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U.S. DEPARTMENT OF ENERGY
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HIGH TEMPERATURE SOLID LUBRICANT MATERIALS FOR HEAVY DUTY AND ADVANCED HEAT ENGINES

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ABSTRACT

Advanced engine designs incorporate higher mechanical and thermal loading to achieve efficiency improvements. This approach often leads to higher operating temperatures of critical sliding elements (e.g. piston ring/cylinder wall contacts and valve guides) which compromise the use of conventional and even advanced synthetic liquid lubricants. For these applications solid lubricants must be considered. Several novel solid lubricant composites and coatings designated PS/PM200 have been employed to dry and marginally oil lubricated contacts in advanced heat engines. These applications include cylinder kits of heavy duty diesels, and high temperature stirling engines, sidewall seals of rotary engines and various exhaust valve and exhaust component applications. The following paper describes the tribological and thermophysical properties of these tribo-materials and reviews the results of applying them to engine applications. Other potential tribological materials and applications are also discussed with particular emphasis to heavy duty and advanced heat engines.

INTRODUCTION

Advanced engine designs offer improved fuel efficiency and reduced emissions but often place higher demands on lubricants and lubrication systems. Improved efficiency results from higher thermal and mechanical loading and reduced emissions are achieved by higher combustion temperatures and reduced oil volumes in the upper cylinder region. These approaches can lead to extremely high operating temperatures of critical sliding elements such as piston ring/cylinder wall contacts and valve stem/guides precluding the use of conventional and even advanced synthetic oils (Ref. 1).

Some of the most challenging tribological problems in advanced heat engines occur with components which are in contact or close proximity to the exhaust gas stream. This occurs in exhaust valve guides/stems, turbocharger components (bearings and seals) and exhaust flow controls (waste gate valves, dampers etc.) For these components, where temperatures can reach 750°C, other tribological solutions, such as solid lubrication, must be considered.

Several solid lubricant coatings and powder metallurgy composites have been developed at NASA for high temperature applications. One example of materials is PS/PM200 composites. Composites of this family are a physical mixture of a metal bonded chrome carbide matrix which provides strength and wear resistance and barium fluoride/calcium fluoride eutectic and silver which act as high and low temperature lubricants (Ref. 2-4). The PS/PM200 materials have been considered as solid lubricant candidates in a variety of sliding applications ranging from cylinder wall coatings for reciprocating stirling cycle engines (Ref. 5) to rotary valve seals on rotorcam engines (Ref. 6)

In addition to the PS/PM200 materials, a new thin metal film lubricant has been recently developed which shows promise for lubricating high temperature metal and ceramic surfaces (Ref. 7). This film is made from a duplex layer of Au and Cr deposited onto alumina and provides low friction and wear in sliding contact from 25 to 1000°C. The Au/Cr film, which is only 2μm thick, can be applied to a finished part without significantly changing dimensions or requiring additional finishing. This film has potential application for ceramic exhaust valve guides and turbocharger components.

The following paper describes the Au/Cr thin film and PS/PM200 lubricant systems currently under development at NASA Lewis Research Center. Past applications, tribological and physical properties and feasibility for use in heavy duty applications will be reviewed. Finally, potential applications with particular emphasis on exhaust gas path components (valves, turbochargers, etc.) will be discussed.

PS/PM200 - BACKGROUND

Sliney has written a number of thorough review papers on the uses and potential of PS/PM200 materials for general heat engines (Ref. 5, 10). One discusses the use of PS200 coatings as cylinder wall coatings for Stirling engines (Ref. 5). In this application PS200 was coated on the inside diameter of a stainless-steel cylinder which was running dry against a stellite-6B piston ring at 760°C Top Ring Reversal Temperature in a hydrogen environment. Testing was conducted for 25 hours

In another paper by Sliney (Ref. 11), the potential applications of PS200 coatings for gas turbine engine bearings and seals are discussed. In this review, Sliney concludes that PS200 coatings are appropriate candidates for gas turbine engine applications.

PS212 coatings were also used to lubricate a partially stabilized zirconia thermal barrier coating (PSZ TBC) used in a rotary engine (Ref. 10). In this application, the PS212 was coated over a thick thermal barrier layer of PSZ to protect the aluminum housing of the engine. The use of the PS212 coating allowed for significantly higher operating temperatures and increased efficiency. Table IV lists application tests of PS/PM200 and their general outcomes.

In all cases, the PS/PM200 materials reduced friction and wear relative to dry, unlubricated systems. However, these materials do not provide the low levels of friction and wear exhibited by conventional liquid lubricants. For these reasons, PS/PM200 materials are appropriate to consider for applications which due to extreme conditions, such as high temperature, preclude the use of better lubricants (such as an oil film).

