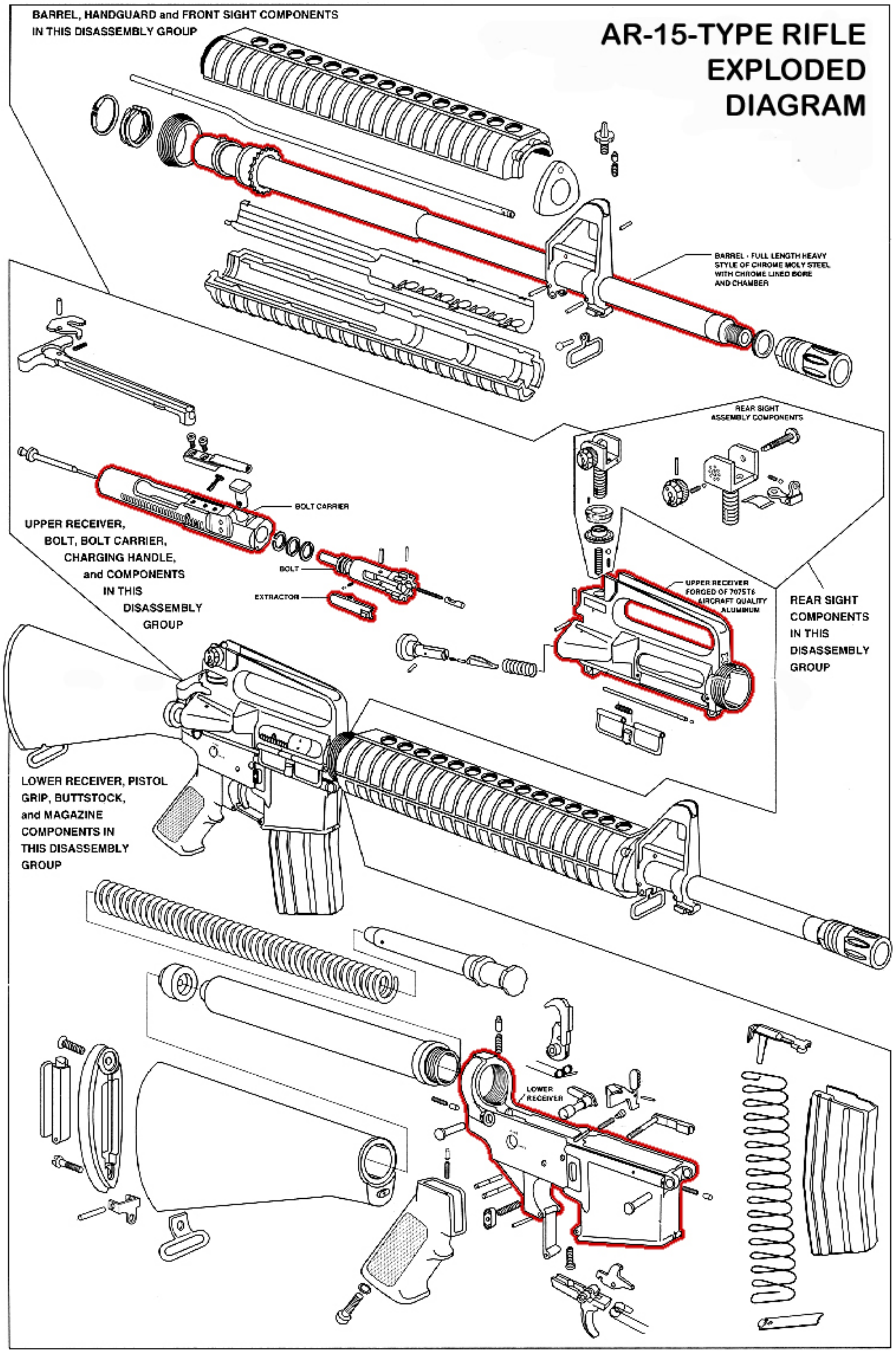
- Diamond is currently the hardest material known to man (although the hypothetical carbon nitride, C_3N_4, is theoretically harder). It is excellent for tribological applications because of its high abrasion resistance, good fatigue strength, high thermal conductivity, good radiation and temperature resistance, chemical and thermal inertness, high corrosion resistance, and environmental compatibility. Of the diamond coatings, diamond-like carbon (DLC) is the most tribological and cost effective coating. With current technology DLC cannot be obtained in thick monolithic shapes and has high internal residual stress. Therefore, DLC may be most advantageously used in its particulate form as an additive in composite coatings, such as is used in Thin Dense Chrome with Diamond Particles (XADC) created by Armology Corporation.

