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A CALCIUM FLUORIDE - LITHIUM FLUORIDE SOLID LUBRICANT COATING FOR CAGES OF BALL BEARINGS TO BE USED IN LIQUID FLUORINE

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16. Abstract

A procedure is described for applying calcium fluoride - lithium fluoride solid lubricant coatings to nickel-beryllium (1.95 Be, 0.50 Ti, remainder Ni) ball bearing cages. The bearings are 50-mm bore bearings with 440-C balls and races. The ability of the fluoride coating to lubricate these bearings will be evaluated in another program under NASA contract NAS 3-11201.

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SUMMARY

Fused fluoride, solid lubricant coatings were applied to machined cages for 50-millimeter bore ball bearings. The cage material is a high strength nickel-beryllium alloy (1.95 Be, 0.50 Ti, remainder Ni).

A suspension of calcium fluoride (CaF_2) and lithium fluoride (LiF) in water was sprayed onto bearing cages that were preheated to 60° C. Water rapidly evaporated from the heated surfaces, and the fluorides deposited as a thin, loosely adherent film. The sprayed deposit was built up to a thickness of about 0.005 centimeter. The coated cages were then heated in a two-zone tube furnace containing an atmosphere of dry hydrogen. The deposits were fused at 900° C for 10 minutes in the furnace hot zone, then moved into the cooling zone where the cages were cooled to 100° C in about 15 minutes. The molten fluorides solidified into smooth, dense, strongly bonded coatings about 0.003 centimeter thick.

Dimensional changes (shrinkage) occurred in the nickel beryllium alloy when it was heated much above 900° C. For example, after 10 minutes at 1100° C, the outside diameter of the bearing cage had shrunk approximately 0.1 percent. No dimensional changes were noticed in the alloy when the coatings were fired at 900° C.

INTRODUCTION

Fluorine is the most reactive oxidizing element known. It is a logical choice therefore, as a high energy rocket propellant. However, materials that are exposed to this corrosive fluid must be selected with great care. For example, the dynamic seals and the bearings in liquid fluorine pumps are very susceptible to chemical reaction with fluorine because the heat generated by friction in sliding or rolling contact increases reaction rates. If reaction rates are too high, excessive corrosive wear occurs - in the extreme case, ignition is possible. On the other hand, fluoridation reactions that occur at a moderate rate are beneficial. They form reaction films which prevent direct metal-to-metal contact and serious adhesive wear.

Research at Lewis Research Center showed that nickel fluoride (NiF_2) films can lubricate sliding surfaces in liquid fluorine (ref. 1). These NiF_2 flims were reaction products formed on the sliding surfaces of nickel base alloys while submerged in liquid fluorine. It was also shown that preapplied coatings of metal fluorides such as lithium fluoride (LiF) and calcium fluoride (CaF_2) can lubricate sliding surfaces in liquid fluorine (ref. 1).

The advantage of preapplied solid lubricant coatings is increased assurance that an adequate lubricating film is present at startup and under conditions where NiF_2 films may not form at a satisfactory rate.

Liquid fluorine lubricated ball bearings for use in fluorine pumps are being evaluated at Aerojet General under NASA contract NAS 3-11201. The bearings are 50-millimeter bore ball bearings with 440-C steel balls and races. Three types of machined bearing cages are being investigated:

(1) Nickel base alloy cages. The cages depend on a fluoride film formed in situ during the bearing tests.

(2) Nickel alloy cages lubricated with preformed 0.003-centimeter thick coatings of 77 weight percent CaF_2 and 23 weight percent LiF.

(3) Self-lubricating composite cages of porous, sintered, nickel-chromium alloy impregnated with fluoride solid lubricants. (One filler is 77 wt.% CaF_2 - 23 wt.% LiF; another is LiF alone. Composites with fluoride fillers as the lubricating components for use in air and in hydrogen are described in ref. 2. Their use as bearing cage materials for dry ball bearings tested in air is decribed in ref. 3.)

The objectives of the work described in this report were

(1) To develop a satisfactory procedure for coating a nickel beryllium alloy (1.95 Be, 0.5 Ti, remainder Ni) with a fused coating of 77 weight percent CaF_2 and 23 weight percent LiF

(2) To coat nickel-beryllium bearing cages for ball bearing tests in liquid fluorine

The nickel-beryllium alloy has high tensile strength extreme hardness, good impact resistance, good ductility and good corrosion resistance. This alloy was selected for coating because it showed the least wear in screening tests of uncoated cage materials which were tested in liquid fluorine at Aerojet General. Some of the important properties of nickel-beryllium are given in the following table (data from ref. 6):