In addition, PS/PM200 lubricants require extensive processing (plasma spraying or and PM processing) and finishing (diamond grinding) for application to a sliding system. These processing requirements add cost and complexity and often limit the widespread use of these materials. To address these issues, the thin film lubricant Au/Cr is under development.

PS/PM200 - MATERIALS SYSTEMS

PS/PM200 is a generic designation for a family of Plasma Spray (PS) coatings or Powder Metallurgy (PM) composite materials which contain typically 60 to 80% metal bonded chrome carbide and 10-20% each of BaF_2/CaF_2 eutectic and silver. Specific numeric designations describe particular compositions. PS200, for example, is a plasma sprayed coating which contains 80% carbide matrix and 10% each of silver and eutectic. PM212 is a powder metallurgy composite containing 70 wt% carbide matrix and 15 wt% each of silver and eutectic. Differing compositions display slightly differing mechanical and tribological properties allowing the composition to be tailored for an application. For instance, PS200, which contains more carbide matrix than PS212, is slightly harder. To make the composites, the three components are physically blended then conventionally plasma sprayed to generate PS200 coatings or processed via a powder metallurgy route shown in Figure 1. Both the material system and powder metallurgy processing are covered under U.S. patents (Ref. 8 and 9). Figure 2 shows the microstructure of PM212. This material system has been designed to provide low friction and wear to sliding contact from below room temperature to about 900°C in reducing or oxidizing environments. Table I gives the material composition and selected thermophysical and mechanical properties of the PM composite. Table II gives representative tribological data for both the coating and powder metallurgy composite. Table III gives thermophysical data needed for assessing engineering feasibility of using PM212 in an application.
Finally, Figure 3 shows a comparison of PM200 strength with conventional bearing/brushing materials (Ref. 3). Even at elevated temperatures, well beyond the capability of bronzes and graphite, PM200 has useful strength for applications such as bushings and valve guides.

THIN METAL FILMS

Thin soft metal films have been used successfully to lubricate metal and ceramic surfaces (Ref. 12-14). These soft films prevent wear and reduce friction in sliding contact by providing an easily sheared layer between the rubbing surfaces. The load capacity of these soft films is greatly enhanced by application over hard bearing substrates. Unfortunately, soft metal lubricants like silver and gold are relatively inert and bond poorly especially to ceramics (Ref. 15). To improve this bond, adhesion enhancing interfacial bond layers of active metals are used. For example, Reference 14 describes the use of titantium as a bond layer for depositing silver onto alumina for room temperature lubrication.

Another lubricant system which has promise is Au/Cr (Ref. 7). In recent laboratory pin-on-disk tests, Au/Cr films have been developed which reduce friction and wear of alumina ceramic specimens. The films are applied by first sputtering a 1000Å thick Cr bond layer onto an alumina test disk. Then a 2μm thick Au lubricant layer is applied. Adhesion is further enhanced by subjecting the specimens to a six hour heat treatment in air at 800°C. Films produced in this manner exhibit friction which ranges from about 0.4 at 25°C to 0.25 at 800°C as shown in Figure 4. Representative wear data is shown in Table V. These Au/Cr films exhibit outstanding wear lives with some tests lasting in excess of 200,000 sliding passes. More recent testing has shown that these films continue to lubricate even at 1000 °C. Current efforts are underway to further characterize this lubricant system at alternate loads and sliding velocities and to evaluate it for us on other high temperature materials like superalloys.

EXHAUST GAS STREAM APPLICATIONS

A common characteristic of the lubrication approaches discussed (Au/Cr films, PS/PM200) is the ability to provide friction and wear reduction to sliding components over a very wide temperature range. This characteristic makes these materials well suited to advanced heat engine components in the exhaust gas stream. A few examples are valve stem/guide contacts, exhaust waste gate valves and dampers and turbocharger bearings and seals.

Compared to piston ring/cylinder wall sliding contacts, these exhaust gas stream components are less highly loaded, and operate at lower velocity (at least for valve guides and waste gate valves) making them well suited to solid lubrication.

For valve guide applications, PS200 or Au/Cr coatings could be applied to the outside diameter of the valve stem. Alternately valve guides could be made from PM200 and run against a conventional valve stem. Figure 5 illustrates a typical valve layout from a heavy duty engine along with lubrication possibilities. By utilizing solid lubrication in this critical area liquid lubrication could be minimized or removed entirely, reducing the potential for oil leakage into the exhaust stream and increasing emissions.

Exhaust waste gate exhaust gas recirculation (EGR) and manifold heat riser valves are another application well suited to solid lubricants. This type of application, shown schematically in Figure 6, usually employs an oscillating shaft or plunger operating in a bushing. Temperatures range from ambient (-25 to 50°C) to high operating temperatures near 700°C. In these applications the duty cycle (total sliding cycles or distance) is lower than for valve guides but nonetheless critical because these components must be free to operate even after being stationary for long periods of time. Greases and conventional solid lubricants (graphite, teflon, MoS_2 for example), lack the thermal stability required. Current designs rely on locating the sliding components in cooler areas but this approach can increase overall size and complexity.