- The most promising future firearms coating lies in composites. Glock and Robar were the first companies to use composite coatings in firearms. Robar uses an electroless nickel and Teflon coating, which it calls NP3. Industrial coating technology is capable of making multicomponent and multilayered coatings. Current technology has also made superlattice, gradient, and nanostructured coatings possible. Future coating technology promises adaptive coatings that have the ability to change their properties to meet the requirements of the operating conditions.

The lack of availability of tribological testing lab equipment was a concern at the beginning of this experiment. After struggling to find sufficient testing equipment, these conclusions will currently rely on tribological evidence gathered by other researchers. Tribological testing of the materials under laboratory test configurations can only be considered as a helpful screening tool that allow only an introductory evaluation of the behavior of coatings. The final choice of the right material combination would be dependent on the results of subsequent field tests. An absolute indicator of tribological performance of a coating is the measurement of its lifecycle in service conditions to gain a complete metric of external chemical, electrical, mechanical, and other loads. Service is the ultimate test, but service tests can be prolonged, expensive, and difficult to control, and premature failures in service can be disastrous. Therefore, low-cost laboratory tests should be conducted to obtain preliminary estimates of a lubricant's potential and to provide a means for production quality control.

This research was successful in (1) identifying a suitable firearm for use with advanced coatings, (2) identifying this firearm's greatest cause of catastrophic failure, (3) comprehensively surveying coatings from the past, present, and future, (4) analyzing the nature of coating tribology, and (5) recommending coating alternatives that will lengthen a firearm's lifecycle while increasing performance and reliability.

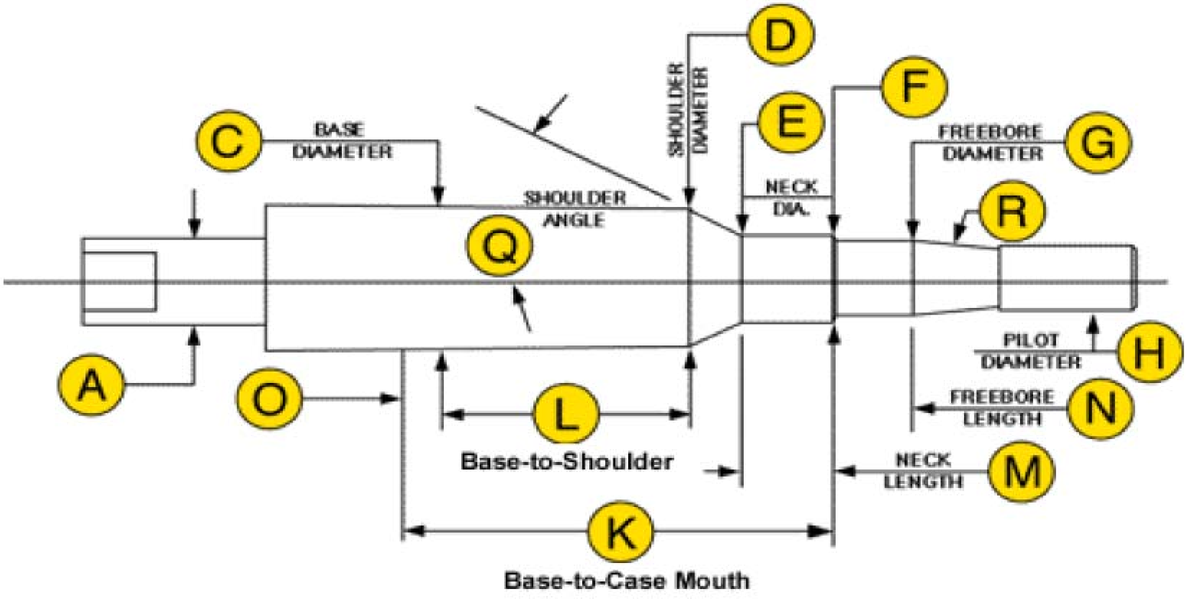
Appendix A: AR15-Type Rifle Exploded Diagram



Appendix B: M16A2 Specifications (98)

Weight:	**US Customary**	**Metric**
Without magazine and sling	7 lb 8 oz	3.40 kg
With loaded magazine and sling	8 lb 13 oz	4.00 kg
Length:		
Rifle with compensator	39.63 in.	100.66 cm
Barrel	20 in.	50.8 cm
Firing characteristics:		
Caliber	223	5.56 mm
Muzzle velocity	3,100 fps	945.5 mps
Chamber pressure	52,000 psi	358,540 kPa
Instantaneous pressure from propellant combustion (17)	60,045 psi	414 MPa
Cyclic rate of fire	700-900 rds/min	700-900 rpm
Maximum rate of fire:		
Semiautomatic	45 rds/min	45 rds/min
Burst	90 rds/min	90 rds/min
Sustained rate of fire	15 rds/min	15 rds/min
Maximum range	3,938 yards	3,600 m
Maximum effective range:		
Individual/point targets	602 yards	550 m
Area targets	875 yards	800 m

