IN-27-CR

92853

P.44

DOE/NASA/0030-2
NASA CR-180808

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(NASA-CR-180808) EXPERIMENTAL EVALUATION OF CHROMIUM-CARBIDE-BASED SOLID LUBRICANT COATINGS FOR USE TO 760 C Final Report (Case Western Reserve Univ.) 44 p Avail: NTIS HC A03/MF A01 CSCL 11H G3/27
N87-27053
Unclas
0092853

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August 1987

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Under Contract NCC 3-30

for

U.S. DEPARTMENT OF ENERGY
Conservation and Renewable Energy
Office of Vehicle and Engine R&D

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Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
NTIS price codes[1]
Printed copy: A03
Microfiche copy: A01

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[1] Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA); Government Reports Announcements* and Index (*GRA* and I); *Scientific and Technical Abstract Reports (STAR);* and publication, NTIS-PR-360 available from NTIS at the above address.

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U.S. DEPARTMENT OF ENERGY
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Office of Vehicle and Engine R&D
Washington, D.C. 20545
Under Interagency Agreement DE-AI01-86CE50162

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E-3713

SUMMARY

This Master's Thesis describes a research program to further develop and investigate chromium carbide based self-lubricating coatings for use to 760 °C. A bonded chromium carbide was used as the "base stock" because of the known excellent wear resistance and the chemical stability of chromium carbide. "Additives" were silver and barium fluoride/calcium fluoride eutectic. The three coating components were blended in powder form, applied to stainless steel substrates by plasma-spraying and then diamond ground to the desired coating thickness.

A variety of coating compositions was tested to determine the coating composition which gave optimum tribological results. Coatings were tested in air, helium, and hydrogen at temperatures from 25 to 760 °C. Several counterface materials were evaluated with the objective of discovering a satisfactory metal/coating sliding combination for potential applications, such as piston ring/cylinder liner couples for Stirling engines.

In general, silver and fluoride additions to chromium carbide reduced the friction coefficient and increased the wear resistance relative to the unmodified coating. The lubricant "additives" acted synergistically in reducing friction and wear. Several coating compositions gave good results in hydrogen, helium, and air to 760 °C.

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CHAPTER 1 - INTRODUCTION

The lubrication of sliding contacts at high temperature has been a major obstacle to the development of heat engines, advanced turbomachinery and spacecraft (ref. 1). Operating temperatures for these applications can reach 1000 °C or higher. There are no liquid lubricants currently available that can withstand temperatures above 400 °C. Therefore, other types of lubricants such as solid lubricants must be used under these conditions.

A solid lubricant is a solid which can shear easily, providing low friction, yet separate sliding surfaces in order to reduce wear. Three of the most common solid lubricants are graphite, molybdenum disulphide and polytetrafluorethylene.

GRAPHITE

Graphite, a form of carbon, is the oldest and most common solid lubricant. Graphite has a hexagonal crystal structure in which large sheets of covalently bonded carbon atoms form platelets. The boundaries between adjacent platelets become preferred slip planes which allow easy dislocation movement and hence low shear strength while the strong covalent bonds between atoms provide compressive strength and, hence, wear resistance.

During sliding, the platelets, sometimes referred to as crystallites, orient themselves so that the preferred slip planes are aligned with the direction of motion. This results in a low bulk shear strength and low friction coefficients. Water vapor and other adsorbed gases on the surface of the platelets decrease bond strength between platelets and further reduce friction. Because of the tribological effect of these adsorbed vapors, graphite is a good lubricant in air but is not a good vacuum lubricant. In vacuum both friction and wear rise dramatically (ref. 2).

MOLYBDENUM DISULPHIDE

Molybdenum disulphide, MoS_2, has a layer lattice structure similar to graphite (fig. 1). Planar hexagonal sheets of molybdenum atoms are surrounded by sheets of sulfur atoms. The bonding between molybdenum and sulfur atoms is strong but bonding between adjacent sulfur atoms is very weak giving MoS_2 planes of low shear strength.

MoS_2, because of the weak bonding between layers of sulfur atoms, is an intrinsic lubricant. It does not require adsorbed gases to reduce friction as graphite does. Therefore, MoS_2 is a good lubricant in vacuum. But in air, MoS_2 reacts with oxygen to form MoO_3 which interferes with the slip process causing higher friction and wear in air (ref. 2). The oxidation rate is slow at room temperature but increases exponentially with temperature. MoS_2 coatings, therefore, have reasonably long wear lives in air at low temperatures, but can only be used for very short durations above 250 °C.

POLYTETRAFLUORETHYLENE

Polytetrafluorethylene (PTFE), is a long chain molecule made by the polymerization of carbon-fluorine monomers. The monomers are covalently bonded together to form long chains. The chains are bonded to one another by weak Van der Waal's forces. Hence, under shear, the long chains easily roll over one another providing low friction while strong carbon to fluorine covalent bonds provide compressive strength and wear resistance (ref. 3).

HIGH TEMPERATURE LIMITATIONS

High temperature adversely affect the three conventional solid lubricants discussed. PTFE losses its compressive strength above 150 °C and cannot separate two sliding surfaces, leading to excessive wear of both the substrate materials and the PTFE.

The beneficial vapors adsorbed in graphite are driven out by high temperatures. This significantly increases friction and wear due to an increase in platelet to platelet bond strength. MoS_2 becomes much more reactive at high temperatures. Since the reaction products of MoS_2 and air, namely MoO_3, interfere with the slip process it is not a good lubricant above about 250 °C except in high vacuum.

Other solid lubricants must be considered to lubricate under severe conditions in both vacuum and various atmospheres where temperatures as high as 1000 °C may be encountered.

HIGH TEMPERATURE LUBRICANT APPLICATIONS

The practical impetus for the development of high temperature lubricants comes mainly from the following areas: space applications, advanced aircraft/automotive turbomachinery and energy conservation research.

Space Applications

Spacecraft surfaces, during re-entry to the earth's atmosphere, and rocket engine components frequently encounter temperatures as high as 1000 °C. Control mechanisms often must undergo sliding contact under these conditions. The traditional approach to these lubrication problems has been to avoid them. Designs are chosen that move essential sliding contacts out of hot areas allowing the use of conventional lubricants. One example of this design approach is the insulating tiles on the space shuttle which provide thermal protection to many of the shuttle's control mechanisms. These designs, however, add to the complexity of the system. Clearly, in space applications where weight, reliability, and simplicity are important factors the need exists for more suitable lubricants.

Aircraft/Automotive Turbomachinery

Recent advances in turbine development for the aerospace and automotive industry have been aimed at increasing the efficiency of gas turbines while maintaining high thrust to weight ratios. The predominant approach to achieve these goals is to increase the turbine inlet temperatures of these engines thereby increasing their thermal efficiency. The need for bearings and lubricants capable of operating at temperatures of 650 °C is not uncommon in experimental turbomachinery (ref. 4). The lubricants used in sliding components such as shaft seals and thrust plates must meet the demanding requirements found here. Even gas hydrodynamic bearings, which ride on a film of air, experience sliding contact during start-up and shut-down and must be lubricated in order to lower starting torque and wear. Currently, sacrificial materials which need frequent replacement are used in these applications. This method is costly and needs improvement.

Energy Conservation Research

The Stirling and Adiabatic diesel engines are high temperature piston engines that achieve high efficiencies by operating at temperatures as high as 760 °C. In the adiabatic diesel, cylinder wall/piston ring lubrication and valve stem lubrication have been major problems. A short term solution is to apply a sacrificial "mist" or spray of oil to the sliding contacts. The oil, however, only provides temporary lubrication because it burns. Over time the burned oil residue chokes the engine requiring a complete teardown and cleaning. A solid lubricant which could control wear without producing undesirable byproducts would be more appropriate.

The Stirling engine is an external combustion engine that uses helium or hydrogen as the working fluid. Cylinder wall/piston ring temperatures reach 760 °C. The current lubrication procedure for this sliding contact is to place the piston ring at the bottom of the piston where the temperatures are lower (fig. 2). This configuration allows the use of more common solid lubricants such as MoS_2 and PTFE. But the annular space created between the piston ring and the top of the piston decreases the overall efficiency of the engine as much as 5 to 10 percent (ref. 5). A better solid lubricant, capable of withstanding these conditions is needed.

Clearly, new solid lubricants that can perform in a variety of environments such as hydrogen, helium, air, and vacuum at high temperatures are essential to the success of these and many other projects.

This thesis project describes a program to further develop an existing solid lubricant system capable of operating from room temperature to 760 °C in air, helium, or hydrogen. This system holds promise for meeting the lubrication challenges presented above.

CHAPTER 2 - MATERIAL SELECTION

A logical path, employing several design gates, was used to develop the high temperature, self-lubricating coating system studied in this program. The general design approach is discussed followed by specific discussion of the materials studied in this program. A flow chart of the design process is outlined in figure 3.

The first step to develop a high temperature solid lubricant is to determine expected operating temperatures and environments. In order for a high-temperature solid lubricant to be successful it must be able to withstand high operating temperatures as well as chemically reactive environments. Thus, the first design gate considered is melting temperature and the second design gate is chemical reactivity with the operating environment and other system components.

A brief review of the periodic table of the elements and standard material handbooks indicates that many metals and most ceramics pass the first design criterion or gate, high melting temperature. These "potential" materials must now be checked for their chemical reactivity with the anticipated environment. Free energy, thermochemical calculations are made to determine which materials will be relatively nonreactive at high temperatures in the operating environment.

At this point we have a list of materials that have high melting temperatures and high temperature chemical stability. The mechanical and physical properties of these candidate materials must now be ascertained in order to proceed to the next design gate. This data is normally acquired from handbooks and through a literature search.

The final design gate is to attain acceptable tribological properties under expected operating conditions. In order for a high temperature solid lubricant to be considered successful it must exhibit low friction and wear properties as well as thermal and chemical stability.

It is likely that no single material which passed the first design gates will also show both low friction and low wear properties. Some materials may be wear resistant but not lubricious and vice-versa. Others may only lubricate over a small temperature range when a large operating temperature range might be encountered.

To overcome tribological behavior deficiencies of some materials it may be necessary to combine several materials together to develop a successful high-temperature solid lubricant system. The logic behind this approach is generic to the formulation of all composite materials: that is to combine the desirable properties of each component without adversely affecting the desirable properties of other components. The chemical reactivities between system components must therefore also be checked. If some components are chemically reactive with one another other materials may have to be chosen.

This design process is an iterative one which will probably lead to many potential lubricant systems. Practicality, safety considerations, cost, and final testing must be taken into account to determine the best lubricant system.

DESIGN APPROACH APPLICATION

This general design approach has been applied to the development of a high-temperature solid lubricant coating, the PS200 coating system, by Harold E. Sliney at NASA Lewis Research Center. The requirements or design criteria of this lubricant system are: (1) the coating must be thermally and chemically stable at high temperatures in air, helium, hydrogen, and vacuum, the proposed operating environments; (2) the coating must display high wear resistance and adherence for extended life applications; (3) the coating must exhibit reasonably low friction coefficients to reduce frictional losses; and (4) the coating must be able to operate over a wide temperature range from room temperature to 900 °C.

Much of the research associated with the materials selection for this lubricant coating system has been completed over the past decade at NASA Lewis. The materials chosen will be reviewed and their function explained.

The coating components are a metal-bonded chromium carbide "base stock" combined with silver and barium fluoride/calcium fluoride eutectic. The chromium carbide base stock provides wear resistance while the silver and eutectic act as low and high temperature lubricants, respectively.

All three of the coating components are chemically and thermally stable throughout the operating temperature range. Appendix A illustrates the thermochemical calculations made to examine chemical reactivity at various temperatures.

The physical properties of the coating components are as follows:

Chromium carbide. - Chromium carbide is a hard, wear resistant ceramic. It has been used successfully in wear control applications (ref. 6). Chromium carbide, however, is not a good lubricant and does not meet the lubrication requirements of the coating system. Other materials must be added to the coating system to provide a lubrication effect.

Silver. - Silver possesses remarkable thermal and chemical stability yet has very low shear strength even at room temperature. This property makes silver a potentially good lubricant. When used in a sliding contact, silver undergoes plastic deformation providing a lubrication effect yet reduces wear by separating the two rubbing surfaces. Silver is a good room to moderate temperature (~350 °C) lubricant but at high temperature, losses its compressive strength and cannot effectively separate sliding surfaces or support loads. Therefore, silver can only be considered as a lower temperature lubricant. It does not function as a wear resistant coating component.

Barium fluoride/calcium fluoride eutectic. - BaF_2, CaF_2, and the Group II fluorides in general, are very stable and have shown to be excellent high temperature lubricants (ref. 7). At temperatures above their brittle to ductile transition temperature, approximately 40 percent of their absolute melting temperature, these ionic solids behave as good lubricants (ref. 8). They exhibit ductile behavior which provides low friction and retain enough compressive strength to support loads and maintain low wear.

Bond Material

In order to apply the active coating components, namely the Cr_3C_2, the eutectic and the silver, in a practical manner, a bond material is used. It functions as a binder by keeping the coating components in a continuous matrix.