Incorporating high temperature solid lubricants can greatly simplify this application. PS200 has been successfully tested in a butterfly type turbocharger waste gate valve as a shaft lubricant coating. Over 3600 hours of engine testing have been successfully accumulated on a large heavy duty diesel engine. Alternately, valve stem bushings could be fabricated, via powder metallurgy processing, from PM212.

In both the valve stem/guide and waste gate applications, the light loads and high temperatures make the use of solid lubricants appropriate. Turbochargers, on the other hand, function well using circulating oil lubrication (Ref. 16). In addition, their high speeds (up to 120,000 rpm) appear to preclude the use of solid lubricants (Ref. 17). However recent developments in both foil gas hydrodynamic bearings (Ref. 18) and high temperature solid lubricants (Ref. 7 and 19) have the potential to enable an alternate lubrication approach for turbochargers.

Foil Gas Bearings are compliant hydrodynamic fluid film bearings which, use ambient air rather than oil as their working fluid. At speeds above about 2000 rpm, foil bearings generate a thin gas film which prevents sliding contact. However, during startup or shutdown and high speed overloading (e.g. due to shocks) back up lubricant coatings prevent wear and damage. Foil Gas Bearings are generally useful at high speeds and light loads. Because air is the working fluid, these bearings have no practical temperature limit up to 700°C (the maximum use temperature of the superalloy foil components). This unique combination of capabilities has led to the successful use of foil bearings for turboalternators and air cycle machines for aeronautics applications.

Two drawbacks which have hindered more widespread use of foil bearings are their limited load capacity (less than 50 psi) and the lack of high temperature start/stop lubricant backup coatings. Recent developments in both bearing technology and tribology have been made to overcome these problems and efforts are currently underway to demonstrate on "oil-free" foil gas bearing supported turbocharger.

Heshmat (Ref. 19) has reported on improved foil gas bearing designs which demonstrate approximately twice the load carrying capacity of conventional designs. These improvements have been achieved through careful optimization of bearing geometry and analysis of the gas film using computers. With load capacities nearing 100 psi at 100,000 rpm, foil bearings are now adequate to handle static and dynamic radial and thrust loading typical of medium size (150 hp) turbochargers.

In terms of backup lubrication, both PS/PM200 composites and Au/Cr films are viable for this application. In fact, PS200 type coatings have been successfully demonstrated as shaft lubricants for foil bearings operating from 25 to 650°C (Ref. 19). In this case, a wide range of PS200 compositions was applied to Inconel X-750 journals and operated against Inconel X-750 foils in a high temperature bearing rig. The bearings were then started and stopped for thousands of cycles. Friction and wear was periodically measured. Figure 7 shows some selected results. Several PS200 coatings performed satisfactorily even after 9000 start stop cycles. For a typical heavy duty truck engine turbocharger, 2000 to 5000 start-stop cycles are required. Therefore the PS200 type technology appears to be suitable. Figure 8 shows a gas bearing test journal after 10,000 start stop cycles at 25 to 650°C.

However, the increased costs associated with plasma spray coating and finish grinding necessitate alternate approaches to lubricating foil bearings in this application. One is to apply sputtered thin (<20 μm) PS/PM200 films using Physical Vapor Deposition (PVD). Initial work at NASA LeRC in this area has been encouraging. Pin-on-disk tests of Au/Cr films indicate lifetimes exceed 200,000 sliding cycles which is roughly equivalent to the number of sliding experienced by a foil bearing during 3000 start/stops. Another possible solution is to use Au/Cr film to directly lubricate either the thin foils or the journal.

In addition to the bearings, floating ring type seals to separate the compressor and turbine gas flows need lubrication. Fortunately, these seals are very lightly loaded and experience only small displacements reducing lubrication requirements. In the seals both PS/PM200 or Au/Cr films may be suitable. However a simple hard facing (e.g. Cr or Cr_2O_3) may be adequate. Figure 9 from Reference 18 shows a possible schematic design for a foil bearing supported turbocharger and the locations of the bearings and seals which require solid lubricants.

The application of foil bearings in heavy duty engine turbochargers would eliminate the need for oil lubrication, auxiliary cooling, and the potential for oil leakage into the intake or exhaust flow stream. Also, since gas foil bearings exhibit significantly lower frictional losses, approximately 3 hp vs. 16 hp for conventional turbocharger, overall engine cycle efficiency can be increased. The application of solid lubricants to foil bearings for "oil-free" turbochargers has the potential to reduce emissions and increase fuel economy. Cost and rotor stability problems remain as critical issues for this application. Current research efforts supported by the Department of Energy, Department of Defense and NASA are underway to address these issues and demonstrate prototype hardware.