Appendix C: .223 Caliber and 5.56 mm Dimensions Comparison



#	Dimension	PTG 223 Rem Match	Clymer 223 Rem	PTG 223 Rem	JGS 223 Wylde	JGS 5.56 Compass Lake	JGS 5.56 Nato	PTG 5.56 Nato	Clymer 5.56 Nato
C	Base Diameter	0.3779	0.3794	0.3804	0.3810	0.3803	0.3803	0.3803	0.3816
D	Shoulder Diameter	0.3568	0.3553	0.3553	0.3572	0.3553	0.3553	0.3553	0.3560
E	Neck @ Shoulder	0.2510	0.2550	0.2550	0.2568	0.2551	0.2551	0.2551	0.2550
F	Neck @ Case Mouth	0.2510	0.2540	0.2540	0.2558	0.2540	0.2540	0.2540	0.2550
G	Freebore Diameter	0.2242	0.2245	0.2240	0.2240	0.2240	0.2265	0.2265	0.2270
H	Pilot Diameter	0.2190	0.2180	0.2190	0.2190	0.2190	0.2190	0.2185	0.2180
K	Base-to-Case Mouth	1.7600	1.7720	1.7720	1.7726	1.7720	1.7720	1.7720	1.7750
L	Base-to-Shoulder	1.4320	1.4340	1.4338	1.4316	1.4338	1.4338	1.4337	1.4380
M	Neck Length	0.2034	0.2200	0.2201	0.2228	0.2202	0.2202	0.2203	0.2180
N	Freebore Length	0.0680	0.0250	0.0250	0.0619	0.0250	0.0566	0.0566	0.0500
Q	Shoulder Angle (Degrees)	23.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0
R	Throat Angle (Degrees)	1.50	3.10	3.10	1.25	1.50	1.20	1.20	2.50

These dimensions were compiled directly from the published blueprints provided by the respective makers. Basic reamer drawing from Clymer's website.

Appendix D: ASTM/ASM Data Sheet for Determining Basic Tribological Parameters

Designation of tribo-system:
Function of tribo-system:

<table>
<tr><th>Structure
Properties</th><th>Tribo-element (1)</th><th>Tribo-element (2)</th><th>Tribo-element (3)</th><th>Tribo-element (4)</th></tr>
<tr><td>Designation</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Composition
Density
Volume</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Geometry
Dimensions
Roughness</td><td></td><td></td><td rowspan="3">Lubricants data (viscosity, etc):</td><td rowspan="3">Environments data (humidity, etc):</td></tr>
<tr><td>Modulus
Hardness
Toughness
Microstructure</td><td></td><td></td></tr>
<tr><td>Other</td><td></td><td></td></tr>
</table>

Operational Kinematics:			
Load, F_N (N)		Velocity, v (m/s)	
Contact area, A (mm^2)		Temperature, T (°C)	
Contact pressure, P (N/mm^2)		Duration, t (h)	

Contact area to wear track ratio		ε_1 (%):	ε_2 (%):
Film thickness to roughness ratio λ:			
Friction coefficient $\mu = F_F/F_N$	Initial:	Max:	Final:

wear data component	wear length W_l	wear area W_q	wear volume W_V	wear coefficient k ($mm^3/N{\cdot}m$)
tribo-element (1)				
tribo-element (2)				

Appendix E: Coating Classification

I. Conversion Coatings (Passivation Processes)
  a. Browning
  b. Black Oxide (Fe_3O_4, Bluing, Blackening)
  c. Color Case Hardening
  d. Carbonitriding (FeN, gas cyaniding, liquid cyaniding, nicarbing, nitrocarburizing, and Tenifer)
  e. Phosphating (Parkerizing)
  f. Anodizing

II. Metallic Coatings
  a. Gold Plating
  b. Nickel Plating
  c. Electroless Nickel
  d. Electroless Nickel and Teflon (NP3)
  e. Chromium Plating (Hard chrome)
  f. Black Chrome
  g. Thin Dense Chrome
  h. Thin Dense Chrome with Diamond Particles (XADC)

III. Organic Coatings
  a. Paint
  b. Phenolic Resin
  c. Nylon
  d. Polytetrafluoroethylene (PTFE, Teflon)
  e. Polyepoxide (Epoxy, Roguard)

