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# Coatings for High-Temperature Bearings and Seals

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## SUMMARY

Research to develop high temperature tribological coatings is very relevant to the needs of numerous advanced technology systems. The attendees at this workshop are obviously aware of the need for high temperature self-lubricating coatings for the LHR diesel, the automative gas turbine, and the Stirling engine. Such coatings are also needed for aircraft engines and for aerodynamic control surface seals and bearings for supersonic and especially hypersonic aircraft. At Mach 3, aerodynamic heating becomes a serious factor and for the National Aerospace Plane (NASP), which will be designed for speeds up to about Mach 25, aerodynamic heating of the airframe will be enormous. The predicted thermal environment in the vicinity of the control surfaces, such as the elevons, involves temperatures of 2000 °C and higher. Of course, thermal protection systems including active cooling with the liquid hydrogen fuel are design options. However, increasing the temperature at which the control surface bearings and seals can operate, reduces weight and complexity. Examples of nonvehicular applications for high temperature tribological coatings included glass manufacturing and metal working.

Conventional solid lubricants such as graphite and molybdenum disulfide ($MoS_2$) are a class of materials with a layer lattice crystal structure which is ideal for the low shear strength associated with low friction. However, these lubricants have very limited high temperature capabilities. Both graphite and $MoS_2$ oxidize in air well below 500 °C. Therefore, it is necessary to creatively screen other classes of candidate materials for chemical and physical properties that are likely to afford the necessary combination of chemical stability and lubricity. One objective of this paper therefore, is to describe a method for the selection of likely candidate high temperature solid lubricants.

## MATERIAL SELECTION

Some material selection criteria are summarized in table 1. The first criterion is that of survivability in the chemical and thermal environment. Thermochemical calculations are useful for estimating chemical reactivity. Reactivity is estimated for the free energies of reaction ($\Delta F$) involved in the assumed reactions of the candidate materials with the environment and at the temperature of interest. Equilibrium constants ($k$) are then calculated from the free energies of reaction using the equation:

$$\log_{10}\left(\frac{1}{k}\right) = \frac{\Delta F}{2.3RT}$$

## TABLE I

Selection Criteria for Composite Lubricant Coatings

1. All Components: Must be Survivors

   Thermochemical stability in the chemical environment at all temperature of interest.
   Compatible thermal expansion properties.
   Adhesion to the substrate.

2. Solid Lubricants: High Degree of Plasticity

   Capable of extensive plastic deformation at low shear stresses.
   Soft: Hv Typically 10 to 50 kg/mm$^2$ at operating temperatures.

3. Wear Control Component: hard, Wear-Resistant, stable chemically and structurally.

A large positive value of $\Delta F$ equates to a small equilibrium constant which is a necessary condition for chemical stability of the reactants (in this case the candidate solid lubricant and the atmosphere). It follows therefore, that if a proposed decomposition reaction of a candidate solid lubricant with its surroundings has a large positive free energy of reaction (equivalent to a very small equilibrium constant), that material is likely to be stable under the assumed conditions.

This approach has some limitations that must be kept in mind. One limitation is that the calculations give no quantitative indication of chemical kinetics. Also, under some nonequilibrium conditions, as when a gaseous reaction product is continuously removed from the reaction site, even reactions with small equilibrium constants may occur at an appreciable rate, especially at high temperatures. Nevertheless, thermochemical calculations can be very helpful in the selection of materials especially when these limitations are kept in mind.

Hardness and ductility or plasticity are among the more important physical properties of solid lubricants. Properties that effective solid lubricants have in common are: (1) they are soft; (2) they have a high degree of plasticity. (The plasticity must be associated with a low yield strength in shear for lubricity, and preferably high elongation and good film coherance and continuity during sliding); and (3) they must exhibit adequate adhesion to the lubricated surfaces. (Obviously, no matter how desirable the other properties of a solid are, that material cannot lubricate if it is not retained at the sliding interface.)