CONCLUDING REMARKS

Advanced engine designs are aimed at increasing fuel efficiency and reducing emissions without sacrificing reliability and durability. These seemingly contradictory goals are being met with improved materials, higher operating temperatures and pressures and new approaches to lubrication problems.

Solid lubrication plays an important role in achieving the design goals especially in the area of exhaust gas stream components. New lubricant materials and systems such as the PS/PM200 composites and Au/Cr films have shown promise in several heavy duty transport and advanced engine applications. The attributes which make them viable lubricant candidates are wide operating temperature range, stability and versatility in application methods. Furthermore, using advanced solid lubricants for cylinder head applications and turbocharger bearings and seals enables "dry" running designs which may significantly reduce emissions and fuel consumption. More efforts, however, are needed to demonstrate these technologies and further develop them for commercial use.

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TABLE I. COMPONENTS OF PS/PM212

Component	Composition, wt %	Composition, vol %	Particle size U.S. sieve no, (μm)
Bonded chromium carbide: 70 wt% of PM212			
Cr_3C_2	45	47	-200 + 400 (74 to 35)
Ni	28	22	
Co	12	10	
Cr	9	9	
Mo	2	1	
Al	2	5	
B	1	3	
Si	1	3	
Silver metal: 15 wt% of PM212			
Ag	100	100	-100 + 325 (150 to 44)
Prefused eutectic: 15 wt% of PM212			
BaF_2	62	52	-200 + 325
CaF_2	38	48	(74 to 44)

TABLE II. TRIBOLOGICAL DATA SUMMARY FOR SINTERED AND HIPped PM212[a]

Temperature, °C	μ		K pin, mm^3/N-m		K disk, mm^3/N-m	
	Sinter	HIP	Sinter	HIP	Sinter	HIP
25	0.35±.05	0.37±.04	$3.2\pm1.5\times10^{-5}$	$1.8\pm.4\times10^{-5}$	$7.0\pm2.0\times10^{-5}$	$0.45\pm.11\times10^{-5}$
350	.38±.02	.32±.07	$3.9\pm1.8\times10^{-5}$	$2.5\pm.3\times10^{-5}$	$3.5\pm1.0\times10^{-6}$	$.85\pm.4\times10^{-5}$
760	.35±.06	.31±.04	$3.6\pm.9\times10^{-6}$	$.07\pm.04\times10^{-5}$	$1.0\pm.6\times10^{-5}$	$2.2\pm.8\times10^{-5}$
850	.29±.03	.29±.04	$4.1\pm2.0\times10^{-6}$	$.83\pm.10\times10^{-5}$	$5.0\pm1.0\times10^{-6}$	≈0, Transfer
Averages	0.34	0.32	2.0×10^{-5}	1.3×10^{-5}	2.2×10^{-5}	$0.88\pm\times10^{-5}$

[a]Uncertainties represent one standard deviation of the mean for the friction coefficients and the data scatter band for the wear data. Data table from reference 3.

[b]Sintered PM212 is approximately 80% dense.

[c]HIPped PM212 is fully dense and exhibits about three times the mechanical strength as sintered PM212.

TABLE III. SELECTED MECHANICAL AND THERMOPHYSICAL PROPERTY DATA OF SINTERED PM212

Property Name	Value	
	at 25°C	at 760°C
Compressive Yield Strength	346 MPa	95 MPa
Tensile Yield Strength	45 MPa	25 MPa
Young's Elastic Modulus	97 GPa	—
Density	5.1 g/cc	—
Thermal Expansion Coefficient	12.7×10^{-6}/°C	17×10^{-6}/°C
Thermal Conductivity	0.10 W/cm-K	0.17 W/cm-K
Specific Heat	.48 W·s/gmK	.68 W·s/gmK
Thermal Diffusivity	.040 cm^2/s	.047 cm^2/s

TABLE IV. PAST APPLICATIONS AND EXPERIENCE USING PS/PM200 IN HEAT ENGINE OR RELATED APPLICATIONS

Component	Application	Outcome
Stirling Engine	Cylinder Wall Coating	25 hours - Successful testing at 760°C in H_2
Foil Bearings	Journal Coating	Accumulated over 30,000 start stop cycles at 650°C
Turbine Engine	Brush Seal Shaft Coating	Coating reduced wear initially but requires finer microstructure for long term use
Rotocam Engine	Rotary Exhaust Valve Face Coating	Successful engine testing coating enables new engine design
Rotary Engine	Sidewall Seal Coating, Apex Seal Material	Lubricated zirconia TBC. Tests to be run on Apex Seal
Process Control Valve	PS200 Coated Valve Stem	Lubricated valve in H_2 from - 200 to 800°C
Exhaust Waste Gate Valve	Coated butterfly valve stem	Lubricated valve for over 3600 hours operation

TABLE V. FRICTION AND WEAR SUMMARY
[Test conditions: 4.9 N load, 1 m/s sliding velocity, air atmosphere, 60 min test.]