IV. Ceramic Coatings
  a. Borides
    i. Nickel Boride (Ni_2B)
    ii. Titanium Diboride (TiB_2)
  b. Carbides
    i. Boron Carbide (B_4C)
    ii. Silicon Carbide (SiC)
    iii. Tungsten Carbide (WC)
  c. Nitrides
    i. Boron Nitride (h-BN, c-BN)
    ii. Carbon Nitride (C_3N_4)
    iii. Chromium Nitride (CrN)
    iv. Titanium Nitride (TiN)
    v. Titanium Aluminum Nitride (TiAlN)
    vi. Titanium Carbon Nitride (TiCN)
  d. Oxides
    i. Chrome Oxide (Cr_2O_3)
    ii. Keronite
  e. Sulfides
    i. Molybdenum Disulfide (MoS_2)
    ii. Tungsten Disulfide (WS_2)

V. Carbon Coatings
  a. Graphite
  b. Graphite Fluoride $(CF_x)_n$

c. Diamond-Like Carbon (DLC,CVD Diamond, ta-C)
d. Tungsten Diamond-Like Carbon (W-DLC)

Appendix F: Galvanic Series in Seawater at 25°C (77°F)

Corroded end (anodic, or least noble)
Magnesium
Magnesium alloys
Zinc
Galvanized steel or galvanized wrought iron
Aluminum alloys 5052, 3004, 3003, 1100, 6053, in this order
Cadmium
Aluminum alloys 2117, 2017, 2024, in this order
Low-carbon steel
Wrought iron
Cast iron
Ni-Resist (high-nickel cast iron)
Type 410 stainless steel (active)
Type 316 stainless steel (active)
Lead
Tin
Copper alloy C28000 (Muntz metal, 60% Cu)
Copper alloy C67500 (manganese bronze A)
Copper alloys C46400, C46500, C46600, C46700 (naval brass)
Nickel 200 (active)
Inconel alloy 600 (active)
Hastelloy alloy B
Chlorimet 2
Copper alloy C27000 (yellow brass, 65% Cu)
Copper alloys C44300. C44400, C44500 (admiralty brass)
Copper alloys C60800, C61400 (aluminum bronze)
Copper alloy C23000 (red brass, 85% Cu)
Copper C11000 (ETP copper)
Copper alloys C65100, C65500 (silicon bronze)
Copper alloy C71500 (copper nickel, 30% Ni)
Copper alloy C92300, cast (leaded tin bronze G)
Copper alloy C92200, cast (leaded tin bronze M)
Nickel 200 (passive)
Monel alloy 400
Type 410 stainless steel (passive)
Type 304 stainless steel (passive)
Type 316 stainless steel (passive)
Incoloy alloy 825
Incoloy alloy 625
Hastelloy alloy C
Chlorimet 3
Silver
Titanium
Graphite
Gold
Platinum
Protected end (cathodic, or most noble)

Appendix G: Budget

The cost of this project will be based on the price of metal samples, various coatings, and lab equipment. An AR15 barrel costs $260 new and $100 used. An AR15 bolt, bolt carrier, and extractor costs $130 new and $80 used (sold as bolt assembly, which includes several other parts that are not of interest). The AR15 upper receiver costs $90 new and $60 used. Since the upper and lower receiver are made out of the same aluminum and the lower receiver is the only federally tracked part of the AR15, this makes the upper receiver better suited for testing in this experiment. These critical parts will be stripped of their original finish and cut into sections for use as substrates for the test samples along with small sheets or bars of the same material, which will be purchased from a supplier. This will allow comparison between purchased AR15 parts and a control group. The metal substrates for use in the samples should not cost more than $150. The cost of the materials will be small in comparison to the cost of the coatings.