A nickel aluminide/cobalt binder is chosen for this coating system for several reasons: (1) the binder is thermally and chemically stable at elevated temperatures, (2) the binder possesses high strength which adds to the wear resistance of the coating, (3) the binder's bulk thermal expansion coefficients closely match those of typical coating substrates such as stainless steel, reducing thermal stresses and cracking, and (4) this binder combined with chromium carbide is commercially available as a plasma spray powder facilitating specimen preparation.

In summary, the coating system consists of a metal-bonded chromium carbide "base stock" which provides wear resistance with silver metal and barium fluoride/calcium fluoride eutectic additions which provide lubrication over a wide temperature range.

Other materials are suitable for this type of composite material. This is particularly true for the low temperature solid lubricant additive. Silver is chosen for its chemical stability, availability, and relative low cost. Different low shear strength materials, gold, for example, could also be used but material waste during the plasma-spray process make lower cost silver more attractive. Also, both silver and the eutectic have been proven as viable solid lubricants in other applications making them logical choices for this composite system (ref. 4).

CHAPTER III - COATING PREPARATION

The conceptual PS200 coating system was developed and tested prior to the beginning of this Master's thesis research project (ref. 9). The optimum coating composition was, however, unknown. It is the goal of this research program to determine the coating composition which exhibits the best overall tribological performance. The following section outlines the composition optimization program undertaken to determine the best coating composition.

COATINGS CHOSEN

The coating composition optimization is a three variable program designed to determine the coating constituent proportions which give the best overall tribological performance on a pin-on-disk tribometer. The three main variables are silver weight percent, BaF_2/CaF_2 weight percent and metal-bonded chromium carbide weight percent.

Due to the complexity and expense associated with preparing and testing each coating composition the overall composition domain was limited. The compositions evaluated can be broken down into four distinct categories; the limiting compositions, the control compositions, the ratio variance compositions, and compositions with a 1:1 ratio of added lubricants. Table I indicates the complete range of compositions tested and the PS200 numbering system by which the compositions are designated.

Limiting Compositions

The coating designated PS218 contains only the metal-bonded chromium carbide with no silver or eutectic. It is evaluated primarily to determine if lubricant additions do, in fact, improve coating performance. The data taken from this composition are considered baseline data to which other compositions can be compared. It was expected that PS218 would be the most wear resistant coating but would also exhibit the highest friction coefficients.

PS213 contains 60 wt % metal-bonded chromium carbide and 20 wt % each of the silver and barium fluoride additions. This coating is a limiting composition because it contains the highest proportion of added lubricants. It was expected that any coatings tested which contain less of the metal-bonded chromium carbide "base-stock" would display excessive wear because the metal binder could no longer form a strong, continuous matrix to support the lubricant additives. Hence, plowing of the coating by hard counterface materials would then occur.

Control Cases

The coatings PS215 and PS216 are compositions that are lacking in one added lubricant. These compositions were chosen to check the validity of the "property addition" premise. That is, it was not yet shown that in this composite coating system the silver acts as a low temperature lubricant and the eutectic acts as a high temperature lubricant. These compositions would verify this theory as well as determine if both lubricants were actually needed in the coating system. PS215 contains 70 wt % of the metal bonded chromium carbide, 30 wt % of silver, and no eutectic while PS216 contains 70 wt % metal bonded chromium carbide, 30 percent eutectic and no silver.

Additive Ratio Variance Coatings

The following compositions designated PS203 and PS204 were tested to determine if small variances in the ratio between lubricant additives had a large effect on the overall coating performance. PS203 contains 85 wt % metal-bonded chromium carbide, 5 wt % silver and 10 wt % eutectic and PS204 contains 85 wt % metal-bonded chromium carbide, 10 wt % silver, and 5 wt % eutectic.

Compositions With a 1:1 Ratio of Added Lubricants

A coating containing 80 wt % metal-bonded chromium carbide and 10 wt % each of the added lubricants (PS200) was tested in a previous study and found to be a good high temperature lubricant (ref. 10). Since this coating with a 1:1 ratio of added lubricants performed well it was decided to test other 1:1 ratio type coatings to find what total added lubricant weight percent gives the best tribological performance. PS212 contains 70 wt % metal-bonded chromium carbide and 15 wt % of each of the added lubricants. PS213 contains 60 wt % metal-bonded chromium carbide and 20 wt % of each of the added lubricants.

TERNARY DIAGRAM

Figure 4 is the ternary diagram for the PS200 series coating system. It gives a graphical representation of the coating compositions evaluated and shows visually how each composition varies from one another. The upper limit at the apex of the triangle is PS218 which contains no added lubricants. The lower limit of the test program is PS213 which contains only 60 wt % of the metal-bonded chromium carbide base stock and 20 wt % each of the silver and fluoride eutectic. Coatings that fall along the line between PS218 and PS213 have 1:1 ratios of added lubricants, namely coatings PS212, PS200, and PS213. PS203 and PS204, on the same horizontal level, contain the same weight percent of the metal-bonded chromium carbide but have varied amounts of added silver or eutectic. Finally, PS215 and PS216, located at the edges of the triangle, contain 70 wt % of the metal-bonded chromium carbide but are lacking in one lubricant or the other.

Coating Powder Preparation

The metal-bonded chromium carbide is commercially available in powder form from the Metco company. It contains approximately 60 wt % chromium carbide and 40 wt % nickel-cobalt binder. Mesh size and composition of each coating component are given in table II.

The silver is purchased in powder form from the Metco or the Fisher Scientific Company. It is 99.99 percent pure. Powder sizes range from -100 to +325 mesh.

The BaF_2/CaF_2 eutectic powder is made by physically mixing reagent grade barium fluoride and calcium fluoride powders in 62 wt %/38 wt % proportions.

These proportions give the eutectic composition which has the lowest melting temperature. Early in the program it was discovered that the ease of coating application (plasma spraying) and coating performance were improved by prefusing the eutectic mixture then regrinding it to proper mesh size. The prefusing is carried out in a nitrogen atmosphere in a clean nickel crucible in a Harper tube furnace at 1100 °C. The resulting fused eutectic block is then crushed in a mechanical crushing machine until the particle size is between 1 and 2 millimeters. The crushed eutectic is further ground in a ball mill using aluminum oxide pellets as the crushing stones. The resulting eutectic powder is then sieved to obtain powder of the correct size for plasma spraying. X-ray analysis of the eutectic prepared by this method indicates that no significant contamination of the powder occurs. By prefusing and regrinding the eutectic, coating samples are very uniform and give consistent test results.

To prepare the coating compositions, the powders are weighed on an analytical balance in the correct proportions for the coating desired. The measured powders are then blended together and are ready for the plasma spray process.

PLASMA SPRAYING

Plasma spraying is the technique used to apply the powder coatings to metal substrate test samples. Plasma spraying is an ideal procedure for applying mixtures of substances that have varied melting temperatures onto surfaces with little substrate heating which can cause thermal distortion.

The basic plasma spray process is as follows: a stream of Argon carrier gas is electrically ionized/heated between an anode and cathode to at least 10 000 K. The coating powder mixture is forced into this hot gas stream where it melts. The hot argon and melted powder mixture then impinges onto the cold (room temperature) substrate. The coating mixture "splats" and adheres to the substrate forming a strong coating. Figure 5 shows the plasma spray process schematically. The substrate is usually held in a rotating or traversing lathe chuck and the plasma spray gun is passed over the part. Many passes are required to buildup the thick (15 mils) coating tested in this study. This process deposits approximately 0.013 cm of coating per pass. Typical plasma spray parameters are given in table III.

Grinding Procedure

The plasma-sprayed surface is a rough, tribologically poor surface. In order to be a good friction and wear surface the rough coating must be diamond ground. Diamond grinding also provides a convenient method of achieving a final dimension or close tolerances.

A diamond grinding procedure was developed in this program to obtain good, consistent wear surfaces from the plasma sprayed coatings. The general procedure is as follows: A number 150 grit diamond grinding wheel is used with deionized water lubrication to grind the coating surface. Initial rough cut grinding passes are made at a depth of no more than 0.0025 cm. When the coating thickness is within 0.0025 cm the grinding depth per pass is reduced to 0.0010 cm. If the grind depths per pass are too large the soft phase materials, namely the silver and eutectic, will be "plucked" from the surface leaving raised carbide rich areas which act as a grinding wheel. If the grinding depth per pass is too small the nickel-cobalt binder material will smear over the entire surface leaving a nickel-cobalt wear surface with no lubricants exposed. Figure 6 shows, schematically, the difference between good and poor wear surfaces. Appendix B explains the grinding procedure in more detail. Figure 7 shows an actual coating surface after diamond grinding. It is clear from this figure that the soft phases are present at the coating surface from the "speckled" appearance of the coating.

CHAPTER IV - APPARATUS AND PROCEDURES

TEST APPARATUS

The pin-on-disk tribometer is a well known, widely used friction and wear tester based on the flat sliding against a round geometry (fig. 8). A hemispherically tipped pin is loaded against a rotating disk. The disk surface, the pin tip or both are coated with the materials to be tested. The pin is held stationary by a torque arm. The drag force or friction force on the arm is measured by a strain gauge. The friction coefficient is defined as the friction force divided by the normal applied load on the pin.

Wear of both the pin and the disk are measured to give an indication of the wear resistance of the sliding couple. As the pin wears, a round wear scar develops on its tip and a circular wear track or groove is worn into the disk wear surface. Rider or pin wear is determined by measuring the size of the round wear scar by photomicroscopy and calculating the wear volume from geometric considerations. Appendix C shows the derivation of the pin wear volume calculations. Disk wear is determined by taking a surface profile across the wear track perpendicular to the sliding direction, calculating the cross section area and multiplying by the average track circumference.

Advantages of the Pin-on-disk Tribometer

The pin-on-disk tribometer has several advantages over other wear test setups. Test conditions are easily varied to simulate many conditions found in actual wear/friction applications such as sliding velocity, temperature, atmosphere, load, and counterface wear materials. Because the pin is hemispherically tipped the pin-on-disk geometry is insensitive to misalignment of the pin and disk specimens. The wear disks and pins are simple to fabricate and the coatings are easily applied to disks. Since most pin-on-disk wear testers can be run at high speeds, accelerated wear data can be taken. The pin-on-disk wear tester is a good apparatus to use to screen materials for further study.

Disadvantages of the Pin-on-disk Tribometer

The pin-on-disk tribometer also has several disadvantages. The sliding geometry, though simple, is not realistic; few machines contain balls loaded in sliding contact against flat surfaces. The contact pressure between a ball or pin and a flat is very high during initial sliding but as wear of the pin progresses and the contact area increases, the contact pressure, an important tribological factor, decreases. The pin-on-disk apparatus alone is only a screening tool and is not a good predictor of future wear life applications. Other more realistic apparatus such as true bearing rigs must be used to further study materials that perform well on the pin-on-disk tribometer.

Test Materials

The specific coatings have been fully described in Chapter II. In this section the wear specimens and details of the spraying procedure are presented.

The coatings are plasma sprayed onto high temperature nickel alloy disks 6.35 cm in diameter and 1.27 cm thick. The disk material composition is given in table IV. The disks are first sandblasted, then a thin bond coat (0.0076 cm) of nickel-chromium powder (80 wt % Ni, 20 wt % Cr) is plasma sprayed onto the roughened surface. The coating mixture is plasma sprayed over the bond coat to a thickness of about 0.038 cm. The coating is then diamond ground to give a total coating thickness (bond coat and lubricant coat) of 0.025 cm. The diamond grinding procedure is outlined in appendix B.

Wear Pins

A number of counterface materials are chosen for evaluation of their sliding behavior against the metal-bonded chromium carbide coatings. The pin materials are chosen because of their thermal and chemical stability and strength at elevated temperatures. They also have to be practical materials for use as engine components, one of the proposed coating system applications. The materials chosen are: a precipitation hardened nickel chromium alloy A; two stainless steels, alloys B and C; a hardened cobalt alloy C; and the PS200 coating on alloy B. Table V gives the Rockwell hardness and the nominal compositions of these materials. The wear pins are hemispherically tipped with a radius of 0.476 cm and are 2 cm long.

Test Apparatus

A pin-on-disk type of apparatus (fig. 8) was used in this study. A hemispherically tipped pin is loaded against a disk by means of dead weights. Friction force is continuously measured by means of a temperature compensated strain gauge bridge. Generally, only the disk is coated, but the pin or both specimens may be coated. The pin generates a 51 mm diameter wear track on the disk. Sliding is unidirectional and the velocity is 2.7 m/s. The specimens are heated by a low frequency induction heater coil located circumferentially around the disk. The surface temperature of the disk is monitored with an infrared pyrometer capable of measuring temperatures from 100 to 1400 °C ±5 percent. Disk surface temperature is measured on the disk wear track 90 deg ahead of the sliding contact.