Disk Specimen	Friction Coefficient			Pin Wear Factor, $mm^3/N\text{-}m*10^{-7}$		
	25°C	500°C	800°C	25°C	500°C	800°C
Unlubricated	0.85±.03	0.69±.05	0.76±.02	23.2±.7	140±15	45±5
Au Coated	0.24±.05	(a)	(b)	1.0±.2	(a)	(c)
Au/Cr Coated	0.40±.05	0.30±.03	0.34±.02	0.60±.20	0.16±.06	1.40±.40

Notes:
-Uncertainties represent one standard deviation of the data. At least six repeat tests were run for each data point given. Data table from reference 7.
[a]Test not run.
[b]Friction was 0.35 until coating delaminated prior to end of 60 min test period.
[c]immeasurable due to excessive coating transfer from disk to pin.

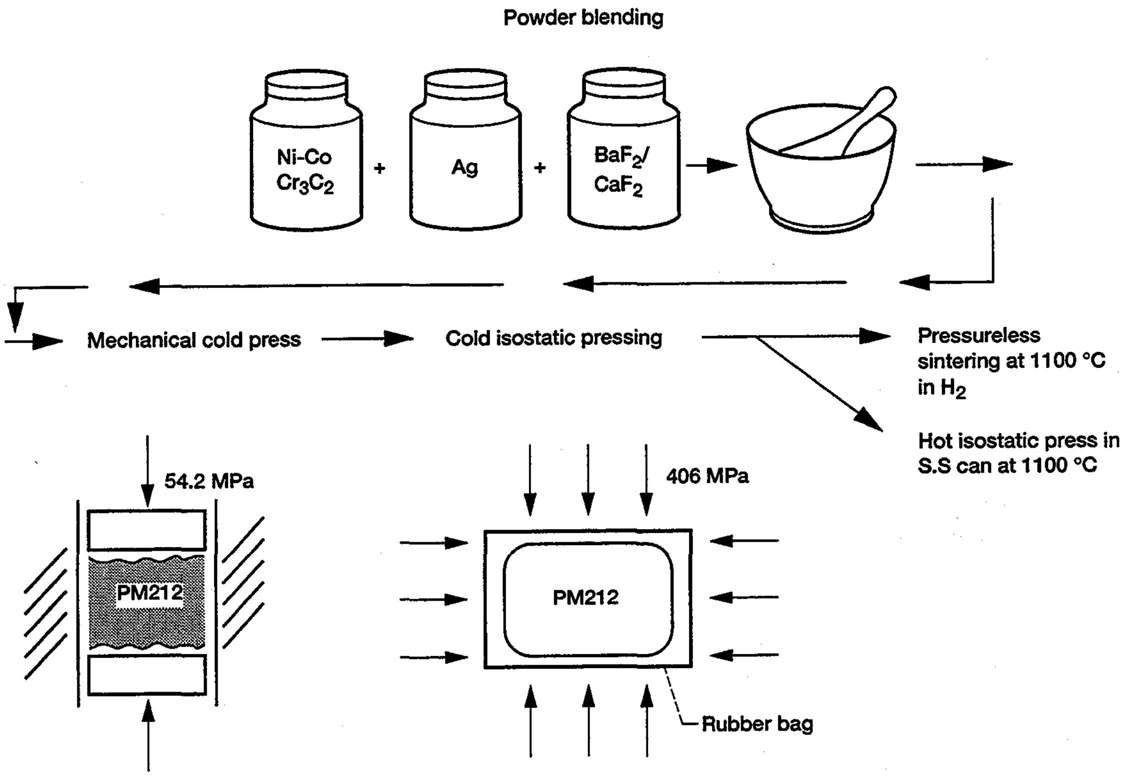


Figure 1.—Powder metallurgy (PM) processing route to make PM212 components.

