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INDUSTRIAL POTENTIAL, USES, AND PERFORMANCE OF SPUTTERED AND ION PLATED FILMS

Talivaldis Spalvins
Lewis Research Center
Cleveland, Ohio

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by Talivaldis Spalvins

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

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SUMMARY

The sputtering and ion plating technology is reviewed in terms of their potential, uses, and performance. Sputtering is not regulated by phase rule relationships. Therefore, it has the capability to form new materials without regard to solid solubility or immiscibility. It offers the greatest flexibility in coating preparation, since coatings can be tailored in any preferred chemical combination, and graded type interfaces (ceramic to metal seals) can be formed. Sputtered and ion plated film characteristics such as the degree of adherence, coherence, and morphological growth which contribute to film performance and reliability are described and illustrated as used in practice. The potential future of sputtered and ion plated films for industrial applications will depend primarily upon greater comprehension of materials selection, possible elimination of restrictions for coating/substrate combinations and the awareness of utilizing the proper desposition parameters.

INTRODUCTION

During the last 15 years sputtered and ion plated films have found an increasing number of nonelectronic applications in many industrial disciplines requiring surface films and protection. A cursory survey of the literature reveals that films containing almost every element in the periodic table have been deposited by sputtering techniques. The intense interest and increased activity in sputtering technology stems from the fact that sputtering provides the greatest versatility in coating and substrate selection. Many materials that are incompatible can be sputter deposited.

The outstanding feature of the sputtering process is the fact that the process is not regulated by classical thermodynamics and Gibb's phase rule relationships. This feature eliminates the restrictions for materials combinations. As a result, coatings can be tailored in any preferred chemical combination, disregarding the restrictive phase rule relationships.

From an industrial point of view, the following unique sputtering features are an integral part of the process: versatility in material deposition, momentum transfer (impact evaporation), sputter-etching, precise controls (stoichiometry, uniformity, thickness) and high flexibility in selecting sputtering modes and configurations. In addition, the sputtering process itself does not degrade the properties of the substrate material. For example, there is not any hydrogen incorporation in high strength steels as is observed during electroplating, creating hydrogen embrittlement or the incorporation of undesirable byproducts or contamination during the deposition. Understanding and knowing how to utilize the above sputtering features surface processes, such as corrosion, wear, erosion, microcracking, etc. can be often controlled and mitigated. It is necessary to adapt an experimental approach to determine the optimum sputtering parameters for a given film/substrate combination.

The objective of this paper is to recognize and highlight some of the unique features and potentials of sputtering and ion plating for practical solutions and to provide a greater comprehension and awareness of the selection of coating/substrate combinations and their characteristics.

SPUTTER COATING POTENTIALS

The most profound feature of the sputtering process originates from the fact that the sputtering process is not regulated by classical thermodynamics and Gibb's phase rule relationships. As a result, one is not forced to remain within the framework of the rigid phase relationships. Any combination of metal and nonmetal elements can be sputter deposited in any composition, without concern for their phase relationships. Therefore, sputtering has the unexplored potential and capability of forming new materials without regard to solid solubilities or immiscibilities. For example, it may not be possible to prepare an alloy of a selected composition of 40% A-60% B, however it is possible to prepare a sputtering target of that composition and stoichiometrically deposit the film. A great variety of these unusual coating compositions can be obtained by simply manufacturing special sputtering targets.

The various types of sputtering targets with regard to their material combinations may be classified as follows: elemental, multielement, multielement compound or mixture, composite and layer type targets. Powders of different materials can be mixed in any ratio and hot pressed into a sputtering target of any size or shape. Alternatively, the composite targets can be constructed of materials of different segments. For example, a planar target can be constructed of pie-shaped sections of different materials as shown in Fig. 1(a), or formed by placing strips or wires of the desired material as shown in Fig. 1(b). Changes in film composition can be controlled by proper area ratio. The layer type target is shown in Fig. 1(c) where the mixture ranges from 100 percent ceramic to 100 percent metal by desired volume increments, forming essentially a target with a reversed composition gradient. This target configuration is especially useful in the manufacture of ceramic to metal seals. Ceramic to metal seals require a graded interface to accomodate the high strains created between the two materials which have differences in thermal conductivity and in the coefficient of thermal expansion. This is particularly important for operations involving thermal cycling. High flexibility in coating preparation can also be achieved with the variation of the many sputtering modes and configurations such as type of potential applied (dc or rf); multiple target utilization, type of gases used (inert or reactive), auxiliary electrodes, magnet utilization (magnetron sputtering) etc. contribute to the extreme flexibility in coating preparation.