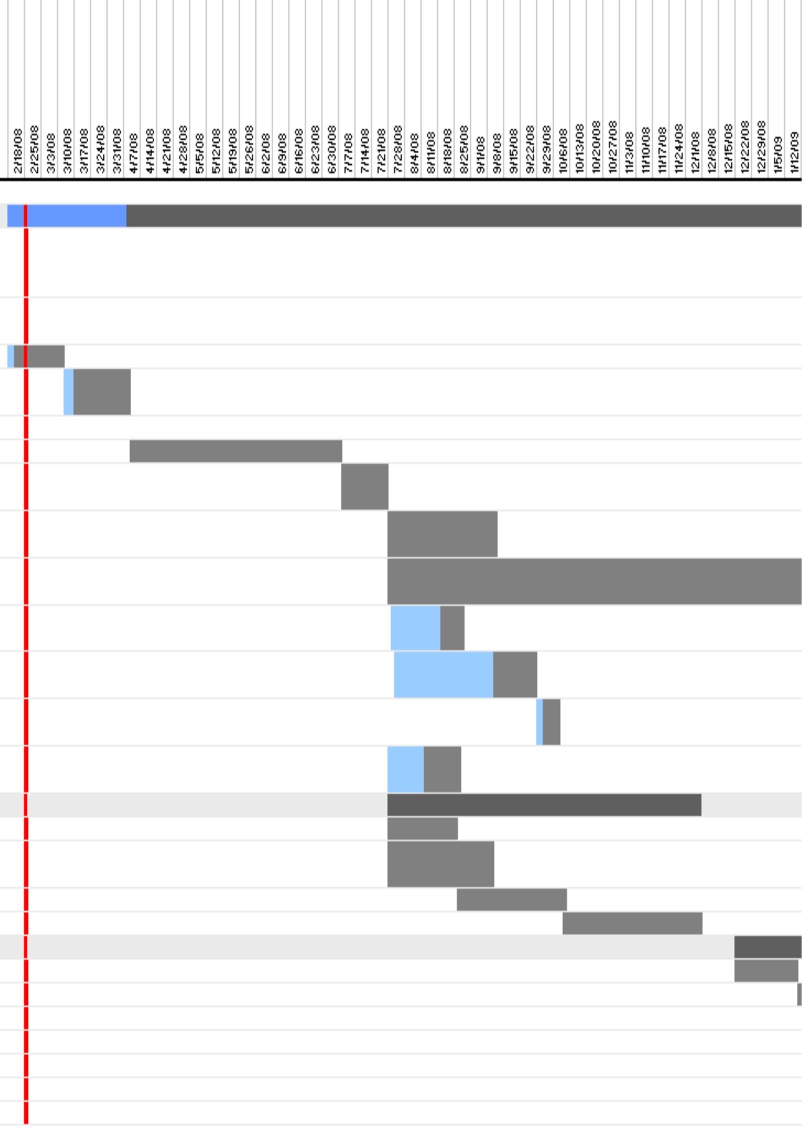
The following prices are what gunsmiths charge for refinishing firearms with traditional coating techniques: hard-chrome plating ($100), bluing ($60), parkerizing ($125), electroless nickel plating ($200), Teflon coating ($100), and anodizing ($60). Prices are only listed for refinishing firearms, but the cost for refinishing small parts is less. Advanced coating techniques should be analyzed to see if a more suitable coating exists. There are potentially viable options, such as the Physical Vapor Deposition (PVD) of either TiN, TiCN, or TiAlN on the steel parts that can cost up to $400. However, PVD cannot be used on aluminum parts because the process requires heating the aluminum above its melting temperature. Since PVD coating is extremely expensive and some of these PVD coatings provide a self-lubricating surface, these coatings would be used best on internal moving parts such as the bolt, bolt carrier, and extractor. The coatings for this project should cost between $200-800 to coat all of the samples. The actual cost includes shipping (see Table 9.1).

Table 9.1. Two proposed budgets and the actual cost.

I. Materials	**Estimated Used Parts**	**Estimated New Parts**	**Cost**
A. Colt AR15 Barrel	$160.00	$295.00	$459.12
B. Colt AR15 Receiver	$100.00	$295.00	$234.12
C. Colt AR15 Bolt Carrier Group	$110.00	$299.00	$314.86
II. Total Budget Requested	**$370.00**	**$889.00**	**$1,008.10**