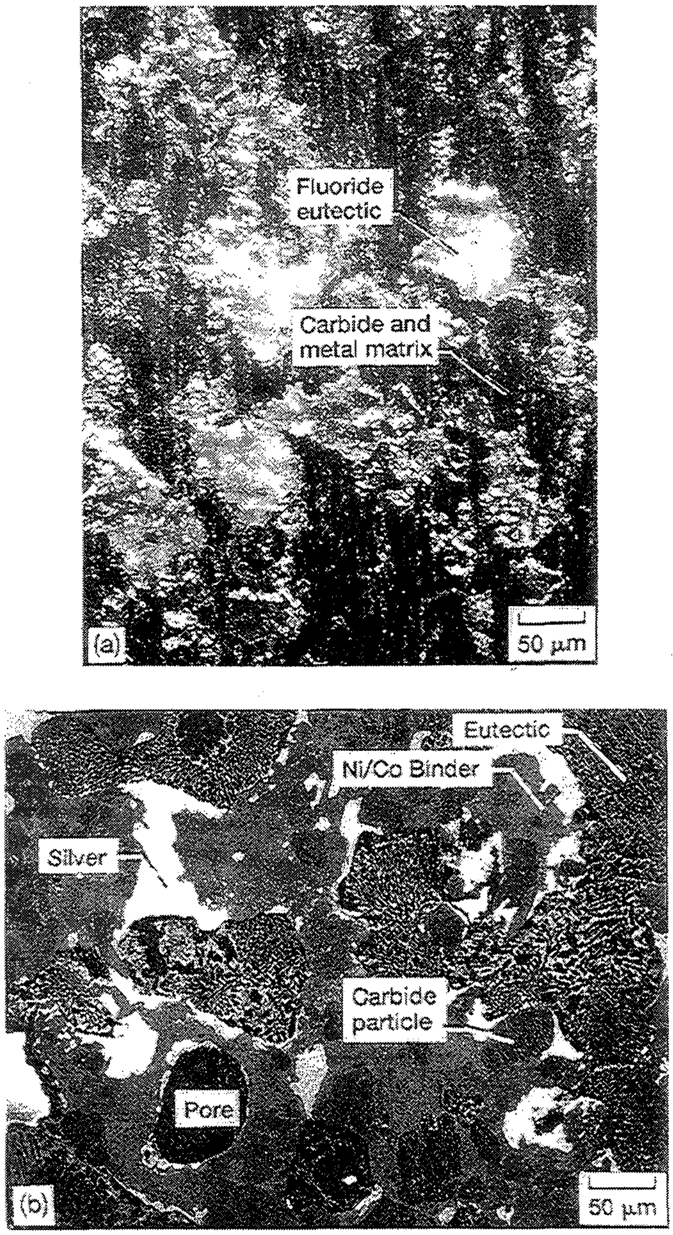


Figure 2.—Compositional photomicrographs of sintered PM212 showing microstructured under oblique optical illumination (a) and backscattered electron imaging (b).

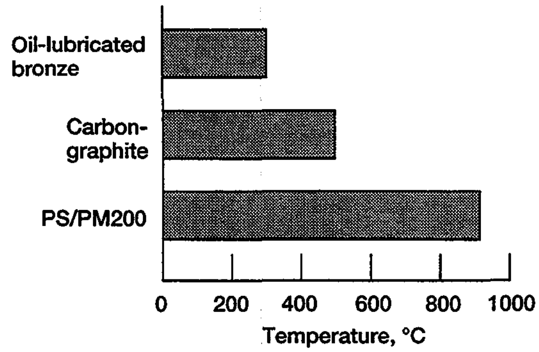


Figure 3.—Maximum use temperatue comparison of PS/PM 200 materials and conventional bearing materials [ref. 3].

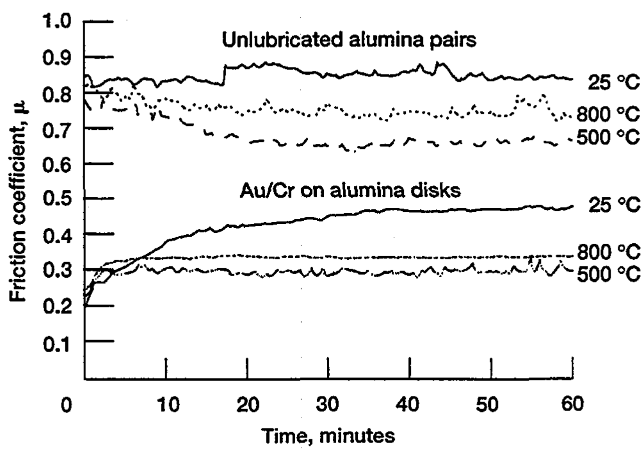


Figure 4.—Friction coefficient vs. time for unlubricated and Au/Cr lubricated alumina specimens. 4.9N load, 1m/s sliding velocity, air atmosphere [ref. 7].

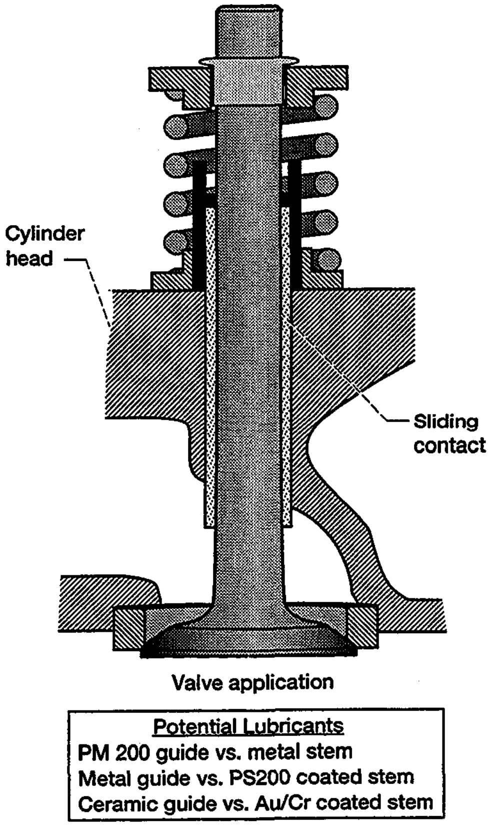


Figure 5.—Schematic of cylinder head cross-section showing valve guide application of high temperature solid lubricants.