CHARACTERISTICS OF SPUTTERED FILMS

The performance and reliability of a coating depends primarily on the degree of adherence, coherence, and morphological growth. The degree of adherence is directly related to surface pretreatment and the type of interface formed. The morphological growth of the film is affected by the sputtering parameters and substrate topography, temperature, and chemistry. The performance of a coating can be attributed to the adhesive strength which depends whether the interface is abrupt or graded. All interfaces represent a break in the normally uniform crystallinity and/or composition. If proper sputtering sequence is not determined an abrupt interface will form, and this involves an abrupt change in such properties as hardness, coefficient of thermal expansion and thermal conductivity. As a result internal stresses are produced which cause microcracks and spalling. To increase adherence and reduce the stresses a graded interface should be formed to distribute the interfacial stresses. In many instances even very thin (10 - 100 Å) interfacial regions may be effective.

The relatively strong adherence of sputtered films can be generally attributed to the sputter-etched (cleaned) surface and the relatively high arrival energies of the sputtered species. The various sputtering approaches can be effectively utilized to reduce the interfacial stresses by matching the properties of a coating and substrate or forming intermediate layers to reduce the large gradients in material disparities.

Film thickness of sputtered films is normally restricted to a maximum of 2 μm, since thicker films tend to be highly stressed and brittle. Therefore it can be implied, that in many applications, proper coating attachment to the substrate is more important than the volume of coating present.

Dense, pore free films can be obtained, since sputtering is generally accomplished from large area targets rather than point sources as in evaporation.[1] The sputtered particles arrive from many different angles thus reducing shadowing effects and there is also strong particle-to-particle cohesion.

The growth morphology of sputtered films is controlled by the particular substrate conditions (temperature, topography, and chemistry) and the sputtering parameters. The objective is to obtain a homogeneous coating growth morphology. By varying the substrate temperature it is possible to obtain thin films with structures changing from essentially amorphous to crystalline. At low temperatures thin films generally have an amorphous structure, because there is little atomic mobility at these temperatures and as a result such films exhibit different properties than do crystalline films. This aspect will be illustrated with sputtered MoS_2 films in the following section.

Since it is practically impossible to prepare surfaces which are atomically smooth over an appreciable area, microdefects and above all, machine and polishing marks are always present. These surface imperfections are preferential nucleation sites - where coating defects originate during sputtering. The coating defects have adverse affects on the coating, they act as stress raisers, therefore weakening the mechanical properties by initiating cracks and creating porosity. These defect structures in the coating can be minimized or possibly eliminated by improving the surface smoothness. It should be noted, that the sputtering technique does not create crystallographic coating defects.

SPUTTERING TECHNOLOGY

With the achievement of high sputtering rates up to 250 μm/hr (10 mils/hr) the process is also emerging as a fabrication technique for depositing thick deposites (foils, sheets) and also for manufacturing intricate mechanical components. On the basis of the sputtering rate consideration two industrial areas of applicating can be distinguished: (a) thin film technology and (b) fabrication technology.

Thin Film Technology

Uses of thin sputtered films. - In the last ten years, sputter deposition has rapidly spread not only in the mechanical areas but continues to proliferate into practically any industrial area which requires films that are difficult or impossible to handle by other techniques. Since the basic physics of the sputtering process is now fairly well understood, and the future of sputtering is not equipment limited, the industrial trend is already apparent; the emergence is toward more automation and widespread applications. In five years probably we will see completely automated sputtering equipment that accepts articles to be plated at one end and produces coated products at the other end. Since the pollution controls become more demanding and more stringently enforced, the sputtering technique offers an excellent alternative, since the process does not produce any effluents.

Typical manufacturing areas where sputtering systems are capable of high volume production are the razor blade (Ref. 1) and the automotive industry (Refs. 2 and 3). The razor blade industry was one of the first to recognize the need for automation. Sputtering systems with different designs have been constructed exclusively for sputter-deposition of razor blades with chormium or chromium-platimum alloy (Cr_3Pt), with the objective of providing corrosion protection and thereby prolong the sharpness of the edge.

Sputter-automation is also emerging very rapidly in the automotive industry where chromium and chromium alloys are sputter deposited on plastic exterior and interior components such as grilles wheel covers, etc.

Typical industrial areas where sputter coatings are having an increased impact are: corrosion and high temperature protection, coatings for tribological applications (friction, wear, lubrication), coating tool tips and cutting tools, decorative coatings, replicating techniques for microscopy, solar cells, coatings for video disks, thin film strain gage sensors, thermocouples for pressure transducers, coating metallic surgical implants etc.