We have used calcium fluoride, barium fluoride, and silver as solid lubricants in our high temperature coatings. Thermochemical calculations indicate that these materials should be chemically stable to high temperatures in air or in hydrogen and this has been experimentally verified. Their hardness-temperature characteristics are given in figure 1(a). Silver is very soft at room temperature with a hardness of about 30 kg/mm$^2$ and this continuously decreases to about 4 kg/mm$^2$ at 800 °C. Thin films of silver lubricate quite well at temperatures up to about 500 °C, but appear to have inadequate film strength to support to load at higher temperatures. The fluorides, on the other hand, are considerably harder than silver at the lower temperatures, but their hardness drops off rapidly with temperature and at about 400 °C, their hardnesses are 30 $kg/mm^2$ or less. Cracks occurred at the corners of the hardness indentations obtained at the lower temperatures on the fluorides samples, but completely ductile behavior was observed above about 200 °C. Brittle to ductile transition temperatures of about 400 °C have been reported for these fluorides (ref. 1). These materials are known to be strain rate sensitive (ref. 2) (at least at low strain rates), and this may be a factor in the apparently lower transition temperatures in the hardness tests. Fluoride coatings have been shown to be lubricious above 400 °C, but ineffective as lubricants at lower temperatures (ref. 3). Therefore, there is an apparent correlation of the brittle to ductile transition temperature with the friction transition temperature.

Since silver films are lubricative at the lower temperatures, and the fluorides discussed are lubricative at higher temperatures than silver, it is reasonable that a composite coating containing silver and the fluorides might be lubricious over a wide temperature range, and this has been shown many times to be the case (e.g., refs. 3 to 5).

## TRIBOLOGICAL PROPERTIES

### Fused Fluoride Coatings

Fused fluoride coatings were prepared by mixing fluoride powders and, in some cases silver powder, into a lacquer. The formulation was applied with a paint sprayer, then fused in an inert atmosphere furnace. The fused coatings were about 0.003 cm thick. The friction-temperature characteristics of coatings with and without silver are compared on figure 1(b). It is clear that the all-fluoride coatings were lubricious only above their brittle to ductile transition temperature, while those with silver were lubricious from room temperature to 800 °C.

The furnace-fused coatings require high temperature processing, which is detrimental to the heat treatment of some alloys. An alternative method is plasma spraying which only minimally heats the substrate. Plasma spraying can also be used to deposit combinations of materials which cannot be applied by the furnace fusion process.

### Plasma Sprayed Coatings

We have reported two series of plasma sprayed coatings containing fluoride solid lubricants: the PS100 and the PS200 series (e.g., refs. 6 and 7). The first series contains stable fluorides and silver with a nichrome binder; the second series contains the same lubricants and chromium carbide with a nickel alloy binder. The proportions of the components can be varied to optimize the coatings for various uses. In general, the PS100 series, which is softer, has been useful where a compliant, but nongalling coating is needed. An example of this type of component (fig. 2), is a compliant shaft seal which is a sometimes desirable alternative to an abradable seal in turbine engines.

When harder, more wear resistant coatings are needed, the PS200 series is preferred. The PS200 concept is summarized on figure 3. As the sketch indicates, the coating is a composite material with the lubricating solids distributed throughout a chromium carbide/nickel alloy matrix. A typical composition contains 10 percent each of silver and calcium fluoride/barium fluorides eutectic in the metal-bonded carbide matrix. The solid lubricant content can be optimized for a particular set of operating conditions. These coatings have reasonably constant friction coefficients over a large temperature range, similar to those shown on figure 2(b) for the fused fluoride coatings. The actual magnitude of the friction coefficient, although relatively constant with temperature, depends on coating composition and the atmosphere; and is typically 0.15 to 0.3.

## APPLICATION TEST RESULTS

Promising results have been obtained with PS200 as a back-up lubricant in compliant gas bearings, as a coating for high speed shaft seals, and as a cylinder liner in a Sterling engine test.

### Gas Bearings

Figure 4 is a gas bearing journal coated with PS200 and finished by diamond grinding. Start-stop tests of this journal in a foil bearing were conducted using the test apparatus shown in figure 5. The surface velocity and torque profiles during a typical start-stop cycle are given on figure 6. The higher torque at the beginning and end of each cycle occurs during sliding contact when the surface velocity is below the critical lift-off velocity for the bearing. The bearing was subjected to 5000 start-stops at 25 °C and another 5000 at 560 °C with no problems. In other similar tests, with PS200-coated journals, the same number of test cycles were completed with bearing temperatures up to 650 °C.