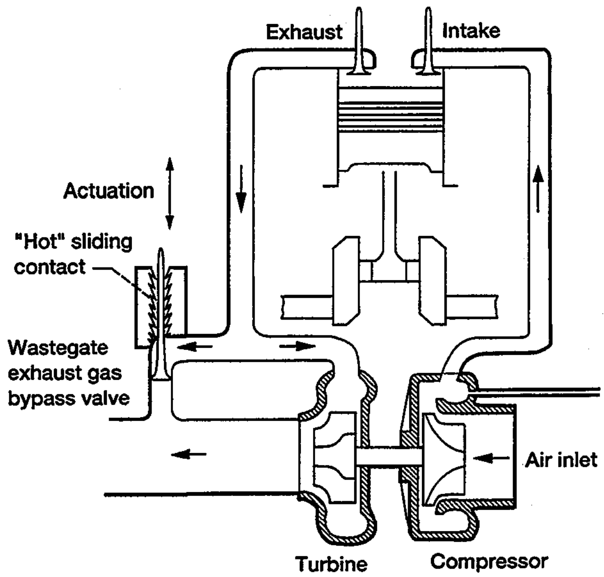


Figure 6.—Schematic illustration of exhaust wastegate valve showing sliding contact area requiring solid lubrication.

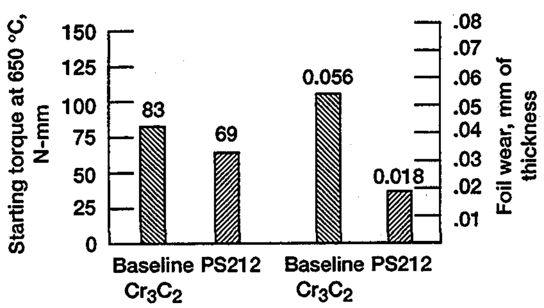
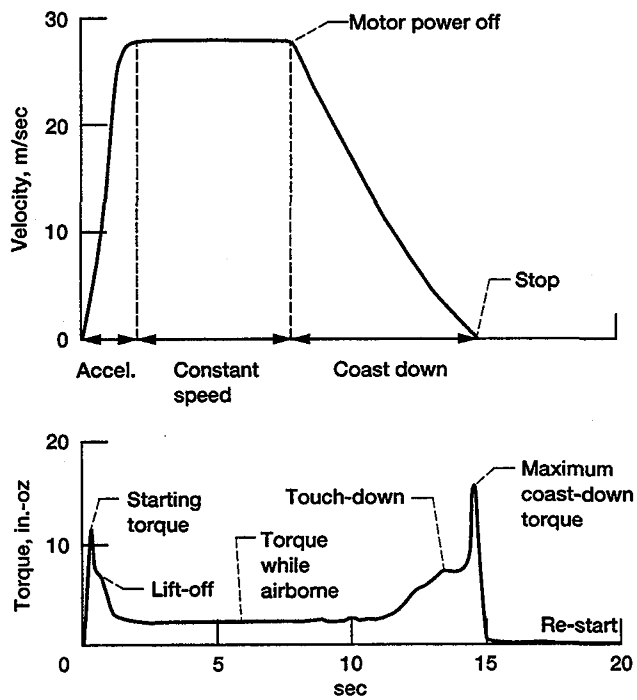
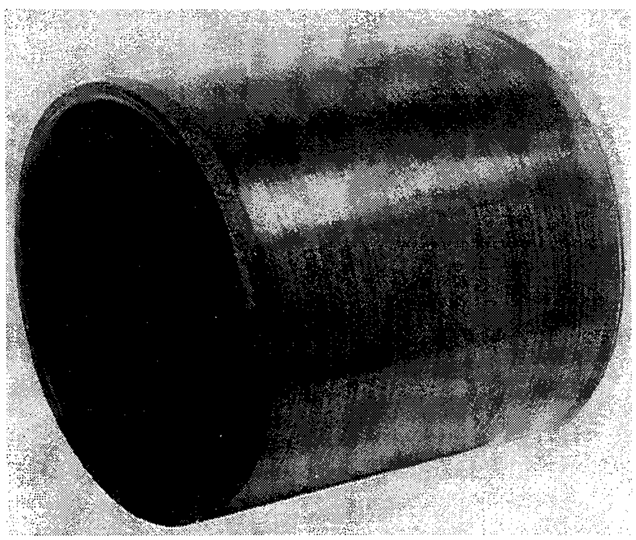


Figure 7.—Friction and wear improvement for foil bearings running against baseline wear resistant coating and PS212 lubricant coating [ref. 19].