Test Procedure

Prior to each set of tests, the disks are heated in a vacuum oven at 150 °C for 3 hr to remove any volatile residue remaining from the finishing operation and subsequent handling. Both the pin and the disk are then cleaned with ethyl alcohol, scrubbed with levigated alumina and then rinsed with distilled water and dried.

Usually, the test duration is 1 hr at each of three temperatures, 25, 350, and 760 °C. Rider wear is measured every 20 min by removing the pin and measuring the wear scar diameter on the hemispherical surface from which the wear volume can be calculated. Locating dowels allow accurate relocation of the test pin.

Disk wear is measured after each hour by recording a surface profile of the wear track, computing the area of removed/displaced coating, and multiplying by the average circumference of the wear track to obtain the wear volume.

The atmosphere of the test chamber is hydrogen or helium; with purities of 99 and 99.997 percent respectively. Some tests are run in moist air. The moist air is supplied from dried, filtered service air, routed through a deionized water filled bubble jar. The relative humidity of the test air is measured with an electronic humidity meter. The relative humidity of the air supplied to the test chamber is 35 percent at 25 °C throughout the tests. The gases are routed through a flow meter at a rate of 0.014 m^3/min. The volume of the test chamber is 0.002 m^3.

Initially, the chamber is purged with nitrogen for 10 min before introducing the test gas. The chamber is then thoroughly purged with the test gas before beginning the friction and wear experiments.

CHAPTER V - EXPERIMENTAL RESULTS AND DISCUSSION

The basic measurement parameters are the friction coefficient, μ, and the wear factor, k. The friction coefficient is defined as the friction or drag force divided by the normal load of the sliding contact. Mathematically, μ is defined as:

$$\mu = \frac{\text{(friction force)}}{\text{(normal load)}}$$

The relationship between friction force and the normal load is linear to a first order approximation. That is, μ is a constant parameter independent of the normal load. The goal of a lubricant is to reduce the friction coefficient thereby reducing energy losses and improving the overall efficiency of a device.

The second basic measurement parameter is the wear factor, K. K is a measure of wear that takes into account load, wear volume, and distance of sliding. Its significance is based upon the assumption that these factors affect a sliding couple linearly. Mathematically, k is defined as:

$$k = \frac{\text{(wear vol.)}}{\text{(load x dist. slid)}}$$

Appendix D gives a further explanation of the wear factor as well as some idea of how it relates to coating performance. In general, however, the lower the wear factor, the better the coating performance.

The error associated with the results presented in this section are outlined in appendix E. The following tests were performed using specimens from the same batch. Due to the high cost of specimen fabrication and testing, repeated tests were generally not performed. More recent work, however, indicates that reasonable error estimates for the data below, unless otherwise stated, are: ±10 percent for the friction coefficient and ±15 to 20 percent for the wear factors.

Pin Material Optimization Results (ref. 11)

Table VI gives the results obtained in the friction and wear experiments with various pin materials sliding on PS200. This coating had previously (ref. 4) shown promise as a backup lubricant for foil bearings. Therefore, it was used to select a single counterface material for the pin material optimization study. Based upon the results shown, alloy C, a hardenable cobalt-chromium alloy was selected as the optimum pin material. Alloy C is used to evaluate the various coating compositions in the composition optimization.

Table VII summarizes the results of the coating optimization study. the metal-bonded Cr_3C_2 formulation with no added lubricants (PS218) provided adequate wear resistance for the counterface material, but the coating wear factors were higher than with the formulated coatings. Friction coefficients with PS218 were very high and erratic and there was a strong tendency to transfer coating material to the surface of the counterface material. Eventually, this resulted in PS218 sliding against PS218, a situation where abrasive wear of the parent coating by hard particles lodged in the softer pin material occurs.

Although very useful for wear control in many applications, chromium carbide coatings have poor tribological performance without solid lubricant additives.

The lowest solid lubricant content was in PS203 and PS204 which contained a total of 15 wt % silver and fluorides. Friction coefficients were high, about 0.5, for both compositions. The results of these tests indicated that slightly varying the ratio of added lubricants had little or no effect on the tribological performance of the coating.

Friction coefficients for PS200 (80 wt % metal-bonded Cr_3C_2, 10 wt % Ag, 10 wt % eutectic) were typically 0.25 to 0.35 in helium and somewhat lower in hydrogen. Wear factors were also lower than those of previous coatings. PS212 and PS213 also contain 1:1 ratio amounts of added silver and eutectic. PS212 contains 15 wt % silver and 15 wt % eutectic and PS213 contains 20 wt % silver and 20 wt % eutectic. PS212 exhibited lower friction coefficients and lower wear factors than PS200. Friction coefficients with PS213 were about the same as PS212, 0.20 to 0.28 but coating wear was higher (see table VI). Therefore, for a 1:1 ratio of the two added lubricants, a total additive content of about 30 wt % appears to be near optimum for this coating system.

Two additional coating compositions were evaluated to check the validity of the "property addition principle." These coatings also helped determine whether both silver and eutectic were really needed in the coating to achieve satisfactory friction and wear performance over the desired temperature range. PS215 contains 30 wt % silver and no fluoride eutectic, while PS216 contains 30 wt % fluoride eutectic and no silver. PS215 exhibited a very erratic stick-slip behavior at 760 °C, and coating wear was high. Excessive transfer of silver to the pin occurred. At 350 °C, the same behavior occurred but in a less severe manner. At room temperature, sliding was smooth and steady friction coefficient of 0.23 was observed. This behavior indicates that silver is a good low temperature lubricant, but (except when used as a thin film) transfers excessively at elevated temperatures.

For PS216 (the composition containing eutectic but no silver) the friction coefficients are about 0.4. This is approximately one-third lower than the unformulated coating, PS218. However, the coating experienced heavy wear and transfer to the pin tip especially at lower temperatures. The results indicate that the addition of eutectic alone in the composition lowers the friction at all temperatures but increases the coating wear and transfer particularly at room temperature.

The tests of PS215 and PS216 do support the "property addition principle" in that neither coating performs well throughout the temperature range. It is only when both lubricants are present, such as in PS212, that the coating performs uniformly well.

Discussion of Coating Optimization Results

The chromium carbide coating system lubricates best when combined with both silver and the eutectic. In fact, the friction and wear properties of the coating are substantially improved with the addition of silver and eutectic up to an additive content of 30 percent. The mechanism for this behavior appears to be the following: when a counterface material is slid against the unmodified coating (PS218), some carbide particles adhere to the counterface surface. When carbide transfer occurs, the sliding becomes one of transferred chromium carbide particles sliding against the parent coating. The pin then abrasively wears the coating. On the other hand, when silver and the eutectic are added to the coating composition, the soft lubricants tend to form a lubricating film that has the effect of preventing carbide transfer. The friction and wear characteristics of the composite coating are continuously improved with the addition of solid lubricant until the concentration of the metal-bonded carbide is insufficient to form a continuous network, thus weakening the coating. This weakening leads to plowing of the lubricants by the counterface material tending to increase friction and coating wear. The data indicates that the matrix breakdown begins at a metal-bonded chromium carbide content of 60 wt %.

Interestingly, the compositions that were lacking in one lubricant or another, PS215 and PS216, behaved very much like the unmodified coating. They both exhibited excessive coating to pin transfer and coating wear was generally high. It is only when both lubricants are present that an effective lubricating film forms on the wear surface.

EDS x-ray analyses of the wear specimens verify that selective transfer of the coating components to the rider does occur. For the unmodified coating (PS218), the carbide transfers and embeds into the riders more predominantly than the nickel-cobalt binder metal. Figure 9 shows the relative concentrations of chromium, nickel, and aluminum outside and on the wear scar. The coating transfer to the pin results in a chromium carbide enriched surface film on the pin which further wears the disk coating. A buildup of the soft phase materials, namely the nickel and the aluminum, occurs at the sliding inlet. This indicates that only the harder material is retained on the pin wear surface while the softer binder material characteristically accumulates at the inlet to the sliding contact.

On the other hand, in a coating containing silver and the eutectic the opposite occurs; the soft phase materials transfer to the pin while the carbide transfer is actually blocked. This effect is illustrated with PS212 (15 wt % silver and 15 wt % eutectic) in figure 10. Clearly, this situation is beneficial to lubrication as the soft lubricants provide a lubricative rather than an abrasive film between the sliding materials.

Both the silver and the eutectic act synergystically to improve the lubrication properties of the coating. Having only one of the two in the coating does not prevent abrasive wear of the coating and the counterface material. Also, each lubricant alone can only lubricate over a relatively narrow temperature range. When both lubricants are present in the coating, the temperature range in which the system can lubricate widens to include the temperature ranges of both the silver and the eutectic.

Atmospheric Effect on Tribological Properties (ref. 12)

Early in the program it was discovered that the friction and wear data of this coating system is greatly influenced by the test atmosphere. The coating performed better in hydrogen, a reducing atmosphere, than in helium, an inert atmosphere, and better in helium than in air, an oxidizing environment. Further tests were performed with PS200 (10 wt % each of silver and eutectic) to study this phenomenon.

The data presented in this section are from specimens from two different batches. At least one specimen from each batch was tested in one atmosphere. Since repeated measurements for each specimen were taken, an error estimate based upon the data scatter can be made. The error estimates are reported along with the average data values and represent one standard deviation of the data points. These errors compare well with the error analysis given in appendix E.

Experimental Results of the Atmospheric Effects Study

The results of the friction and wear experiments are summarized in table VIII and shown graphically in figs. 11 to 13. The data support previous results which indicate that the test atmosphere does significantly affect the friction and wear behavior of the coating. Tests in hydrogen given the lowest friction and wear results. Friction coefficients are generally 0.23±0.05 and coating wear factors (k) are low 6.4×10^{-10} $cm^3/(cm\text{-}kg)$. See appendix B for an explanation of the wear factor k. In helium the friction coefficients are 25 percent higher, that is, 0.29±0.03, and the coating wear factor increases by 50 percent. Pin wear follows the same trend as the coating wear. In general then, the friction and wear of the coating and counterface material increase as the test atmosphere becomes less reducing in the following order: hydrogen → helium → air.

Discussion of the Atmospheric Effects Results

After the wear tests were completed, x-ray photoelectron spectroscopy (XPS) analysis of the coating specimens was performed to determine the phases and compounds present on the wear surface. The XPS-analysis verified the presence of the constituents of the coating and also indicated that no impurities were added to the coating during the preparation process.

As previously discussed, friction and wear are the lowest in hydrogen, higher in helium, and highest in air. X-ray diffraction analyses provided a clue for a plausible explanation of this trend.

A comparison of x-ray diffraction peak intensities (peak heights) for coatings tested to 760 °C in the three atmospheres showed that only the chromic oxide level was affected by the test atmosphere. The relative chromium oxide concentration levels were approximated from the intensities of the diffraction peak for the (110) plane of the chromic oxide crystal structure with no correction for adsorption or fluorescence. The relative chromic oxide levels were obtained simply by normalizing the peak heights relative to the air atmosphere case.

As would be expected, the relative concentration level of chromic oxide on the wear tracks is highest for specimens run in air and lowest for specimens run in hydrogen. In spite of the high purity of the bottled test gases, chromic oxide is found on the wear tracks of specimens run in helium and in hydrogen due to residual oxygen and possibly water vapor present in the test chamber.

Figure 14 is a graph of the average friction coefficient versus the relative chromic oxide level normalized to the chromic oxide level in air. The data points are limited in number, but the trend indicates that there is a direct relationship between the friction coefficient and the level of chromic oxide present at the sliding interface for this coating system.

Chromic oxide is a hard, refractory compound that is a good anti-wear material when applied as a smooth, adherent coating (ref. 6). In this instance however, the chromic oxide that forms on the plasma sprayed coating apparently acts as an abrasive component in the sliding contact, thereby increasing friction and wear.

To determine other factors influencing the friction and wear behavior of the coating, energy dispersive spectra (EDS) x-ray analyses of the rider wear scars were performed. These analyses indicated that the amount of silver transfer from the parent coating to the rider wear scar is much lower for specimens run in air than in helium or hydrogen. Previous studies indicate that silver transfer has a beneficial effect on the tribological performance of the coating. Thus the lower levels of silver transfer for specimens run in air may be inhibiting its lubricating function in these cases.

It is difficult to prove that the high levels of chromic oxide present on samples run in air, inhibit beneficial silver transfer. It is likely, however, that both high chromic oxide levels on the wear track and reduced silver transfer to the rider wear scar are significant factors contributing to higher friction and wear.

The effect of prefusing the eutectic is evident by comparing the friction and wear data in table IX. Friction coefficients are 15 to 20 percent lower, counterface wear is 20 to 30 percent lower and coating wear remains about the same for coatings prepared by this improvement processing method. They are also more uniform and easier to plasma spray. Therefore, prefusing the fluoride eutectic has been adopted as a standard part of the coating procedure.