### High Speed Shaft Seals

PS200 has shown promise for use as a shaft seal material for turbine applications. At the very high speeds typical of such applications, friction coefficients as low as 0.1 and very low wear rates have been observed.

### Stirling Engine Cylinder Liner

PS200 was also evaluated in a Stirling engine test to evaluate the concept that improved fuel efficiency could be achieved in the Stirling engine if "hot piston rings" were used. The lubrication of the piston ring/cylinder contacts in the Stirling engine is a challenging high-temperatures tribological problem. Metal temperatures as high as 600 to 1000 °C occur near top dead center of the cylinder walls. The working fluid in the engine thermodynamic cycle is hydrogen. The lubricant coating, therefore, must not only provide low friction and wear, but also must be thermochemically stable in a strongly reducing hydrogen atmosphere.

In current designs of the Stirling engine, the piston rings are made of reinforced polytetrafluroethylene (PTFE). They are located in ring grooves near the bottom of the piston where the temperatures are relatively low and do not degrade the PTFE. This arrangement results in a long annular gap from the top of the piston to the piston ring. This gap is known as the "appendix gap" and it is the source of parasitic energy losses (ref. 8). It therefore would be desirable to minimize the appendix gap by locating the top ring in a groove near the top of the piston. A schematic of the ring locations in the baseline piston and in a piston with an added hot ring are shown in figure 7. It was determined by means of pin on disk tests that Stellite 6B is a good tribological material in sliding contact with PS200 in hot hydrogen.

A four cylinder automotive Stirling engine known as the Upgraded MOD I was used as the test engine. The engine was designed by Mechanical Technology Inc. (MTI) under a DOE contract managed by the Stirling engine Project Office at NASA Lewis Research Center. MTI modified the design by enlarging the cylinder bores to allow them to be coated with PS200 and by redesigning the pistons to allow them to be fitted with Stellite 6B "hot piston rings". The engine was tested for 22 hr at various speeds and a top ring reversal temperature of 700 °C. The results were compared to those obtained in baseline tests where the hot rings were removed and replaced with filler rings. This provided a direct comparison of an engine with and without a long appendix gap. Efficiency gain varied from 0 to 7 percent depending upon engine operating conditions. These gains were over and above any frictional losses introduced by the "hot rings." For example, figure 8 shows that at 5 Mpa mean operating pressure, no gain in engine efficiency was observed at 1000 rpm but up to a 7 percent gain was measured at 2000 and 4000 rpm. Over all test condition the efficiency gain averaged approximately 3 percent. Seal leakage measurements showed about a 30 percent reduction with the hot rings in place. In addition, cylinder wall temperature measurements indicated less cylinder heating in the appendix gap area. Figure 9 shows that this project moved forward from the selection of materials based upon their chemical and physical properties, through experimental research and development, to a successful engine test that verified computational analyses.

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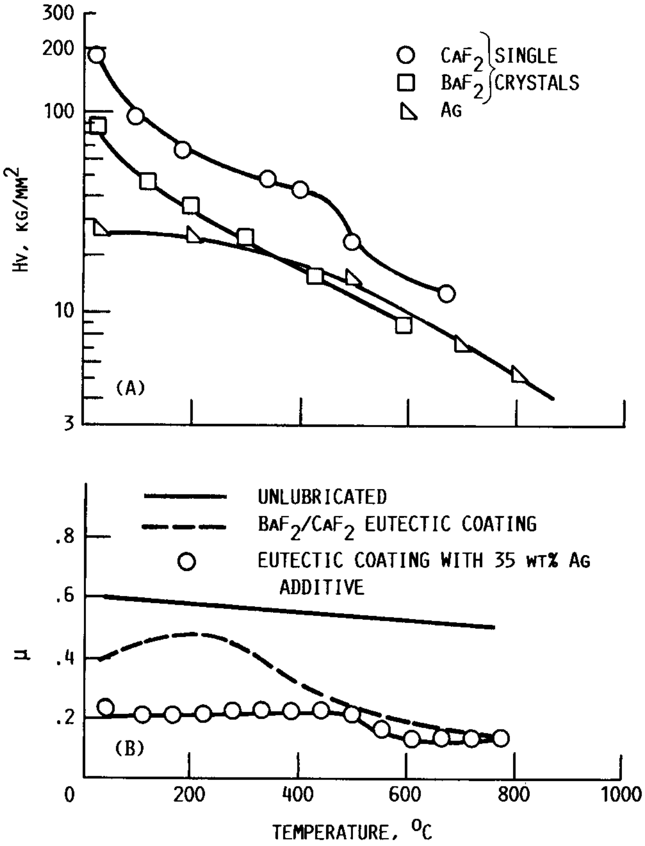