Appendix G: Timeline

WBS	Tasks	Task Lead	Start	End	Duration (Days)	% Complete	Working Days	Days Complete	Days Remaining
1	Background Research	Greg	9/14/07	1/22/09	497	42%	355	207	290
1.1	Research which firearm is most produced and has the greatest market for customization.		9/14/07	11/02/07	50	100%	36	50	0
1.2	Identify critical parts, which could result in a catastrophic malfunction.		11/03/07	1/01/08	60	100%	42	60	0
1.3	Order critical parts.		1/02/08	3/11/08	70	70%	50	49	21
1.4	Find out what these critical parts are made of and how they typically fail.		3/12/08	4/08/08	28	20%	20	5	23
1.5	Research possible traditional coatings.		11/03/07	1/01/08	60	100%	42	60	0
1.6	Research possible advanced coatings.		4/09/08	7/07/08	90	0%	64	0	90
1.7	Identify the coatings that can be used on each of the critical parts.		7/08/08	7/27/08	20	0%	14	0	20
1.8	Find vendors that can provide these coatings.		7/28/08	9/10/08	45	0%	33	0	45
1.9	Research available data on surface coating performance characteristics.		7/28/08	1/23/09	180	0%	130	0	180
1.10	Identify the variables that best characterize the performance characteristics.		7/29/08	8/27/08	30	70%	22	21	9
1.11	Select which standards and specifications will be used for this experiment.		7/30/08	9/27/08	60	70%	43	42	18
1.12	Identify which laboratory equipment is required for this experiment.		9/28/08	10/07/08	10	30%	7	3	7
1.13	Send request for research grant to the appriopriate DOD research group.		7/28/08	8/26/08	30	50%	22	15	15
2	Prepare for Experiment	Greg	7/27/08	12/06/08	133	0%	95	0	133
2.1	Obtain metal samples.		7/27/08	8/25/08	30	0%	21	0	30
2.2	Find vendors that can provide these coatings.		7/27/08	9/09/08	45	0%	32	0	45
2.3	Prepare metal samples for coating.		8/26/08	10/09/08	45	0%	33	0	45
2.4	Send samples to vendors for coating.		10/09/08	12/07/08	60	0%	42	0	60
3	Conduct Experiment	Greg	12/22/08	6/03/09	164	0%	118	0	164
3.1	Conduct adhesion testing.		12/22/08	1/15/09	25	0%	19	0	25
3.2	Conduct wear testing.		1/16/09	2/09/09	25	0%	17	0	25
3.3	Conduct friction testing.		2/10/09	3/06/09	25	0%	19	0	25
3.4	Conduct corrosion testing.		3/07/09	3/31/09	25	0%	17	0	25
3.5	Evaluate findings.		4/01/09	4/15/09	15	0%	11	0	15
3.6	Repeat any necessary testing.		4/16/09	5/10/09	25	0%	17	0	25
3.7	Write thesis.		3/07/09	6/04/09	90	0%	64	0	90



Glossary

Accuracy – includes precision and the closeness of the mean or center of impact to the aiming point on the target. The ability of a weapon to hit the target at the point aimed at; lessens with range and is dependent upon the caliber, power of the cartridge fired, the weapon used and its sighting system (telescopic sights offer greater accuracy at longer ranges), climatic influences, and the user.

Action – the heart of the rifle. The main part that all the rest of the parts are attached to, also called the receiver.

Anode – the terminal where current flows in.

AR15 variants – includes the original AR15 and subsequent designs, such as the M16/A1/A2/A3/A4, the M4, and all civilian variations of the AR15. These weapons are lightweight, gas-operated, air-cooled, magazine-fed, shoulder-fired weapons that can be fired in either automatic, three-round bursts, or semi-automatic.

Assault rifle – a small arm that uses a rifle-type round that is smaller and lighter than a rifle but larger than an SMG. Usually has selective fire and almost always fires a lower-energy round than a true riddle.

Barrel –chambers the cartridge for firing and directs the projectile. The rifle barrel assembly is air-cooled, contains compensator and front sight assembly, and holds the two handguards and the sling swivel.

Barrel life –the expected lifetime of a barrel, normally expressed in seconds or at most minutes; tells the user how many rounds he may expect to fire at sustainable accuracy by the division of barrel life by barrel time.

Blank – a partially formed gun barrel requiring machining or some other operation to produce a finished barrel. Rifle barrel assembly is air-cooled, contains compensator and front sight assembly, and holds the two handguard assemblies and the sling swivel.

Bolt – provides stripping, chambering, locking, firing, extraction, and ejection of cartridges using the drive springs and projectile propelling gases for power. The rotating mechanical device used in the 19th and 20th centuries to load and unload a rifle. Consisted of the bolt lever, the bolt itself, the firing pin, firing pin spring, sear, and extractor. Still in use today in some military rifles, especially for sniper use. In the assault rifle is the component that holds and supports the base of the round while it is being chambered, fired, extracted.

Bolt action – any rifle using a rotary bolt.

Bolt carrier assembly – carries bolt assembly to chamber, and fires the weapon. Contains the firing pin, extractor, bolt assembly, ejector, and bolt cam pin.

Bore – the hole through the barrel of a firearm measured from land to land. The hole running down the length of the barrel through which the bullet is projected.

Breech – the rear end of the bore of firearm where the cartridge is inserted into the chamber. That part of the rifle that is open to allow the introduction of cartridges to load or reload the weapon, or closed when the rifle is either safe or loaded and ready to fire. It is located immediately behind the chamber. Sometimes the term is used to signify the chamber, but this is strictly inaccurate.

Caliber – a particular cartridge size and operating pressure. The caliber can be a numerical description; 5.56 X 45 or 7.62 X 39, it can be a numerical composite; .30-06 ("Caliber thirty, model of 1906") or it can be a name; .300 Winchester Magnum. Calibers can have several names; the .30-06 was called ".30 Gov't" and in Europe is known as "7.62 X 63". Cartridges of a caliber can be loaded to different pressures. The .257 Roberts is loaded to +P as well as standard pressure.