CHAPTER VI - CONCLUSIONS

In general, the addition of the solid lubricants silver and fluoride eutectic to the metal-bonded chromium carbide coating does significantly improve its tribological characteristics. Also, the test atmosphere has a significant effect on the friction and wear characteristics of the coating system. The following specific conclusions from this work can be made:

1. A mechanism describing the effect of the lubricant additives on the coating system is: in the absence of the solid lubricant additives, chromium carbide particles transfer from the coating and embed into the surface of the softer counterface pin alloy. This leads to abrasive wear of the remaining parent coating. The presence of silver and BaF_2/CaF_2 additions in 1:1 ratio amounts are effective in reducing friction and wear. These additions formed lubricative films on the sliding surfaces which effectively inhibit transfer of carbide particles to the counterface material and prevent self-abrasion of the coating.

2. The best of the counterface alloys evaluated for these coatings is a hardenable cobalt alloy C. Favorable results were also obtained with a formulated coating sliding against itself.

3. The optimum results are obtained with alloy C sliding on a coating consisting of 70 wt % bonded chromium carbide and 15 wt % each of silver and BaF_2/CaF_2 eutectic (PS212). Friction coefficients are typically 0.2±0.05 and very low wear is observed from 25 to 760 °C.

4. The results of this study suggest that some of the compositions described may be valuable for coating sliding contact components in advanced heat engines. The results in hydrogen are especially applicable to the Stirling engine.

5. The friction and wear of a chromium carbide based coating (PS200) is affected by the atmosphere present during sliding. Friction and wear properties are better in inert or reducing atmospheres than in air.

6. The test atmosphere is one factor that controls the formation of chromic oxide which seems to have an adverse effect on the tribological properties of the coating and may be inhibiting beneficial silver transfer.

7. There may be a direct relationship between chromic oxide levels present on wear surfaces and the friction coefficient.

8. The test data indicate that coating behavior can be improved if the formation of chromic oxide can be reduced and if silver transfer from the parent coating to the pin can be enhanced.

APPENDIX A - THERMOCHEMICAL CALCULATIONS

The calculation of chemical reactivities between potential lubricant materials and expected operating environments is illustrated in this appendix (ref. 7). Equilibrium constants for presumed reactions are calculated at several temperatures to determine the relative stability of the proposed lubricant material. Small produce partial pressures (less than 10^{-4}) indicates that the material is stable under the environmental conditions being considered. The following are calculations of the chemical reactivity between CaF_2 and hydrogen at 760 °C.

The presumed reaction is as follows:

$$1/2\ CaF_2 + 1/2\ H_2 = 1/2\ Ca + HF$$

hence, the expression for the equilibrium constant is:

$$K_{hydrogen} = \frac{P_{HF}}{(P_{hydrogen})^{1/2}}$$

where P_{HF} and $P_{hydrogen}$ represent the partial pressures of the hydrogen-fluoride and hydrogen gas respectively. A hydrogen partial pressure of 1 atm is assumed for these calculations.

The pressure of the hydrogen-fluorine gas is used to determine the relative reactivity of the CaF_2. By using tabulated values for the equilibrium constant, K, it is seen that the hydrogen-fluorine partial pressure is insignificant under these conditions:

$$K_{hydrogen} = 1.0\text{x}10^{-13} \text{ at } 760\ °\text{C}$$

$$P_{HF} = 10^{-13} \text{ atm}$$

No significant reaction. Therefore CaF_2 is stable in hydrogen at 760 °C. A similar calculation for CaF_2 in oxygen yields $P_{HF} = 10^{-27}$; no significant reactivity. Thus CaF_2 is stable in both oxygen and hydrogen at temperatures as high as 760 °C. Calculations for other materials and environments are done in a similar manner.

APPENDIX B - RECOMMENDED GRINDING PROCEDURE

(1) Use diamond grinding only

(2) Use water as lubricant - use no oil

(3) Initial grinding depth should be 0.0025 cm

(4) Final cuts should be 0.001 to 0.0015 cm

- Taking too deep a cut, i.e., 0.01 cm, will pluck softer phases (Ag and BaF_2/CaF_2) from surface.
- Taking too light a cut, i.e., less than 0.001 cm, will smear the metal-bonded chromium carbide. This will result in an "orange peel" type finish.

(5) Ground surface should be matte not glossy and have a speckled appearance representing the three separate phases.

APPENDIX C - PIN WEAR VOLUME CALCULATIONS

The volume of material worn from a hemispherical surface is a function of the hemispherical radius and the wear scar diameter. Mathematically, the volume equation is defined as follows:

$$V = 0.167\pi h(3a^2 + h^2)$$

where

a = wear scar radius

$h = r - (r^2 - a^2)^{1/2}$

r = radius of curvature

APPENDIX D - EXPLANATION OF WEAR FACTORS

The wear factor (K) used in this paper is a coefficient which relates the volume of material worn from a surface to the distance slid and the normal load at the contact. Mathematically, K is defined as:

$$k = \frac{V}{(S \times W)}$$

where

W = normal load at the sliding contact in kilograms

S = total distance slid in centimeters

V = volume of material worn away in cubic centimeters

The physical interpretation of the numeric value of the K factor is as follows:

$$K = \frac{10^{-8} \text{ cm}}{\text{cm-kg}} \text{ high wear}$$

$$K = \frac{10^{-9} \text{ to } 10^{-10} \text{ cm}^3}{\text{cm-kg}} \quad \text{moderate to low wear}$$

$$K = \frac{10^{-11} \text{ cm}^3}{\text{cm-kg}} \text{ very low wear}$$

Some authors prefer wear factor units of $mm^3/(N\text{-}m)$. Conversion to these units can be made to a close approximation by multiplying our units by 10^4.

APPENDIX E - ERROR ANALYSIS

The experimental error for the data presented in this thesis can be analyzed in two ways. One is the precision with which the measurements are made; an external error analysis. Another method is to define the error in a statistical manner based upon similar data sets; an internal error analysis.

The External Error Analysis

The external error is based upon the precision with which physical measurements such as friction coefficient, rider wear factor, and coating wear factor can be made (ref. 13).

The friction coefficient, μ, is defined as the friction force between two materials in relative motion divided by the normal force of the contact.

$$\mu = \frac{(\text{Friction force})}{(\text{Normal force})}$$

The external error associated with μ can arise form uncertainties in the magnitude of the applied load and inaccuracy in the measurement of the friction force. The friction force is measured with a calibrated strain gauge bridge. The uncertainty of this measurement system is approximately 3 percent. The load is applied by means of a dead weight system. Friction in the pulleys which transmit the applied load to the specimens and the load chamber feed-through system introduces an error of 5 percent. These uncertainty estimates are based upon calibration measurements of the test rig components. The overall error of the friction coefficient is estimated as the resultant of its parts:

$$\mu_{\text{external}} = ((3\ \text{percent})^2 + (5\ \text{percent})^2)^{1/2} = \pm 6\ \text{percent.}$$

The error of the K factor is dependent upon the inaccuracy in the measurement of the distance slid, load, and wear volume. The following are typical estimates for the errors:

Error of wear volume = ±11.5 percent

Error of distance slid = ±2 percent

Error of load = ±5 percent

$$K_{\text{rider external}} = ((11.5)^2 + (2)^2 + (5)^2)^{1/2} = \pm 12.7\ \text{percent.}$$

The coating wear factor equation has the same general form as the rider wear factor equation, however the uncertainty of the wear volume is slightly smaller, 10 percent. Thus the uncertainty of the coating wear factor is:

$$K_{\text{coating external}} = ((10)^2 + (2)^2 + (5)^2)^{1/2} = \pm 11.9\ \text{percent.}$$

The Internal Error Analysis

The internal error is based upon data scatter from comparable tests and is strongly dependent upon variations in specimen material properties. Since preparation and characterization of plasma-sprayed coatings involves many variables and is very difficult, significant variations in material properties can be exhibited between different batches of samples. Within the same batch or rather with specimens fabricated at the same time with identical raw materials the data scatter is reasonable and compares with the external error estimate. However, data from similar tests but different batches do not correlate well. Friction coefficients are reproducible within 20 percent but wear factors may vary as much as an order of magnitude.

Although the magnitudes of the data for similar specimens but from different batches do not always correlate well, the trends in the data do. For example, a PS212 coating specimen will generally display better tribological properties than a PS200 specimen from the same batch but may exhibit worse tribological properties than a PS200 specimen from a different batch. Similarly, coatings run in air will always show higher friction and wear than similar coatings from the same batch run in helium or hydrogen. Therefore, the trends in the data are repeatable both within the same batch of specimens and between different batches but the actual numbers may overlap significantly for data from different batches.

Because of the high complexity and expense of fabricating and testing the wear specimens, the sample number of identical tests within the same batch is necessarily small and a meaningful statistical analysis of the data is not usually possible. A compromise of both the external and internal error estimates must be made when analyzing this tribological data.

The following overall error estimate is chosen which most accurately describes data from specimens from the same batch:

Error in μ = ±6 percent

Error in K_{rider} = ±12.7 percent

Error in $K_{coating}$ = ±11.9 percent

and when comparing data from different batches:

Error in μ = ±20 percent

Error in K_{rider} = within an order of magnitude

Error in $K_{coating}$ = within an order of magnitude

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TABLE I. - COMPOSITION AND IDENTIFICATION NUMBER OF COATINGS EVALUATED

Composition	Wt %		
Identification number	Bonded Cr_3C_2	Silver	Eutectic
PS200	80	10	10
PS203	85	5	10
PS204	85	10	5
PS212	70	15	15
PS213	60	20	20
PS215	70	30	0
PS216	70	0	30
PS218	100	0	0

TABLE II. - COMPOSITION OF THE THREE MAJOR COATING COMPONENTS

Component	Composition, wt %	Particle size
Bonded Chromium Carbide		
Ni Al Cr_3C_2 Co	28 2 58 12	-200 + 400 Mesh
Silver Metal		
Ag	100	-100 + 325
Eutectic		
BaF_2 CaF_2	62 38	-200 + 325

TABLE III. - TYPICAL PLASMA SPRAY PARAMETERS

Parameter	Material, value
Arc gas	Argon 1.4 m^3/hr
Powder carrier gas	Argon 0.4 m^3/hr
Coating powder flow rate	1 kg/hr
Amperage	450 to 475 A
Voltage	32 V
Gun to specimen distance	≈15 cm

TABLE IV. - THE NOMINAL WEIGHT PERCENT COMPOSITIONS OF THE SUBSTRATE MATERIALS

Pin material	59 Co, 30 Cr, 4 W, 2 Ni, 1 Fe, 1 C, 1.5 other
Disk material	70 Ni, 15 Cr, 7 Fe, 2.5 Ti 1 Al, 1 Mn, 1 Co, 2.5 other
NiCr	80 Ni, 20 Cr

TABLE V. - NOMIAL COMPOSITION AND ROCKWELL HARDNESS OF CANDIDATE PISTON RINGS MATERIALS

Pin material code	Pin material	Element wt %														Rockwell hardness
		Ni	Cr	Co	C	Fe	Al	Si	Ti	Mo	Mn	B	W	N	Cb	
Alloy A	Inconel X-750	70	16	1	0.1	7.5	1	----	2.5	----	1	---	--	----	---	R_c40
Alloy B	XF818	18	18	--	.2	54.6	--	0.3	---	7.5	.15	0.7	--	0.12	0.4	R_c18
Alloy C	Stellite 6B	2	30	59	1	1	--	.75	---	.75	1.25	---	4	----	---	R_c42
Alloy D	Nitronic 60	8	18	--	.1	61.8	--	4.0	---	----	.8	---	--	.12	---	R_c28

*Note: Compositions taken from manufacturer's data. Hardness values taken at room temperature.

TABLE VI. - SCREENING OF PIN MATERIALS AGAINST PS200 COATING

[Test conditions: 0.5 kg, load; 2.70 m/s, sliding velocity, 38.97 kPa, chamber pressure.]

Pin material	Temperature, °C	Friction coefficient, μ		Wear Pin wear factor, K, cm³/cm-kg		Wear Coating wear factor, K, cm³/cm-kg	
		He	H2	He	H2	He	H2
Alloy A	760	0.41	----	4×10^{-10}	-------	--------	-------
	350	.41	----	2×10^{-9}	-------	Average value 1.7×10^{-9}	-------
	25	.45	----	2×10^{-9}	-------		-------
Alloy D	760	.40	----	4×10^{-10}	-------	Average value 1.6×10^{-9}	-------
	350	.46	----	3×10^{-10}	-------		-------
	25	.45	----	2×10^{-10}	-------		-------
Alloy B	760	.40	----	6×10^{-10}	-------	Average value 8.6×10^{-9}	-------
	350	.30	----	3×10^{-10}	-------		-------
	25	.30	----	2×10^{-10}	-------		-------
PS200	760	.29	----	2×10^{-10}	-------	Too small to measure	-------
	350	.28	----	4×10^{-10}	-------		-------
	25	.31	----	6×10^{-10}	-------		-------
Alloy C	760	.35	0.20	7×10^{-11}	5×10^{-12}	9.2×10^{-10}	9×10^{-10}
	350	.25	.25	2×10^{-11}	1×10^{-11}	8.2×10^{-11}	6×10^{-10}
	25	.38	.24	5×10^{-11}	2×10^{-11}	1.7×10^{-9}	2×10^{-10}

TABLE VII. - FRICTION AND WEAR SUMMARY FOR VARIOUS COATINGS AGAINST ALLOY C IN HELIUM AND HYDROGEN

[Test conditions: 0.5 kg, load; 2.7 m/s, sliding velocity; and 38.97 kPa, chamber pressure.]