Performance of sputtered films. - To illustrate the performance of sputtered films in the mechanical area, the discussion herein will be confined to the tribological materials: (a) soft, solid film lubricants (Au, Ag, MoS_2, PTFE) and (b) hard, wear resistant refractory compound films (TiC, WC, Cr_3C_2, Cr_3Si_2, etc.). These films in the thickness range (2000 - 6000 Å) have been sputter-deposited on sliding and rotating bearing surfaces to reduce wear, lower the coefficient of friction and increase the endurance life of the mechanical components.

Sputtered MoS_2, Au, Ag films are most widely used in the aerospace and aircraft industry. These sputtered lubricant films, for example, are of invaluable importance where tolerances are close, reliability requirements are high, and the wear minimization of wear debris formation is critical. MoS_2 films can be directly sputtered on any bearing components (races, cage, and balls) with strong adherence. Due to the strong adherence extremely thin films (2000 Å) are more effective than thicker films applied by other techniques (Ref. 4). These thin sputtered MoS_2 films under vacuum conditions display a very low coefficient of friction 0.04.

Figure 2 illustrates how the coefficient of friction is affected by the change in the crystalline size (Ref. 5). It is interesting to note that an amorphous type structure displays a high coefficient of friction and has no lubricating properties. On the other hand, the crystalline structure displays a low coefficient of friction and good lubricating properties. Simply by controlling the substrate temperature during the sputtering process the coefficient of friction can be varied accordingly as seen in the transition region.

In the application of hard refractory compound films (carbides, nitrides, silicides) sputtering is essentially the only reliable direct technique (without using binders) for the deposition of compounds. These wear resistance films, because of their hardness and brittleness, are highly sensitive to surface conditions and the mode of application. Strong adherences have been obtained where a graded interfacial region has been formed to reduce the internal stresses (Refs. 6 and 7). Especially with the hard, brittle coatings the internal stresses increase with the coating thickness. Even if a strong adherence is established delamination or separation can occur within the coating. Consequently, a critical thickness effect exists. For instance this critical thickness effect has been determined for sputtered TiC during sliding friction experiments (pin on disk) at different loads (Ref. 7) and the results obtained are shown in Fig. 3. For films less than a critical thickness, the coefficient of friction was in the range of from 0.2 to 0.3. For coatings thicker than the critical value, the coefficient of friction was between 0.6 and 0.8. Another approach to improve carbide coating adherence, gain some toughness, and reduce internal stresses, is by preparing special cermet targets, by adding a metallic binder such as cobalt (Ref. 8).

Significant improvement in bearing life (as measured by running time to failure of the coating) has been obtained with angular contact stainless steel bearings, where the races and cages were sputter coated with a 1000 Å thick underlayer of Cr_3Si_2 and subsequently sputtered with MoS_2 film about 6000 Å. This duplex coating extends the bearing life (five fold) over MoS_2 films directly applied as shown in Fig. 4.

Sputtered PTFE (polytetrafluoroethylene) films are used for tribological applications, and these films display excellent adherence and uniformity and are pore free not only on metal substrates but also on glass, wood and paper surfaces (Ref. 9). Figure 5 shows sputtered PTFE on paper. Preliminary results with sputtered PTFE films indicate that the coefficient of friction is comparable to that of the original PTFE which may vary from 0.08 to 0.2 (Ref. 10). The coefficient of friction for PTFE depends on the load, sliding speed and film thickness. Sputtered PTFE films have been applied to surgical needles (cataract operations) as shown in Fig. 6 where they have to function as a lubricant to reduce the friction during the insertion and removal.

Video disks are being sputter deposited with a thin layer of a solid lubricating film to protect the sound fidelity of the records.

Fabrication Technology

The high sputtering rates up to 250 μm/hr are introducing a new manufacturing approach. For sputtering to be a viable fabrication technique, the sputtering rate becomes a prime consideration from an economical standpoint. Thicknesses up to, but not limited to 0.63 μm, have been achieved. Very intricate inner and outer cylindrical structures with coolant passages for thrust chambers are being developed. A typical inner layer with machined coolant passages and a completed chamber section with sputtered outer layer is shown in Fig. 7.