FIGURE 1. - EFFECT OF TEMPERATURE ON MICROHARDNESS AND FRICTION COEFFICIENTS OF COATING MATERIALS. FRICTION MEASURED FOR CAST INCONEL PINS SLIDING ON 0.04-MM THICK COATINGS FUSION-BONDED TO PRECIPITATION-HARDENED INCONEL X-750 DISKS IN AIR AT 2.3 M/S UNDER 500-GM LOAD, 4.8-MM PIN TIP RADIUS.

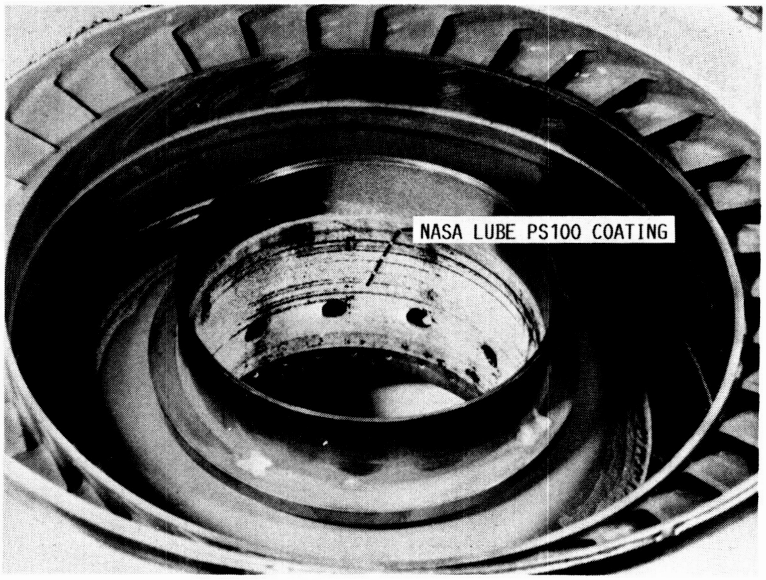
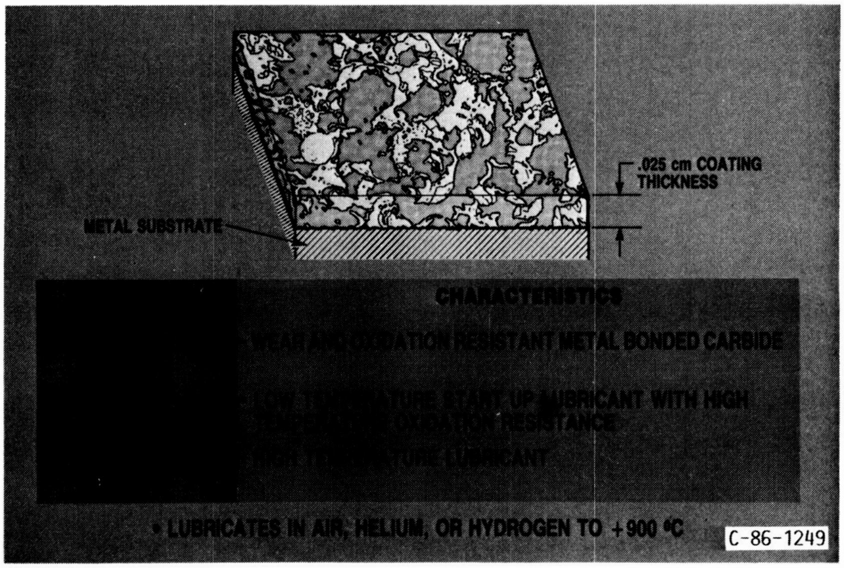


FIGURE 2. - COMPRESSOR/TURBINE SHAFT SEAL-OPERATORS AT 650 °C.