Coating, PS number	Atmosphere	Temperature, °C	Average, μ	Pin wear factor, K cm^3/cm-kg	Coating wear factor, K cm^3/cm-kg
PS200 Cr_3C_2-Ag-Eut. (80-10-10)	He	760	0.35	7×10^{-11}	9.2×10^{-10}
		350	.25	2×10^{-11}	8.2×10^{-11}
		25	.38	5×10^{-11}	1.7×10^{-9}
PS203 (85-5-10)		760	.50	1.5×10^{-10}	Average value
		350	.45	Not measurable	3.4×10^{-9}
		25	.47	7.5×10^{-10}	1.3×10^{-9}
PS204 (85-10-5)		760	.50	4.3×10^{-10}	1.0×10^{-9}
		350	.50	7×10^{-11}	1.1×10^{-10}
		25	.47	1×10^{-11}	1.1×10^{-10}
PS212 (70-15-15)		760	.26	4×10^{-10}	5.0×10^{-10}
		350	.20	6×10^{-10}	2.4×10^{-10}
		25	.21	5×10^{-11}	8×10^{-12}
PS213 (60-20-20)		760	.28	3×10^{-10}	6×10^{-10}
		350	.20	3×10^{-11}	4×10^{-10}
		25	.21	2×10^{-12}	2×10^{-10}
PS215 (70-0-30)		760	.35	Not measurable	1×10^{-8}
		350	.34	Not measurable	Erratic
		25	.23	4×10^{-11}	Erratic
PS216 (70-0-30)		760	.40	Not measurable	$8.\times10^{-9}$
		350	.42	Not measurable	2.4×10^{-9}
		25	.42	1×10^{-11}	1.2×10^{-8}
PS218 (100-0-0)		760	.60	7×10^{-11}	2×10^{-9}
		350	.50	2×10^{-12}	4×10^{-10}
		25	.55	1×10^{-12}	1.4×10^{-9}
PS218 (100-0-0)	H_2	760	.50	Not measurable coating transfer to rider surface	2.8×10^{-9}
		350	.48		1.2×10^{-9}
		25	.35		1.7×10^{-9}

TABLE VIII. - FRICTION AND WEAR SUMMARY OF PS200 SLIDING AGAINST COBALT ALLOY

[Test conditions: 4.9 N load, 2.7 m/s sliding velocity, 38.97 kPa chamber pressure.]

Test Atmosphere	Temperature, °C	Average friction coefficient, μ	Average rider k factor, $mm^3/(m\text{-}N)$	Average coating k factor, $mm^3/(m\text{-}N)$
H_2	760	0.18±0.05	$0.75\times10^{-7}\pm0.35$	$7.6\times10^{-6}\pm1.9$
H_2	350	.26±.06	$1.25\times10^{-7}\pm.35$	$4.5\times10^{-6}\pm2.1$
H_2	25	.26±.04	$2.0\times10^{-7}\pm.35$	$7.0\times10^{-6}\pm3.8$
Average value	---	.23±.03	$1.33\times10^{-7}\pm.35$	$6.4\times10^{-6}\pm1.6$
Helium	760	.28±.04	$5.62\times10^{-7}\pm2.4$	$8.7\times10^{-6}\pm.7$
Helium	350	.26±.03	$3.44\times10^{-7}\pm1.9$	$8.2\times10^{-6}\pm.5$
Helium	25	.32±.03	$4.17\times10^{-7}\pm1.2$	$1.5\times10^{-5}\pm.23$
Average value	---	.29±.03	$4.4\times10^{-7}\pm1.2$	$1.04\times10^{-5}\pm.4$
Air	760	.30±.03	$5.16\times10^{-6}\pm1.1$	$1.5\times10^{-5}\pm.2$
Air	350	.37±.04	$2.35\times10^{-6}\pm1.0$	$1.0\times10^{-5}\pm.2$
Air	25	.28±.03	$1.31\times10^{-6}\pm.8$	$2.1\times10^{-5}\pm.2$
Average value	---	.32±.05	$2.94\times10^{-6}\pm2$	$1.5\times10^{-5}\pm.5$

TABLE IX. - AVERAGE DATA FOR PS200 COATING WITH BOTH PREFUSED AND NONPREFUSED EUTECTIC

[Test conditions: Specimens run in hydrogen atmosphere, 0.5 kg load, 2.7 m/s sliding velocity, slid against hardened cobalt alloy. Values given are averages over temperature range.]

Powder preparation	Nonprefused fluoride eutectic	Prefused fluoride eutectic
Average friction coefficient	0.28±0.03	0.23±0.03
Average pin wear factor k, $cm^3/(kg\ cm)$	$1.5\times10^{-11}\pm0.3$	$1.2\times10^{-11}\pm0.2$
Average coating wear factor k, $cm^3/(kg\ cm)$	$6.5\times10^{-10}\pm0.7$	$6.3\times10^{-10}\pm0.5$

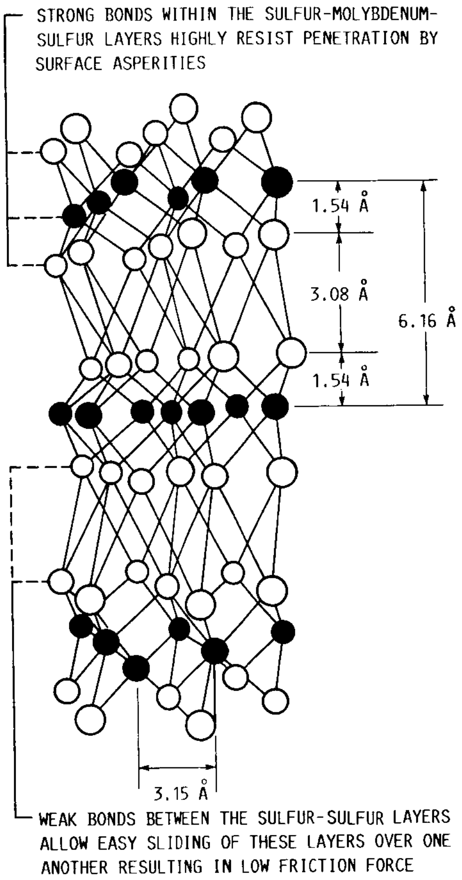

FIGURE 1. - CRYSTAL LATTICE STRUCTURE OF MoS_2.

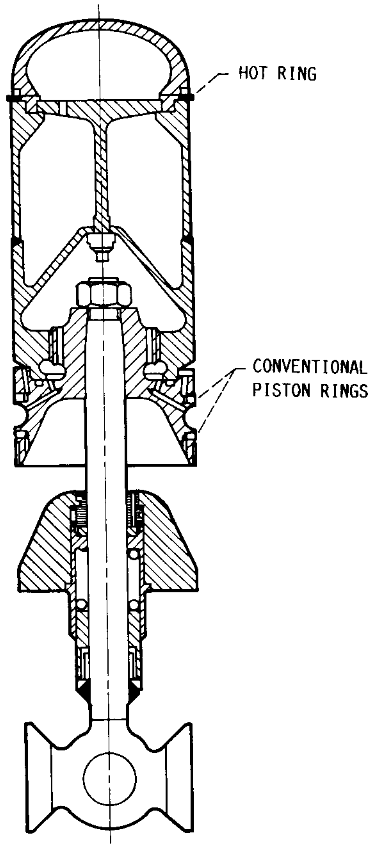

FIGURE 2. - STIRLING ENGINE PISTON SHOWING "HOT RING" WHERE TEMPERATURES REACH 760 °C. HIGH-TEMPERATURE LUBRICANT NEEDED FOR THIS APPLICATION.

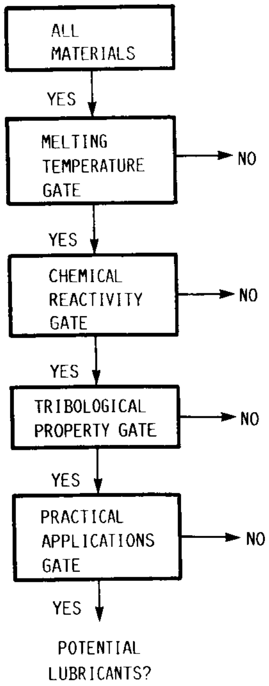

FIGURE 3. - FLOW CHART DIAGRAM OF THE DESIGN PROCESS.

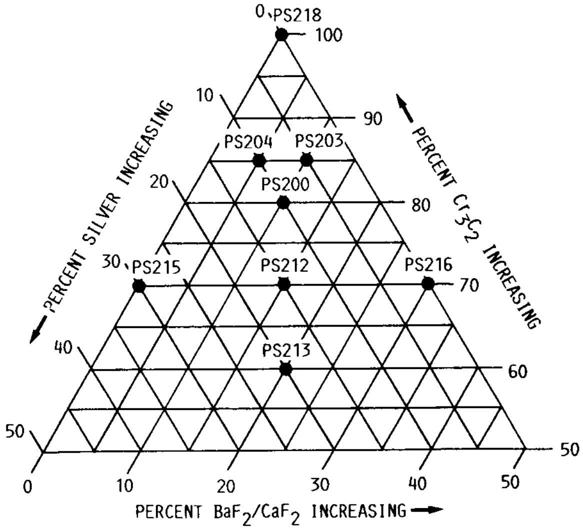

FIGURE 4. - PSEUDO-TERNARY DIAGRAM OF THE LUBRICANT SYSTEM.

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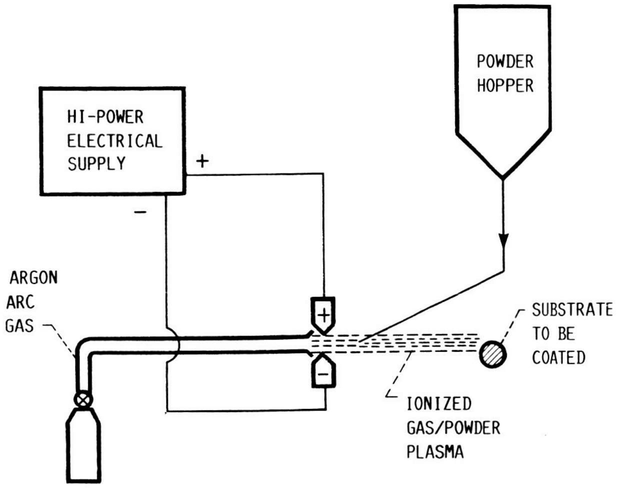
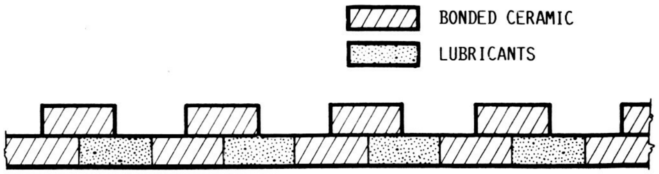
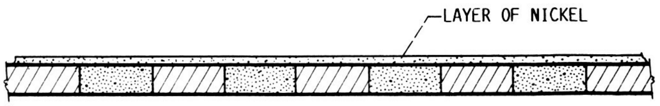


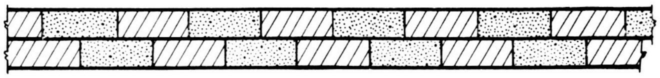
FIGURE 5. - SCHEMATIC OF THE PLASMA-SPRAY PROCESS.



GROUND COATING FROM WHICH SOFT LUBRICANTS HAVE BEEN "PLUCKED" FROM THE SURFACE. POOR SURFACE.



GROUND COATING IN WHICH NICKEL BOND MATERIAL HAS BEEN SMEARED OVER COVERING LUBRICANTS. POOR SURFACE.



CORRECTLY GROUND COATING. BOTH THE LUBRICANTS AND BONDED CERAMIC ARE PRESENT AT SURFACE.

FIGURE 6. - HYPOTHETICAL CROSS-SECTION ILLUSTRATION OF DIAMOND GROUND SURFACES.

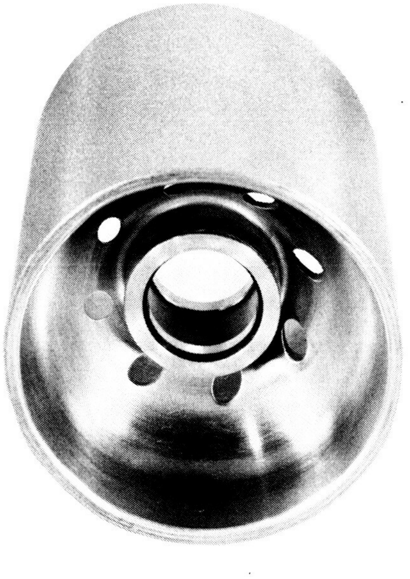


FIGURE 7. - DIAMOND GROUND PART.