ION PLATING

Characteristics of Ion Plating and Ion Plated Films

With wider industrial applications of ion plating, the process is often more difficult to identify since it is referred in the literature by other names such as "ion vapor deposition", "glow discharge vapor deposition", "ionization electrostatic plating", "bias sputtering" and possibly others. In ion plating the specimen to be coated is the cathode to which a potential of 3000 - 5000 volts is applied, and the coating material is evaporated in the glow discharge by a suitable evaporation source such as resistively heated filaments, electron beams or induction heated crucibles. The ion plating process is more energetic than sputtering, because the process uses a high substrate bias of several thousand volts to accelerate the positively ionized evaporant atoms into the substrate. In a conventional sputtering configuration (Refs. 11 and 12), such high bias on the specimen would allow no net deposition since re-sputtering would exceed the sputtering rates. In ion plating the specimen to be coated is sputter cleaned prior to deposition and is maintained clean at a high bias, during the deposition.

The two characteristics of ion plating which have received attention are the (1) flux of high energy ions and neutrals and (2) the high throwing power. These two features of the process make this technique far superior to any other deposition technique in terms of the excellent adherence and ability to coat uniformly 3-dimensional couplex surfaces. The excellent film adherence is generally attributed to the formation of a graded-fused interfacial region, even when the film and substrate materials are mutually incompatible.

The factors which are believed to contribute to the excellent adherence are the sputter etched surface, the high flux of the energetic ions and neutrals and the surficial heating effects which accelerate diffusion and facilitate surface reaction, without necessitating bulk heating. All the foregoing reasons are operative in providing excellent adherence.

Strongly adherent fully dense (pore free), and uniform-continuous films can be obtained at lower nominal thickness using ion plating. The type of interface formed not only provides the superior adherence, but it also improves mechanical properties such as yield strength, tensile strength and fatigue life. Typical load elongation curves for nickel and inconel tensile specimens ion plated with a 1500 Å copper and gold film are shown in Fig. 8. The ion plated specimens show an increase in tensile and yield strength of from 5 to 8 percent. Ion plating effects on the fatigue life are shown in Fig. 9. Nickel fatigue specimens plated with a 1500 Å film of copper or gold had a 23 to 27 percent increase in fatigue life, respectively. Similar results have been reported (Ref. 13) wherein steel fatigue specimens were ion plated and electroplated with gold and then fatigue tested. The results obtained are presented in Fig. 10. The ion plated film increased the fatigue limit, while the electroplated film had no noticeable effects.

The throwing power and film uniformity has been determined where metallic films were ion plated onto the front and back surfaces of a flat plate as a function of gas pressure. These results are shown in Fig. 11, Ref. 14. It can be seen that the ratio of film thickness on the front surface to that of the back surface approaches unity at the higher argon pressures. What this means in practice is that 3-dimensional surfaces, internal surfaces of tubes, screw threads etc. can be coated without specimen rotation as shown in Fig. 12.

APPLICATIONS AND PERFORMANCE

The applications of ion plated films are basically derived from the two unique features discussed previously. However, the full potential of ion plating has not yet been realized, and its more limited use arises from the fact that only several vacuum equipment manufacturers presently market the equipment and then on a limited scale.

Most ion plated films have been used for tribological applications in order to reduce friction and wear, and as protective films to increase corrosion resistance.

Soft, metal ion plated gold films (2000 Å) on nickel and tool steel surfaces gave a lower coefficient of friction and longer endurance lives when friction tested (pin on disk) under vacuum conditions in comparison to other deposition techniques (Ref. 11). Similar results were also obtained with indium, lead and silver films (Ref. 15). The reason for the lower coefficient of friction is believed to be caused by surface hardening created by the alloying effects in the surface. The greater endurance life is attributed to the improved adherence.

The aircraft industry has developed a continuous coating capability where small components such as threaded steel and titanium fasteners are ion plated with aluminum for production purposes (Ref. 16).

Other application areas include decorative coatings for jewelry or any type of novelty item. Probably the most important feature of a gold decorative coating is its nobility. This is valueless, however, if the coating is porous. Ion plating offers an excellent solution. Due to the exceptional adherence, strike coats for electroplating materials which would be otherwise very difficult or impossible to plate can now be performed. Ion plating of metallic surfaces can be used to facilitate their joining by conventional soldering and brazing techniques. Due to the high throwing power porous components can be sealed for vacuum and hydraulic applications. Ion plating of plastics with a metallic coating is of great interest in many industrial applications. Impregnation of fiber or glass wool with metal can be successfully performed further, for reclamation purposes worn-out mechanical components, such as aircraft pistons can be refinished by material buildup.