Start-stop and torque profiles



PS200 coated journal after successful completion of 5000 start-stops at 25 °C and 5000 start-stops at 560 °C.

Figure 8.—Foil gas bearing after testing over wide range of temperature from 25 to 560 °C.

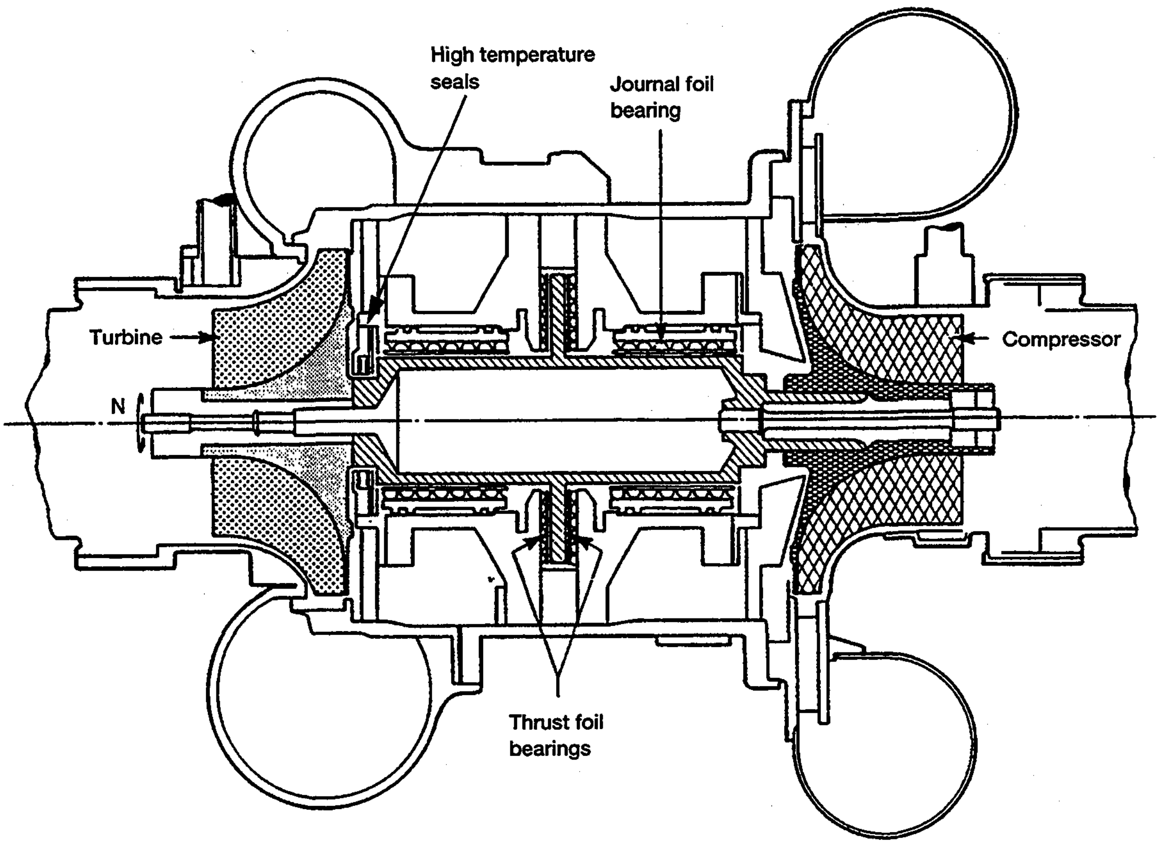


Figure 9.—Schematic cross section of foil gas bearing supported turbocharger. Adapted from ref. 20.

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13. ABSTRACT ***(Maximum 200 words)***

Advanced engine designs incorporate higher mechanical and thermal loading to achieve efficiency improvements. This approach often leads to higher operating temperatures of critical sliding elements (e.g. piston ring/cylinder wall contacts and valve guides) which compromise the use of conventional and even advanced synthetic liquid lubricants. For these applications solid lubricants must be considered. Several novel solid lubricant composites and coatings designated PS/PM200 have been employed to dry and marginally oil lubricated contacts in advanced heat engines. These applications include cylinder kits of heavy duty diesels, and high temperature stirling engines, sidewall seals of rotary engines and various exhaust valve and exhaust component applications. The following paper describes the tribological and thermophysical properties of these tribomaterials and reviews the results of applying them to engine applications. Other potential tribological materials and applications are also discussed with particular emphasis to heavy duty and advanced heat engines.

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