Carbine – a shorter version of a standard rifle, sometimes. This is usually a rifle that has been cut down both in length of barrel and in weight in order to make it easier to carry (U.S. tradition has it that a carbine has a barrel length of 22 inches or less). Originally intended for use by cavalry, carbines were also issued to gun crew. In World War II and subsequently, carbines were issued to all front-line troops who were not riflemen, such as drivers, officers, radiomen, and so on.

Cartridge – a single, loaded round of ammunition. Originally a paper container for the powder, which also served as wadding. Nowadays it signifies the complete assembly of primer, case, propellant, and bullet that goes to make a round of ammunition, the composite round.

Case – the container component of a cartridge that is filled with the propellant and has the primer fitted to it.

Catastrophic malfunction – any malfunction that cannot be resolved with immediate action, and requires the use of tools or disassembly for resolution.

Cathode – the terminal where current flows out.

Chamber – the recess in the rear of a barrel where the cartridge rests during firing. The rear part of the barrel into which the cartridge is loaded and where it is fired.

Chamber pressure – the pressure created in the chamber by the expanding gases caused by firing the weapon. These gases force the bullet along the barrel and can be tapped to provide extraction and reloading energy in the breech block. Pressures reach 55,000 pounds per square inch or more.

Cleaner, Lubricant, and Protectant (CLP) – is used to clean all areas, internal and external, of powder fouling, corrosion, and dirt. Specifically it is used to clean the bore, chamber, locking lugs, gas tube, and bolt carrier assembly.

Compensator – a muzzle brake whereby some of the propellant gases following the bullet are diverted to lessen the upward jump of the muzzle on firing, especially in automatic or burst firing. Also seen on anti-materiel rifles to reduce the recoil to a small extent.

Cook-off – the firing of a round due to the chamber inducing enough heat in the cartridge propellant to cause spontaneous combustion.

Critical parts – any parts that cause a catastrophic malfunction.

Crown – the chamfering at the end of the barrel. A properly crowned barrel evenly releases the bullet without disturbance, and aids accuracy.

Ejector – a mechanism on firearms that ejects the fired or unfired shell clear of the gun. Normally a fixed stud in the bolt or breech block housing (the riddle body) that is hit by an extracted round on its based that causes the case to be thrown away from the breech.

Erosion – wear in the leade and throat of a barrel, due to the hot gases of combustion. Once sufficiently worn, a barrel begins to lose accuracy. The wearing-away of the bore by gas, chemical, or mechanical action. All barrels suffer from erosion when fired, and excessive erosion degrades accuracy to such an extent that the weapon needs to be rebarreled or discarded.

Extractor – the hooked device which draws the cartridge out of the chamber when the breech mechanism is opened. The device fitted to the rear of the chamber in earlier weapons, or integrally to the bolt, whereby the cartridge is gripped for extraction.

Extreme conditions – "include, but are not limited to exhaust trails, gun-blast surfaces, rocket-blast areas, hull bottoms, leading edges, areas that may trap or be exposed to fumes from exhaust, guns or rockets, or surfaces subjected to temperatures above 121°C(250°F) as the result of thermal radiation, aerodynamic heating, or other sources of heat." (61)

Fayed surface – two or more surfaces are joined or fitted closely or tightly together.

Feedramp – the portion of the receiver between the magazine and the chamber.

Firing Pin – the part of the firing mechanism of the weapon that strikes the primer and causes the propellant to ignite.

Fouling – accumulation and deposition of non-living material on hard surfaces. In firearms the carbon from the burnt powder can build up on the metal surfaces inside the firearm. The deposits created within the chamber, barrel, body, piston housing, and so on of the modern rifle, in the barrel and chamber in older weapons, which can cause jamming, misfires, and other failures. Caused by the propellant failing to be completely consumed on firing, and often seen as a shower of sparks at the muzzle in older weapons.

Furniture – the parts of a weapon that make it comfortable to hold and carry. The term derives from the fact that most early weapons used wood to form the butt (stock) and the fore end. The butt allows the weapon to be fired from the shoulder; the fore end protects the firer's hands from excessive heart from the barrel.

Grain – an old measure of weight, used in the precious metal industry. An average ounce weight equals 437. 5 grams.

Gun – any weapon that fires a projectile. Loosely applied to all manner of weapons; a generic term.

Headspace – the distance between the breech face and the face of the bolt, between which is sandwiched the cartridge rim. Rimmed cartridges normally extend behind the breech face to an extent, whereas rimless cartridges can be held within the chamber.

Hot Dipping – one of the oldest processes for applying metallic coatings involves immersing the article into a bath of molten metal, and very little, if anything, is done to change the coating's properties after removal from the molten bath.