CONCLUSIONS

The potential future of sputtered and ion plated coatings for industrial applications will depend primarily upon the greater comprehension of materials selection. Such comprehension includes the elimination of restrictions (e.g., classical thermodynamics and phase rule relationships) for coating/substrate combinations, and the awareness of utilizing the proper deposition parameters.

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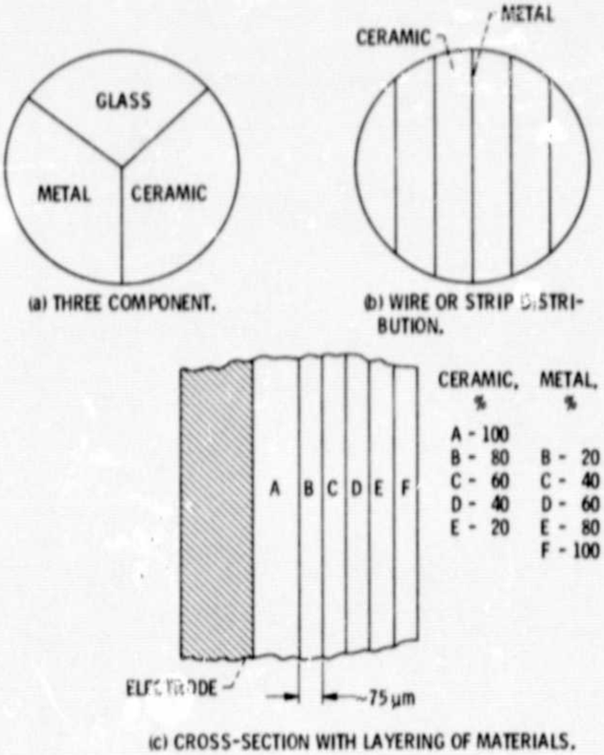


Figure 1. - Construction of sputtering targets.

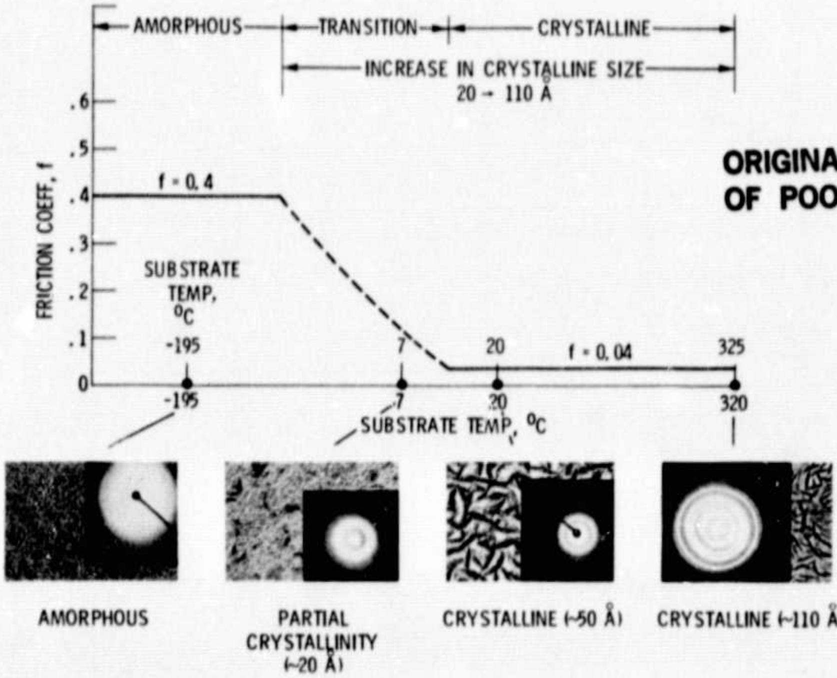


Figure 2.- Substrate temperature effects on MoS_2 film morphology and friction coefficient.

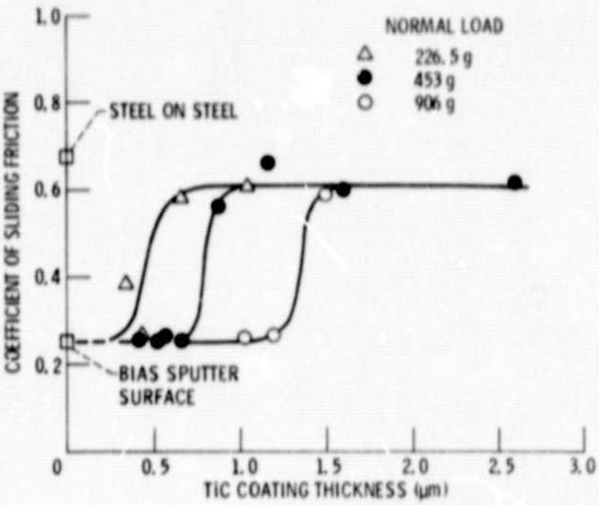


Figure 3. - Coefficient of sliding friction after 20 cycles for steel rider on sputtered TiC film as a function of film thickness (sliding speed was 1.5 cm/s) (ref. 7).