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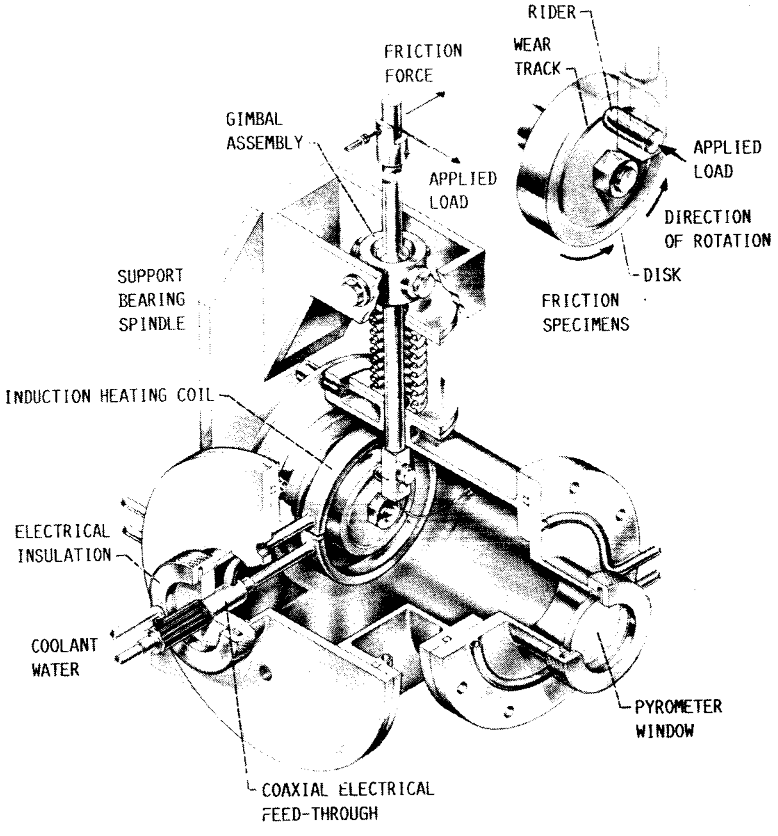

FIGURE 8. - HIGH-TEMPERATURE FRICTION APPARATUS.

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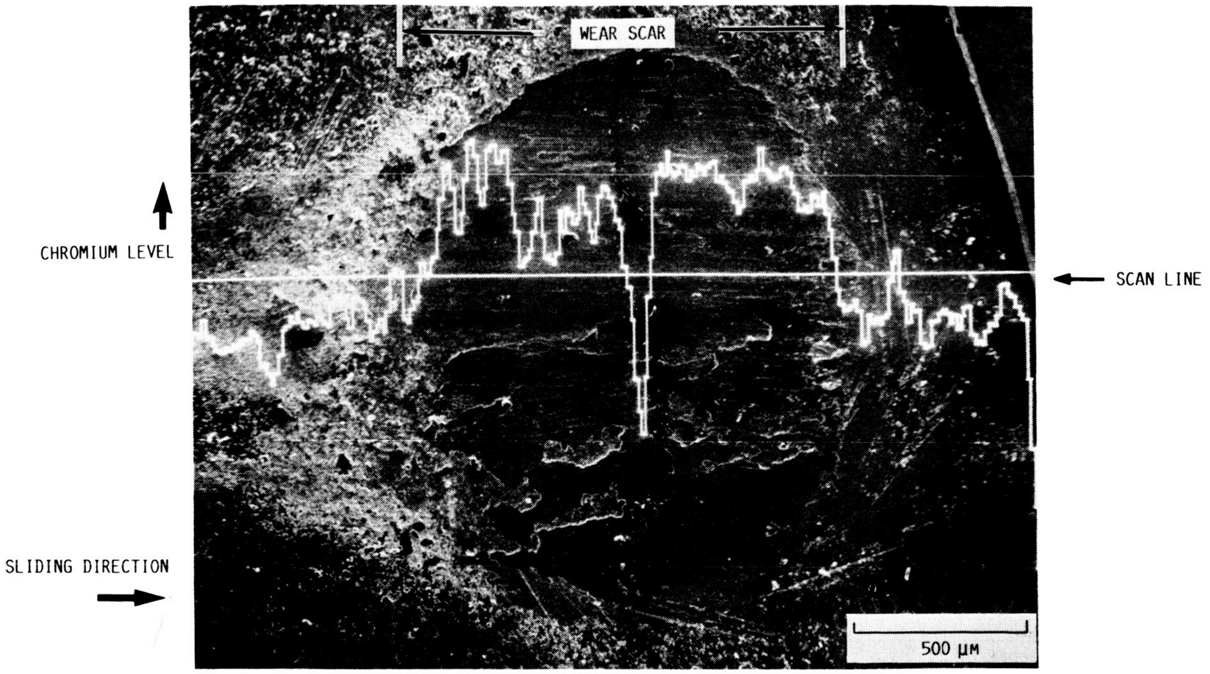
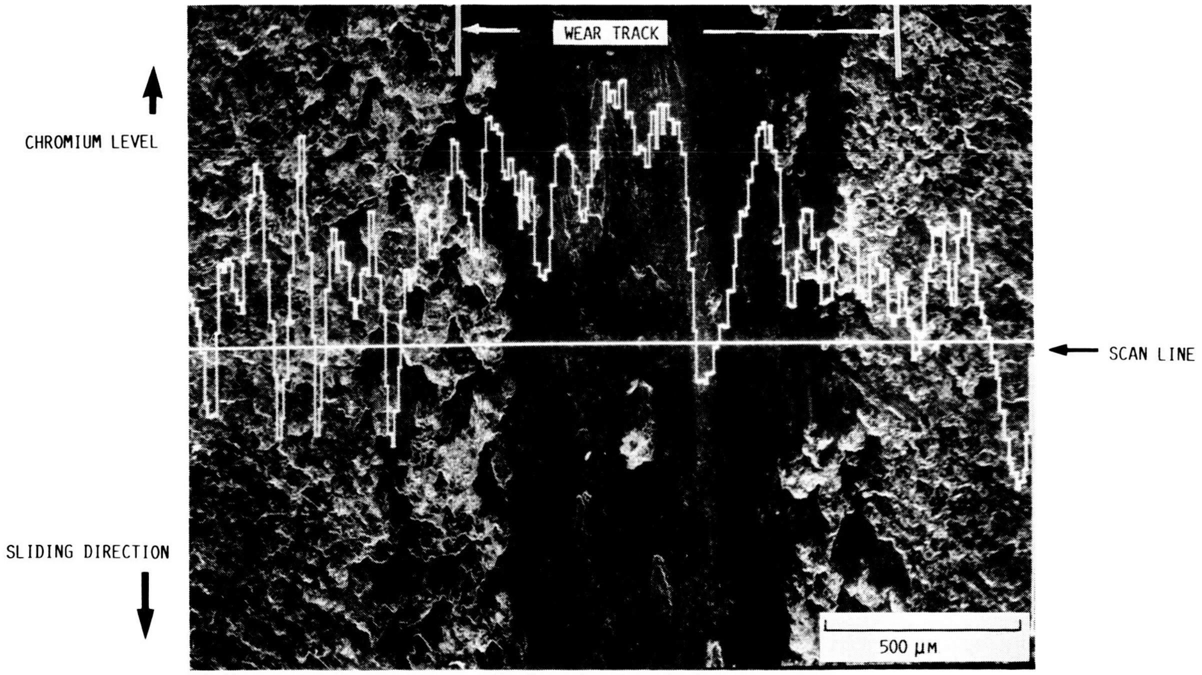
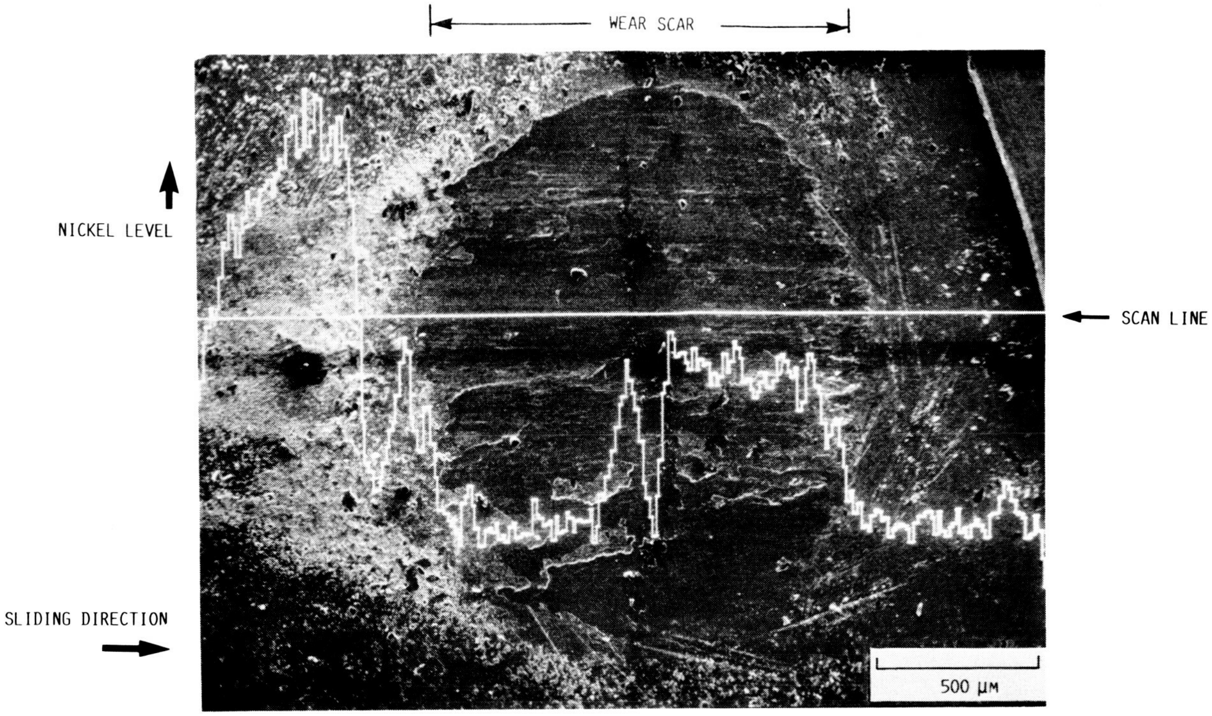


(A) CHROMIUM DISTRIBUTION IN VICINITY OF WEAR SCAR.

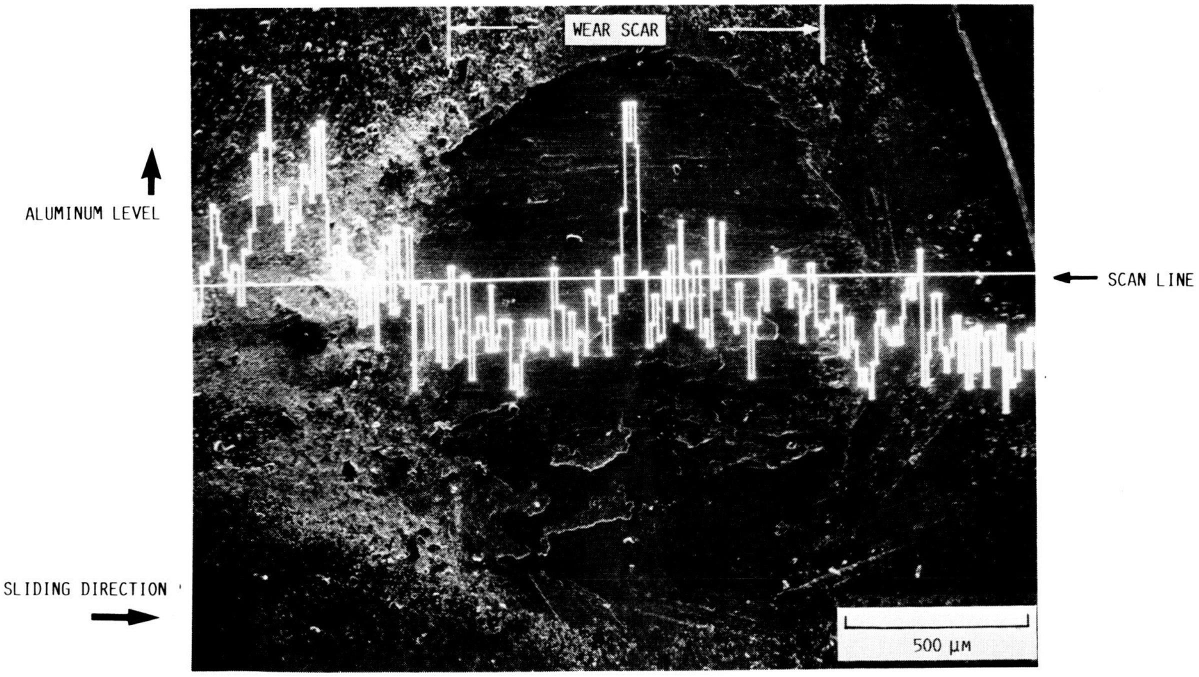


(B) CHROMIUM DISTRIBUTION IN VICINITY OF WEAR TRACK.