CHARACTERISTICS

WEAR AND OXIDATION RESISTANT METAL BONDED CARBIDE

LOW TEMPERATURE START UP LUBRICANT WITH HIGH TEMPERATURE OXIDATION RESISTANCE

HIGH TEMPERATURE LUBRICANT

- LUBRICATES IN AIR, HELIUM, OR HYDROGEN TO +900 °C

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FIGURE 3. - CONCEPT OF PS200-A PLASMA SPRAYED COMPOSITE, SOLID LUBRICANT COATING.

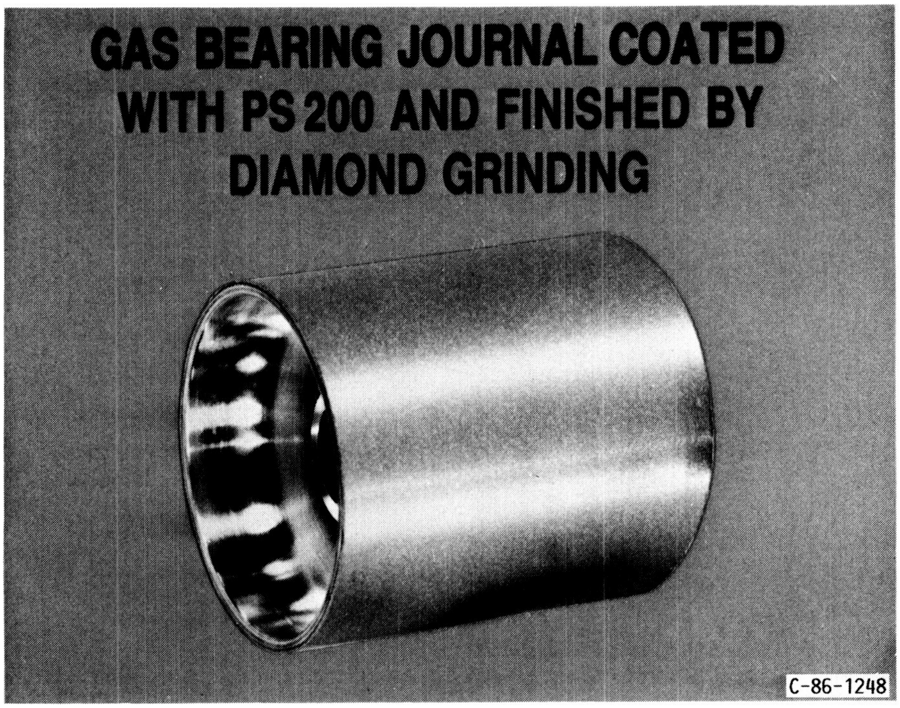

FIGURE 4. - A FLUID FILM BEARING APPLICATION.

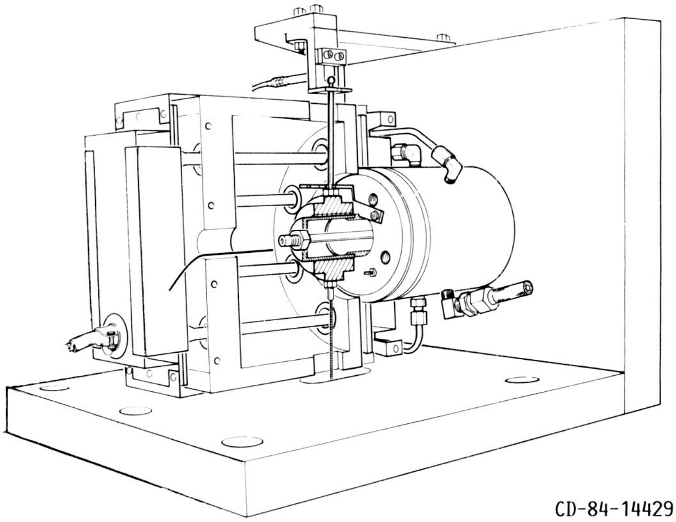

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FIGURE 5. - FOIL BEARING TEST MACHINE.