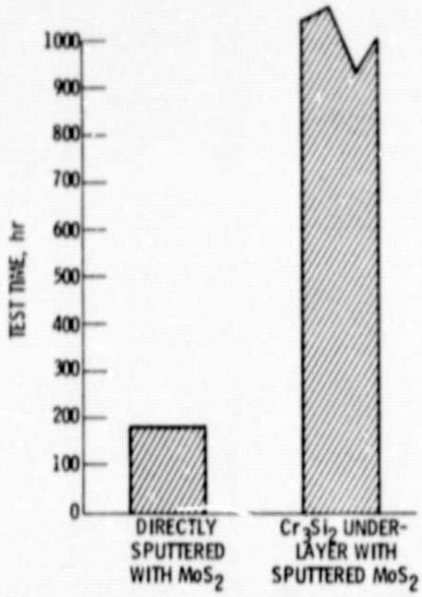


Figure 4. - Endurance lives of 400C stainless-steel ball bearings with sputtered MoS_2 films on races and cage - with and without a Cr_3Si_2 underlayer.

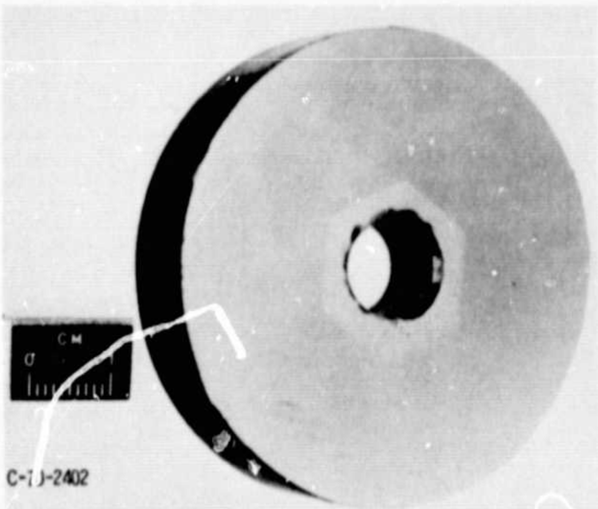


Figure 5. - Sputtered PTFE on paper.

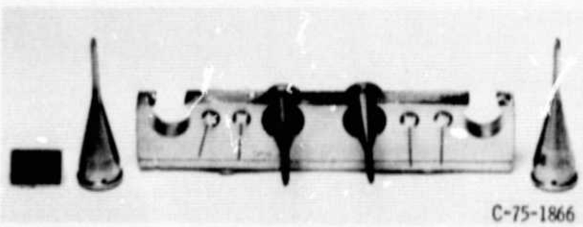


Figure 6. - Hypodermic needles and protective housings with sputtered teflon.