Ignition – the primer initiates ignition, and ignition takes place at about 500°C.

Immediate action – the process of resolving a malfunction by checking to ensure parts are secure and in place, and cycling the weapon to clear any obstructions.

Killing power – a rather inaccurate term for the ability of weapon or its projectile to effect lethal force on the target. Sometimes used by those in awe of a particular weapon, such as Dirty Harry's .44 Magnum.

Lands – that portion of the original bore surface of a rifle barrel which lies between the grooves. The raised portion or ridges between the groves in a rifled bore.

Leade – the leade or lead, which is the distance between the mouth of the cartridge and the point at which the rifling engages the bullet. The gap between the front of the chamber and the commencement of the rifling (sometimes called the leade). Also, a term meaning to aim in front of a moving target by a specific amount.

Lower Receiver – contains the trigger assembly, sear, hammer assembly, selector lever, rifle grip, bolt catch, and buttstock assembly. The lower receiver provides firing control for the weapon and provides storage for basic cleaning materials.

Lug – a lug on the barrel which secures the barrel to the frame. Lugs on the front of a bolt or breech block which rotate into slots to lock the action for firing are termed locking lugs. On lever-action rifles, the locking lugs of the bolt and receiver require intermediate locking blocks that slide into place. Many lever-action rifles are not as strong as bolt-action rifles, and are not chambered for cartridges as strong.

Maximum Average Pressure (MAP) – is the recommended maximum pressure level for loading commercial sporting ammunition. It is usually measured with Piezo transducers.

Muzzle – the bullets exit point in the end of the barrel.

Muzzle energy – the kinetic energy of a round on exit from the muzzle. High muzzle energies mean longer ranges and increased penetration of bullets (i.e. increase killing power).

Muzzle velocity –the speed at which a bullet leaves the muzzle of the riddle, measure in feet per second (fps) or meters per second (m/s).

Pickling – the soaking of metal in an acid to remove the hardened scale or oxide that develops from hot working. Steel is often pickled before it is cold worked. For environmental reasons shot blasting has largely replaced pickling.

Precision – refers to the dispersion of the bullets about their own mean or center of impact. A precise rifle should yield a tight shot group.

Proof Load – the greatest load than can be applied to a piece, as a beam, column, etc., without straining the piece beyond the elastic limit.

Receiver – the metal part of the gun that houses the breech and firing mechanisms, sometimes called the frame. Also called the breech on earlier weapons.

Rifle – a long-barreled, rifled weapons, fired from the shoulder, used for accurate shooting to 600 yards or more. Rifles are still found that are bolt operated, but they are few and far between, mainly reserved for sniping work. Today the AK-47 is perhaps the most recognizable rifle in the world, closely followed (in proliferation) by the Heckler & Koch G3 and the U.S. M16.

Rifling – spiral grooves cut or swaged into the bore of a barrel. The bullet passing down the barrel is rotated by the rifling, stabilizing the bullet for its trip to the target.

Seam – an unwelded lap or fold on the surface of metal usually produced during a rolling or forging. May appear to be a crack.

Sear – a catch in the firing mechanism of a gun that engages in a bent in the breech block or restrains the firing pin, thus inhibiting firing until the trigger is pulled.

Self-loading – a firearm that automatically extracts, ejects, and reloads another cartridge ready for firing. Also known as auto-loading. The term also applies to self-loathing rifles, assault rifles, machine guns, submachine guns, and machine pistols.

Soldering – joining two pieces by heating them and introducing a different metal into their gap.

Solid Film Lubricant (SFL) – is the authorized touch up for the M16A2 Rifle and M4/M4A1 Carbine and may be used on up to one third of the exterior finish of the weapon.

Stripping – the procedure of removing any existing finish from metal and today means doing this by either acid bath or electro deplating tank.

Trigger – the part of the firing mechanism pulled or squeezed that releases the hammer or firing pin.

Twist – in regards to defects in steel bar stock, it is a distortion caused by the rotation of the ends of a bar in opposite directions. In regards to rifling, it is the amount of pitch in a rifle barrel's rifling; determines rate of spin a bullet will have when it leaves the end of the rifle barrel. In other words, it is the distance moved down the barrel for the bullet to make one complete revolution.

Upper Receiver – provides support for the bolt carrier assembly. The upper receiver contains the rear sight assembly, ejection port, ejection port cover, and housing for the key and bolt carrier assembly and bolt assembly.

Useful-Life – is defined as the number of rounds that are fired without exceeding the assigned or chosen tolerance on extreme spread.

Welding – joining two parts by heating their edges until the metal melts, and adding a filler to the joint.

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