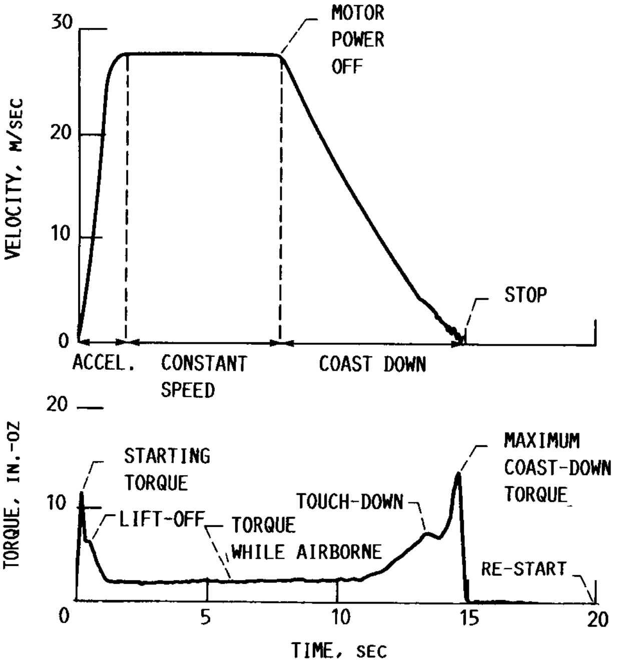
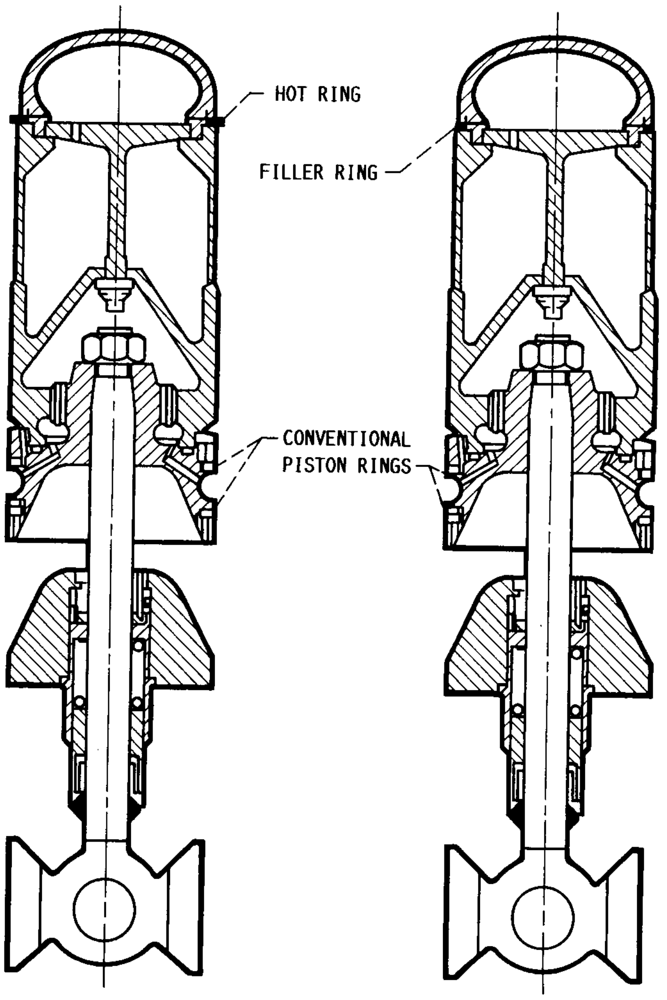


FIGURE 6. - TYPICAL TORQUE PROFILE OF A FOIL BEARING DURING A SINGLE START/STOP CYCLE.



MOD I ENGINE PISTON WITH HOT RING

MOD I ENGINE PISTON WITH FILLER RING

FIGURE 7. - STIRLING ENGINE PISTON CONFIGURATIONS.