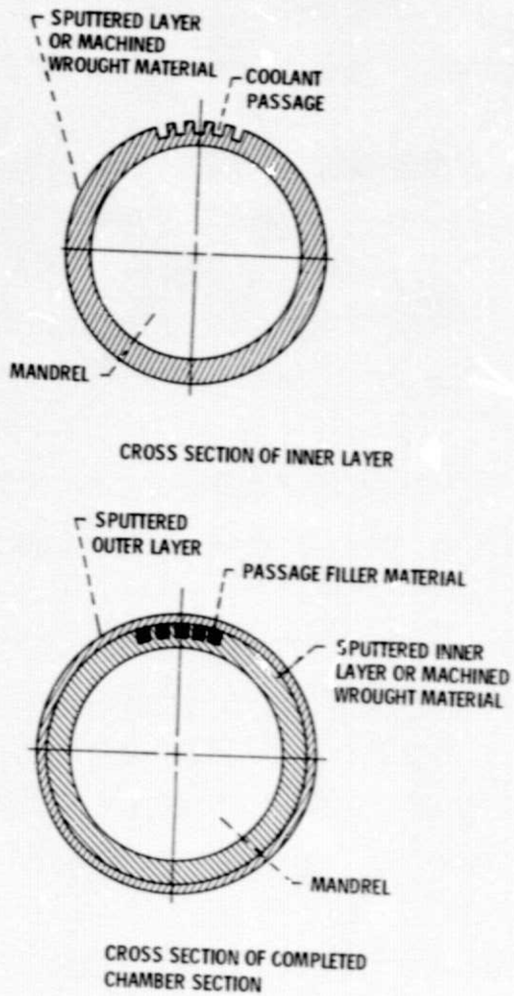


Figure 7. - Fabrication of thrust chambers

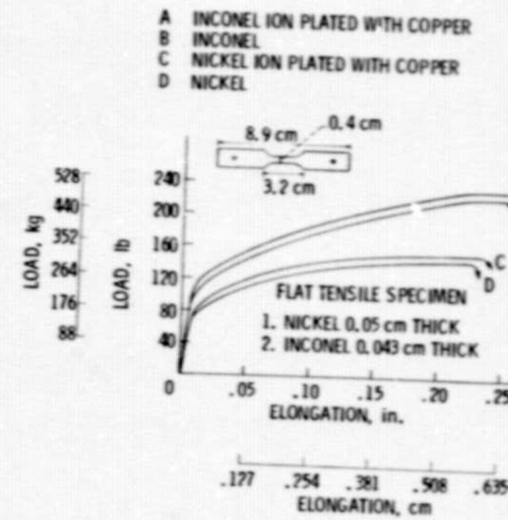


Figure 8. - Load elongation curves during tensile tests.

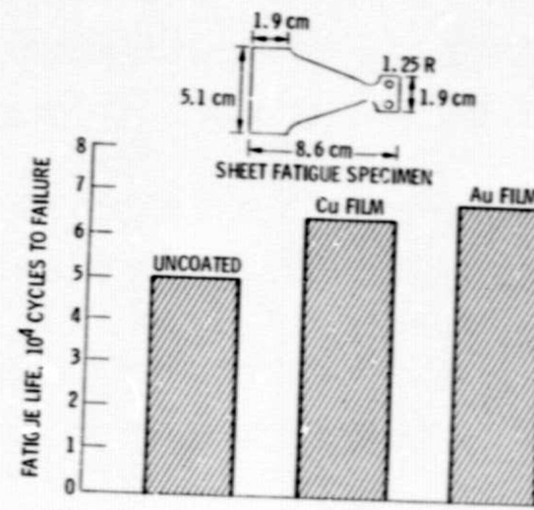


Figure 9. - Effect of copper and gold ion plated films (1500 Å) on the fatigue life of nickel.

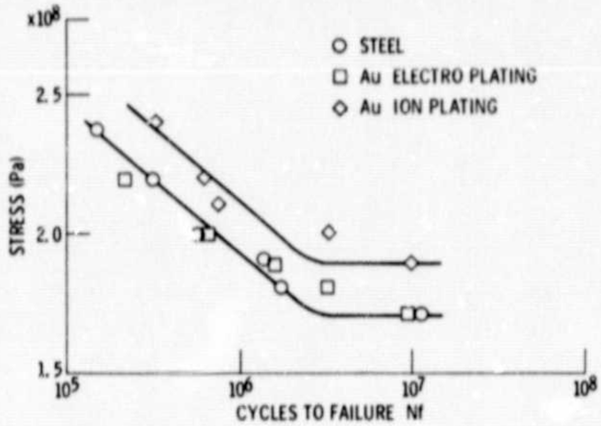


Figure 10. - Effect of ion plating on the fatigue property of low carbon steel (ref. 13).