FIGURE 9. - EDS X-RAY DISTRIBUTIONS ON WEAR SPECIMENS: PS218 (WITHOUT SOLID LUBRICANT ADDITIVES) AFTER SLIDING AGAINST HARDENED COBALT ALLOY C. TEST CONDITIONS: HELIUM ATMOSPHERE, 0.5 KG LOAD, 2.7 M/SEC, SLID FOR 3 HR.



(C) NICKEL DISTRIBUTION IN VICINITY OF WEAR SCAR.



(D) ALUMINUM DISTRIBUTION IN VICINITY OF WEAR SCAR.

FIGURE 9. - CONCLUDED.

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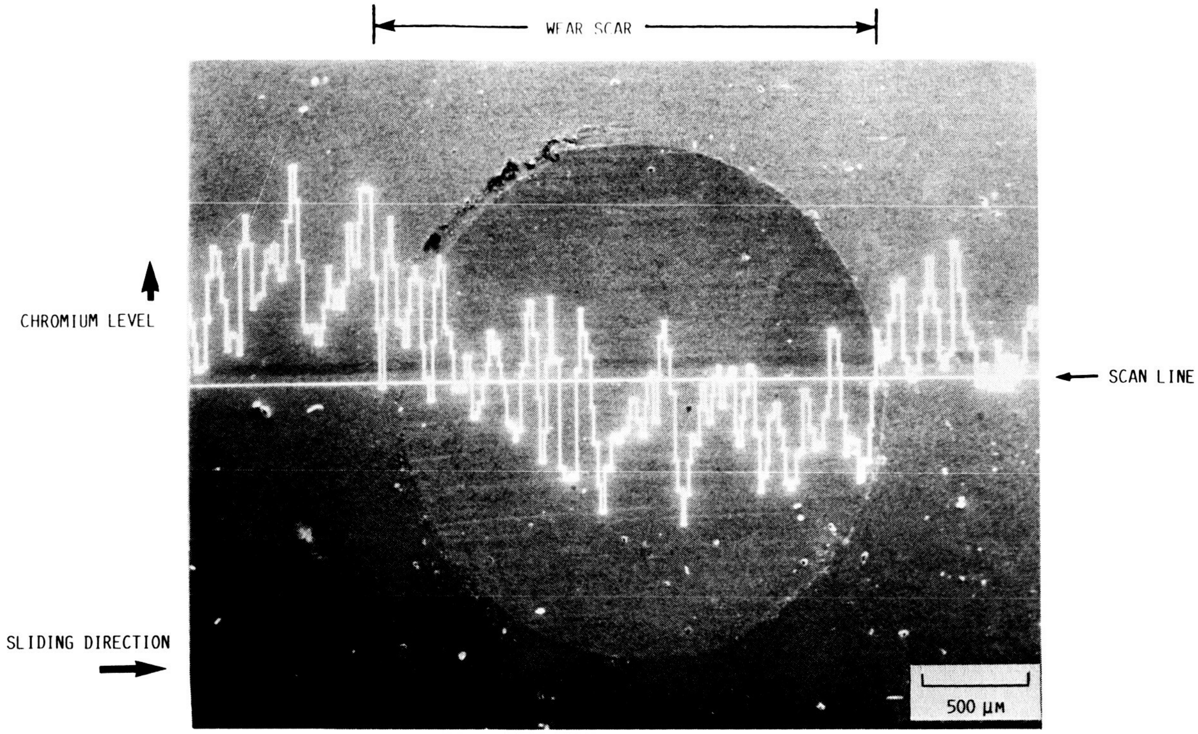
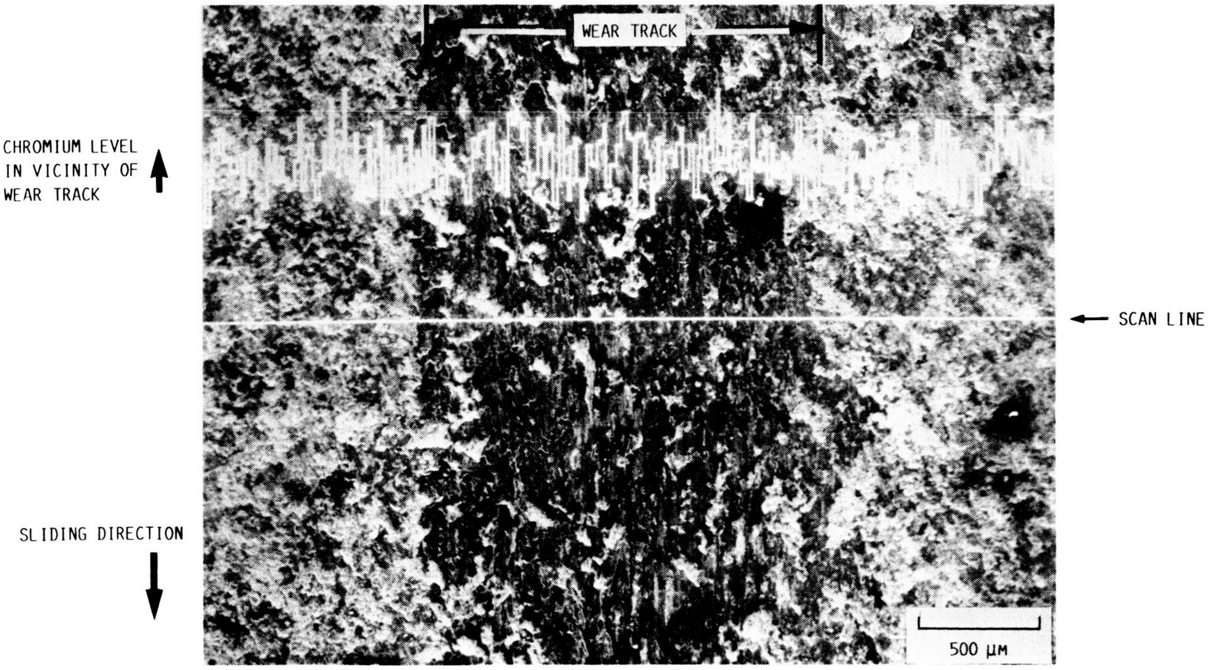
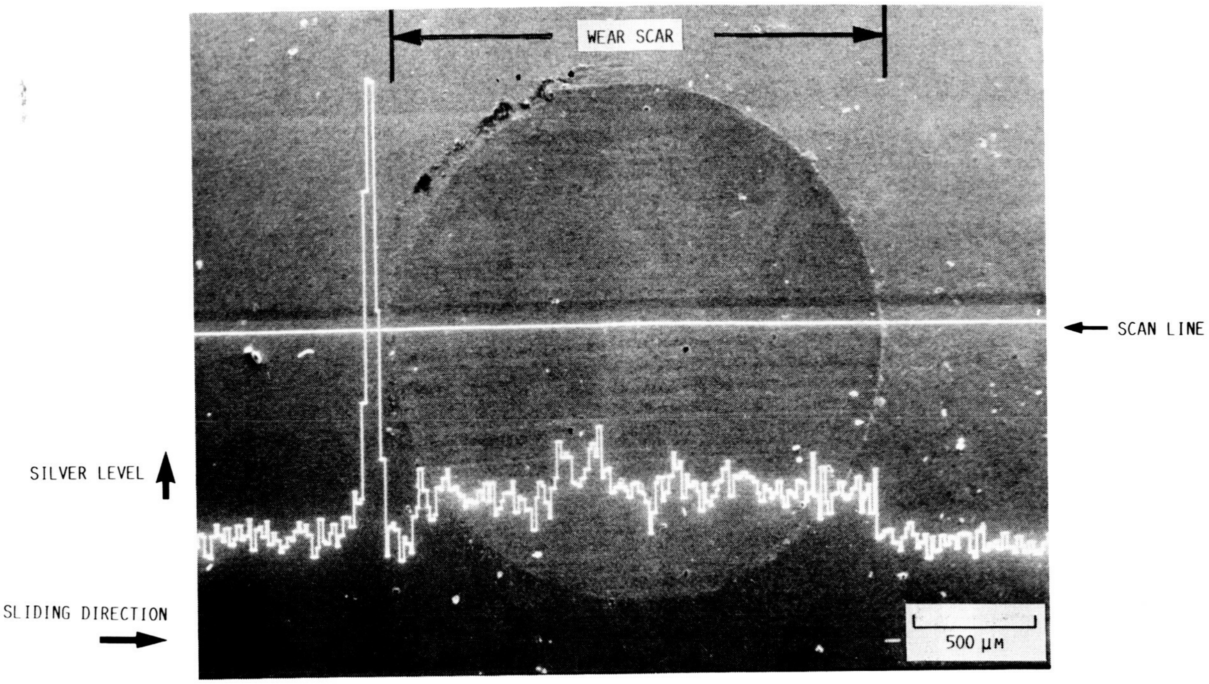


(A) CHROMIUM DISTRIBUTION IN VICINITY OF WEAR SCAR.

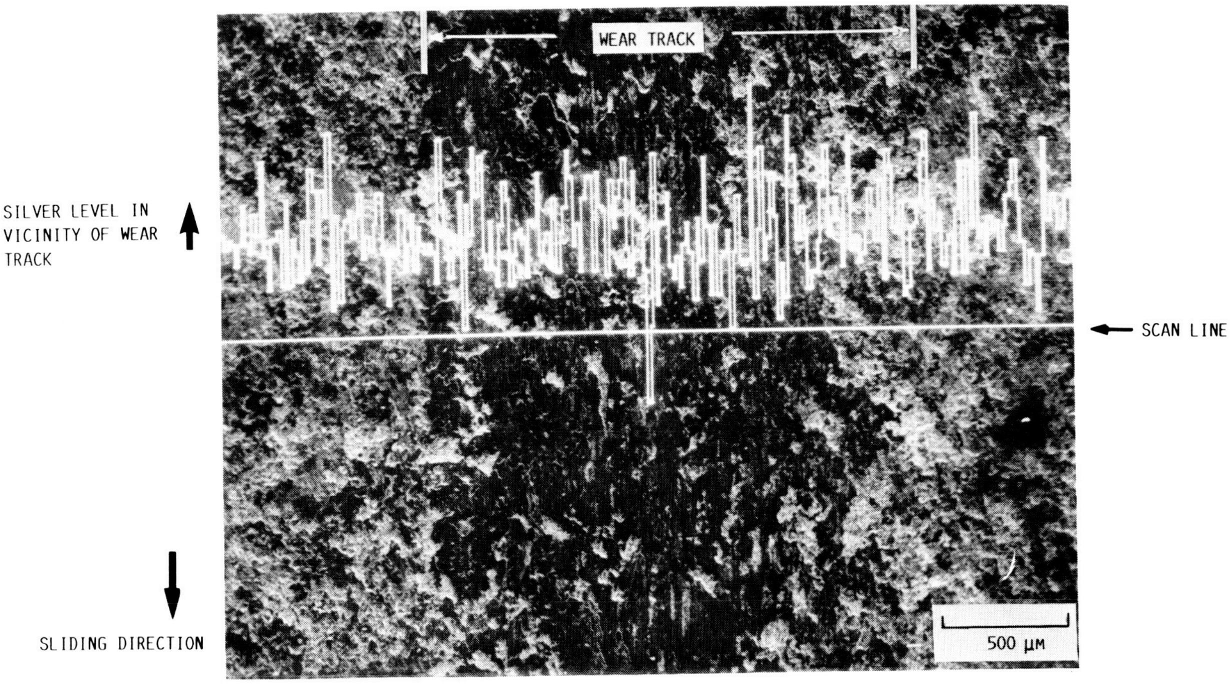


(B) CHROMIUM DISTRIBUTION IN VICINITY OF WEAR TRACK.

FIGURE 10. - EDS X-RAY DISTRIBUTIONS ON WEAR SPECIMENS: P212 (WITH SOLID LUBRICANT ADDITIVES) AFTER SLIDING AGAINST HARDENED COBALT ALLOY C. TEST CONDITIONS: HELIUM ATMOSPHERE, 0.5 KG LOAD, 2.7 M/SEC, SLID FOR 3 HR.



(C) SILVER DISTRIBUTION IN VICINITY OF WEAR SCAR.



(D) SILVER DISTRUBUTION IN VICINITY OF WEAR TRACK.

FIGURE 10. - CONTINUED.