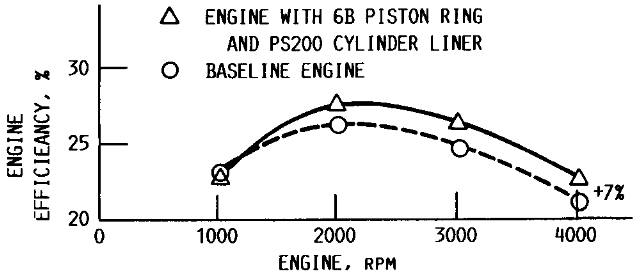
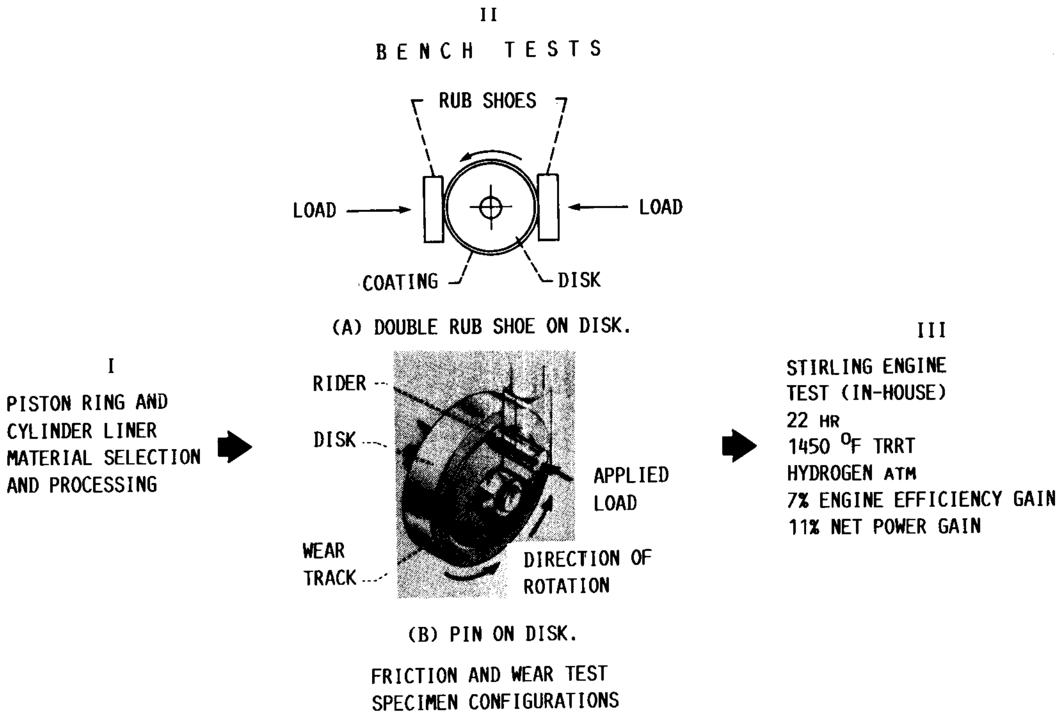


FIGURE 8. - STIRLING ENGINE EFFICIENCY USING "HOT PISTON RING" CONCEPT COMPARED TO BASELINE ENGINE. 4-CYLINDER ENGINE, HYDROGEN WORKING GAS, 5 MPA MEAN OPERATING PRESSURE.



I

PISTON RING AND
CYLINDER LINER
MATERIAL SELECTION
AND PROCESSING

II

BENCH TESTS

(A) DOUBLE RUB SHOE ON DISK.

(B) PIN ON DISK.

FRICTION AND WEAR TEST
SPECIMEN CONFIGURATIONS

III

STIRLING ENGINE
TEST (IN-HOUSE)
22 HR
1450 °F TRRT
HYDROGEN ATM
7% ENGINE EFFICIENCY GAIN
11% NET POWER GAIN

FIGURE 9. - PHASES OF "HOT PISTON RING" PROJECT WITH THE STIRLING ENGINE PROJECT OFFICE.

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16. Abstract

Criteria are discussed for predicting the probable lubricating ability of candidate solid materials from a consideration of their basic chemical and physical properties. The properties considered to be of importance in the model are thermochemical potential, adhesion, low hardness, plasticity, yield strength in shear, and brittle-to-ductile transition characteristics. A review of the selection and tribological testing of materials, which were selected for use in self-lubricating composite coatings by employing this model, is given. Two series of plasma-sprayed coatings with good tribological properties over a wide temperature spectrum are described. The PS 100 series of coatings contain oxidatively stable solid lubricants in a nichrome matrix. The PS 200 series contains the same solid lubricants in a very wear resistant metal-bonded chromium carbide matrix. Examples are given of applications of these coatings in high speed shaft seals, sliding contact bearings, and Stirling engine cylinder liners.

17. Key Words (Suggested by Author(s))
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