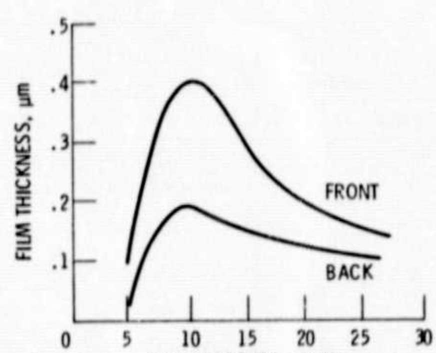
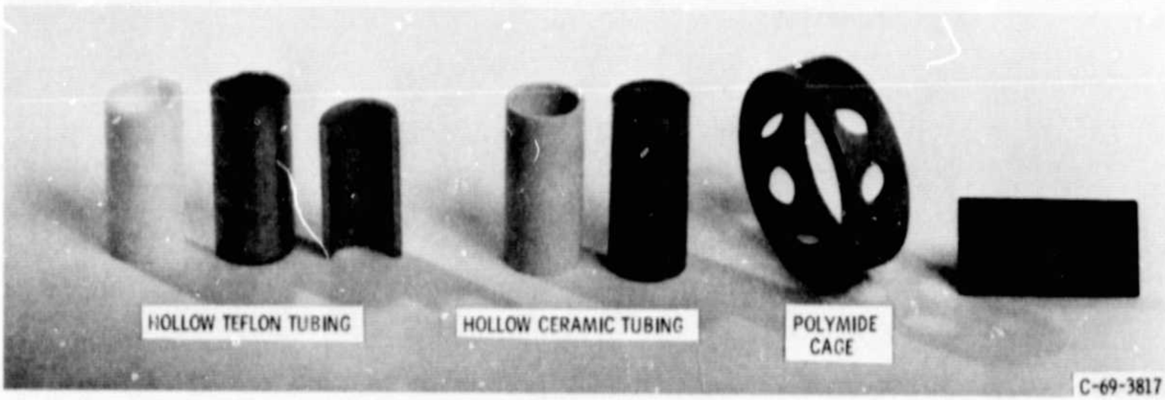
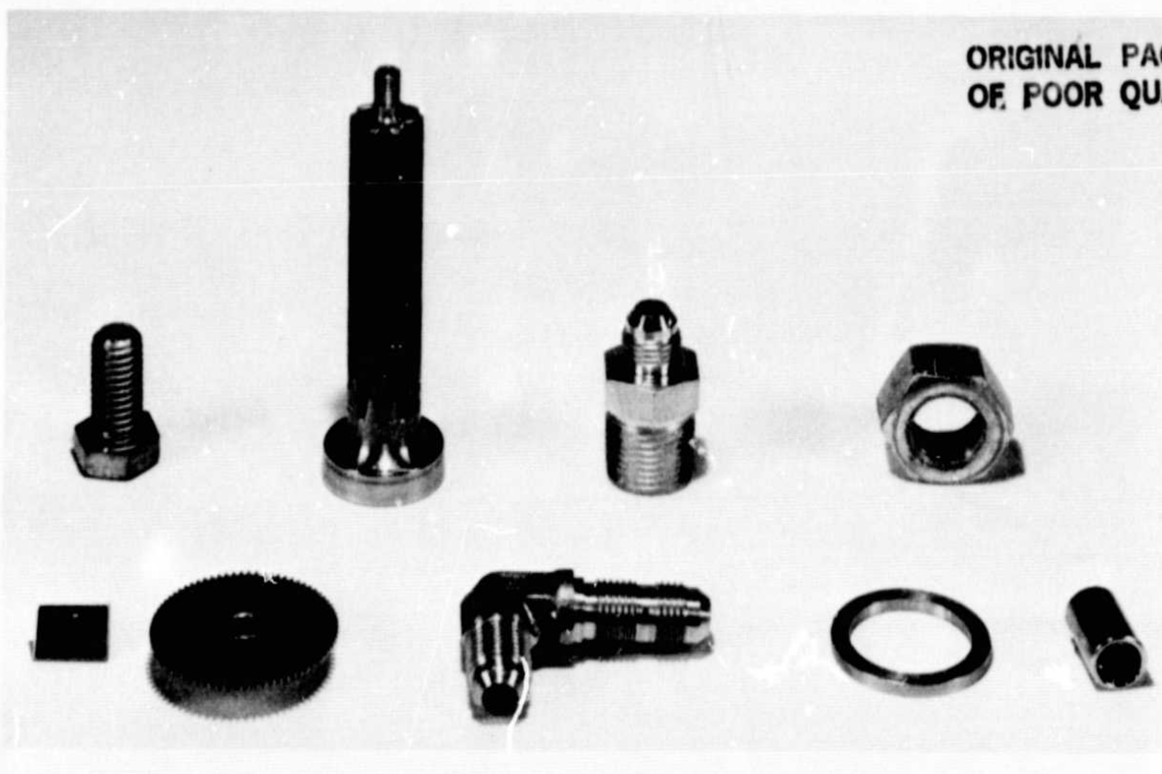


Figure 11. - Film thickness on front and back surfaces of a flat plate specimen as a function of argon pressure (ref. 14).



(a) COATED INSULATORS.



(b) COATED INTERNAL AND EXTERNAL METALLIC SURFACES.

Figure 12. - Ion plated insulators and objects with metallic coating.

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16. Abstract

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