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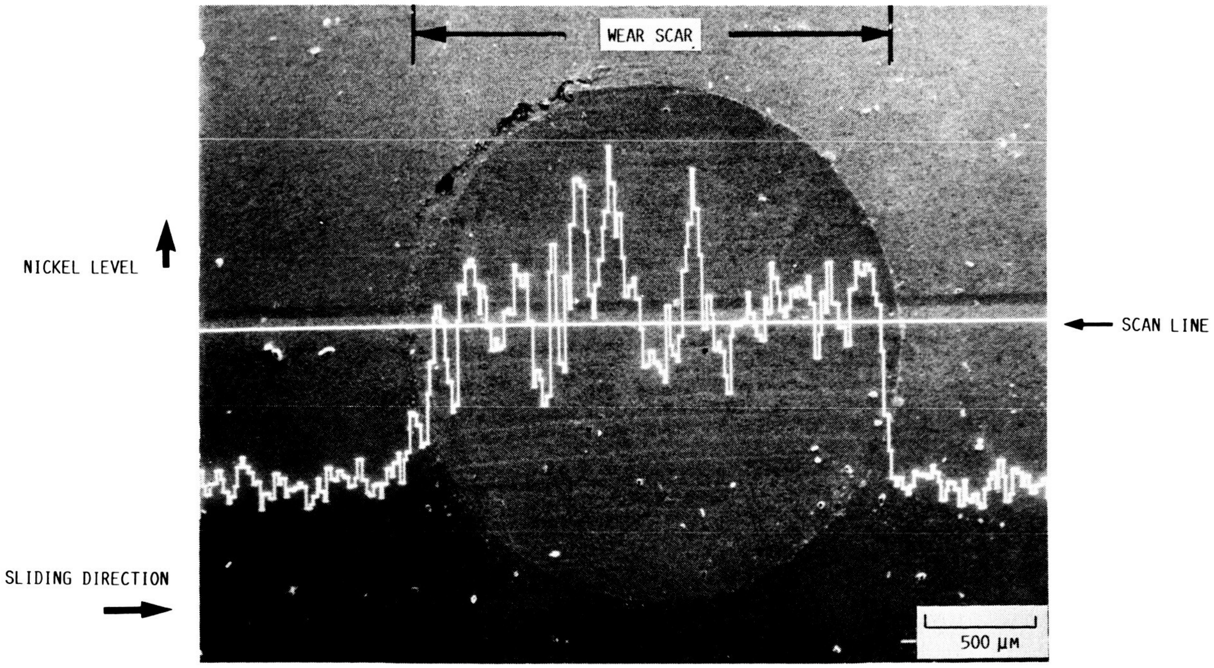
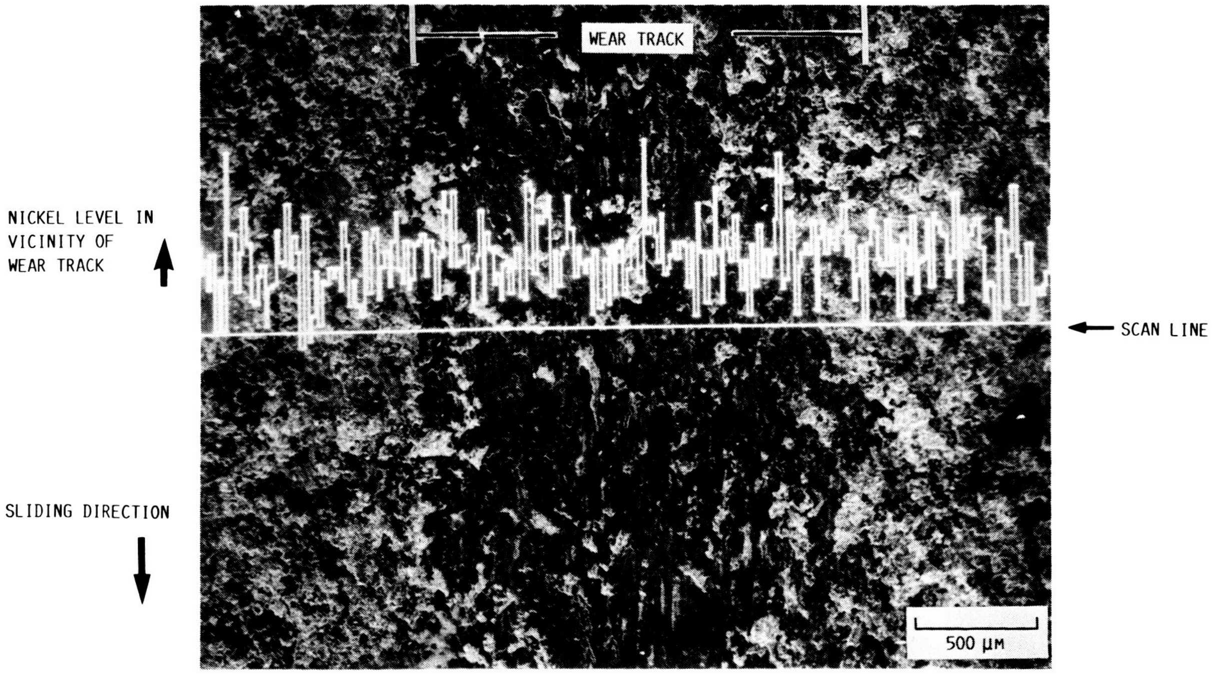


(E) NICKEL DISTRIBUTION IN VICINITY OF WEAR SCAR.



(F) NICKEL DISTRIBUTION IN VICINITY OF WEAR TRACK.

FIGURE 10. - CONCLUDED.

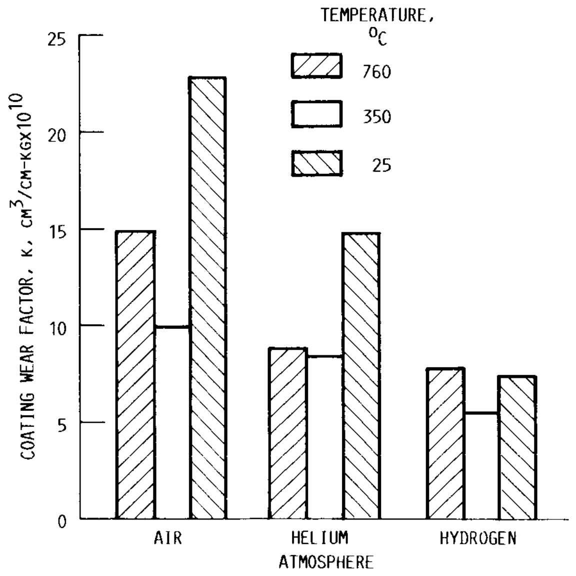


FIGURE 11. - DISK COATING WEAR FACTOR, K, FOR THE PS200 COATING IN VARIOUS ATMOSPHERES. TEST CONDITIONS: 2.7 M/S SLIDING VELOCITY, 38.97 kPa CHAMBER PRESSURE, 4.9 N NORMAL LOAD.

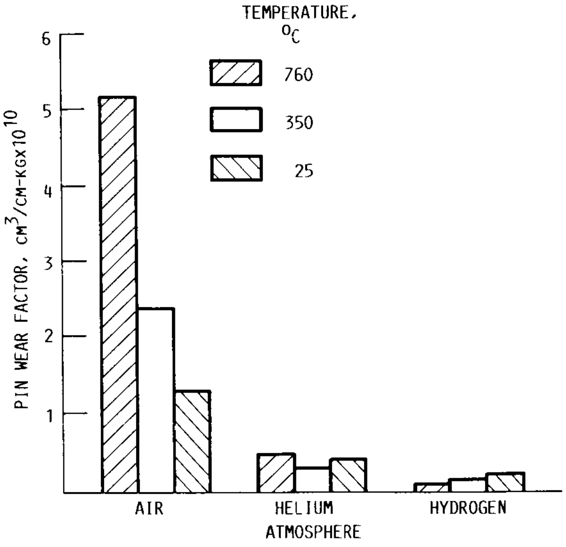


FIGURE 12. - PIN WEAR FACTOR, K, FOR THE HARDENED COBALT ALLOY TESTED AGAINST THE PS200 COATING IN VARIOUS TEST ATMOSPHERES. TEST CONDITIONS: 2.7 M/S SLIDING VELOCITY, 38.97 kPa CHAMBER PRESSURE, 4.9 N NORMAL LOAD.

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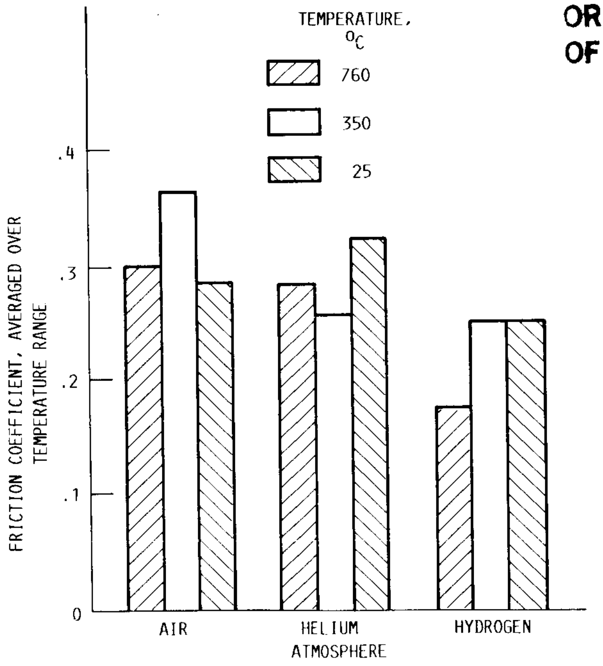

FIGURE 13. - FRICTION COEFFICIENT FOR PS200 SLIDING AGAINST HARDENED COBALT ALOY IN VARIOUS ATMOSPHERES. TEST CONDITIONS: 2.7 M/S SLIDING VELOCITY, 4.9 N LOAD, 38.97 kPa CHAMBER PRESSURE.

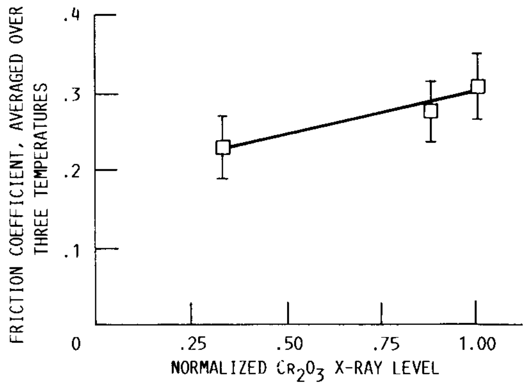

FIGURE 14. - AVERAGED FRICTION COEFFICIENT VERSUS RELATIVE WEAR TRACK Cr_2O_3 CONCENTRATION LEVEL NORMALIZED TO THE AIR CONCENTRATION LEVEL. TEST CONDITIONS: 2.7 M/S SLIDING VELOCITY, 4.9 N LOAD. ERROR BARS REPRESENT ONE STANDARD DEVIATION OF THE DATA POINTS.

NASA
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Space Administration

Report Documentation Page

1. Report No.
NASA CR-180808

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Experimental Evaluation of Chromium-Carbide-Based
Solid Lubricant Coatings for Use to 760 °C

5. Report Date
August 1987

6. Performing Organization Code

7. Author(s)
Christopher Della Corte

8. Performing Organization Report No.
E-3713

9. Performing Organization Name and Address
Case Western Reserve University
Cleveland, Ohio 44106

10. Work Unit No.
505-63-01

11. Contract or Grant No.
NCC 3-30

12. Sponsoring Agency Name and Address
U.S. Department of Energy
Office of Vehicle and Engine R&D
Washington, D.C. 20545

13. Type of Report and Period Covered
Contractor Report

14. Sponsoring Agency ~~Code~~ Report No.
DOE/NASA/0030-2

15. Supplementary Notes
Final Report. Prepared under Interagency Agreement DE-AI01-85CE50162. Project Manager, Harold E. Sliney, Materials Division, NASA Lewis Research Center, Cleveland, Ohio 44135. C. Della Corte, Case Western Reserve University and NASA Resident Research Associate at Lewis Research Center.

16. Abstract
This Master's Thesis describes a research program to further develop and investigate chromium carbide based self-lubricating coatings for use to 760 °C. A bonded chromium carbide was used as the "base stock" because of the known excellent wear resistance and the chemical stability of chromium carbide. "Additives" were silver and barium fluoride/calcium fluoride eutectic. The three coating components were blended in powder form, applied to stainless steel substrates by plasma-spraying and then diamond ground to the desired coating thickness. A variety of coating compositions was tested to determine the coating composition which gave optimum tribological results. Coatings were tested in air, helium, and hydrogen at temperatures from 25 to 760 °C. Several counterface materials were evaluated with the objective of discovering a satisfactory metal/coating sliding combination for potential applications, such as piston ring/cylinder liner couples for Stirling engines. In general, silver and fluoride additions to chromium carbide reduced the friction coefficient and increased the wear resistance relative to the unmodified coating. The lubricant "additives" acted synergistically in reducing friction and wear. Several coating compositions gave good results in hydrogen, helium, and air to 760 °C.

17. Key Words (Suggested by Author(s))
High temperature lubricant
Solid lubricants for heat engines

18. Distribution Statement
Unclassified - unlimited
STAR Category 27
DOE Category UC-96

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No of pages
40

22. Price*
A03

SA FORM 1626 OCT 86

*For sale by the National Technical Information Service, Springfield, Virginia 22161