Physical constants	
Specific gravity	8.84
Thermal expansion coefficient (68° to 1022° F or 20° to 550° C	8.0×10^{-6} (14.4×10^{-6})
Modulus of elasticity, psi (GN/m^2)	27 - to 30×10^{6} (190 to 210)
Electrical resistivity, $\mu\Omega$-cm	23.8
Typical annealed properties	
Tensile strength, psi (MN/m^2)	105 000 (725)
Yield strength (2 percent), psi (MN/m^2)	45 000 (472)
Elongation, percent	40
Rockwell hardness	B-70

COATING PROCEDURE

After some preliminary difficulties, a procedure was found for satisfactorily coating the nickel-beryllium alloy cages. One problem was the formation of undesirable residues from the liquid carrier used in spraying the coating. Another problem was dimensional instability of the cages if they were overheated when the coating was fired. These difficulties will be discussed later in this report.

The following procedure produced satisfactory coatings:

(1) Mix dry, reagent grade powders of calcium fluoride (CaF_2) and lithium fluoride (LiF) in the proportion 77 weight percent CaF_2 - 23 weight percent LiF.

(2) Sandblast the part to be coated to a surface roughness of about 1 micrometer (40 μin.) rms.

(3) Add 15 grams of mixed powders to 50 milliliters of distilled water (convenient volume for a standard 3-oz air brush bottle), and shake to suspend the solid particles.

(4) Spray suspension with an air brush. The air brush should be equipped with the type of spray adjusting tip used for air-brushing porcelain enamel suspensions. The part to be coated should be preheated and maintained at about 60° C. This is conveniently done with a warm air blower.

(5) Build up the coating thickness to an estimated 0.005 centimeter by repeated passes with the air brush.

The coating thickness can be measured with a four place micrometer at various stages of spraying, but extreme care is necessary because the coatings are very loosely bonded in the as-sprayed condition. With experience, it is possible to visually estimate the coating thickness to about ±25 percent of the measured thickness. Visual estimation of coating thickness is possible because only about one-tenth of the total as-sprayed coating thickness is deposited with each pass of the air brush. Therefore, it is possible to observe a gradual transition in appearance of the coated surfaces from a metallic appearance, through a hazy, filmed over appearance, to an opaque chalk-white just before the coating reaches the desired 0.005 centimeter thickness.

(6) Fuse the coating by heating in a dry hydrogen atmosphere for 10 minutes at 900° C. (In this work, a two-zone hydrogen tube furnace was used. The hot zone was a ceramic tube in which temperature was maintained at 900° C and the cold zone was a water jacketed cast iron tube.)

(7) Cool specimens in hydrogen atmosphere. (In this work the specimen cooled from 900° C to about 100° C in 15 minutes when the specimens were moved into the cooling zone of the furnace.)

(8) The fused coatings should be 0.002 to 0.004 centimeter thick.

Some examples of coated bearing cages are shown in figure 1. The coatings are dense, strongle bonded, and have a uniform, light gray color. The coatings have a dull finish but are transluscent under strong illumination.

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Figure 1. - Nickel-beryllium bearing cages coated with fused fluorides.

DISCUSSION

The friction and wear properties of fused fluoride coatings in liquid fluorine, and the use of fluoride solid lubricants for dynamic seals in fluorine were reported in reference 1. A coating that gave favorable results was sprayed from a suspension which contained CaF_2 and LiF. The weight ratio of the two solids was 77 CaF_2-23 LiF. Therefore, CaF_2-LiF coatings were chosen for evaluation as lubricants for ball bearings to be operated in liquid fluorine. There was no prior experience in coating nickel-beryllium alloy with this composition.

Lacquer was the first liquid used in this work as a suspending agent for the fluoride powders. It held the powders in suspension reasonably well and was also beneficial as a binder for the as-sprayed, coatings. However, lacquer left a sooty residue after the coatings were fused in hydrogen. Consequently, the liquid carrier was changed to distilled water. Water was not a good suspending agent and frequent agitation was necessary in order to maintain a sprayable suspension. Nevertheless, because no undesirable carbonaceous residues were possible, water was chosen as the liquid carrier.

The binary phase diagram for the CaF_2 - LiF system, which is given in figure 2, was used as a guide in choosing a firing procedure for the coatings. According to this diagram, complete melting of the composition 77 weight percent CaF_2 - 23 weight percent LiF should occur at about 1075° C. However, melting begins at the eutectic temperature (769±4° C) where the molten phase has the composition 57 weight percent LiF - 43 weight percent CaF_2 and the remaining CaF_2 is solid. As the temperature is increased, more CaF_2 melts, and the melt composition follows the liquidus curve until, at 1075° C, all CaF_2 melts and the melt composition is 77 weight percent CaF_2 - 23 weight percent LiF.

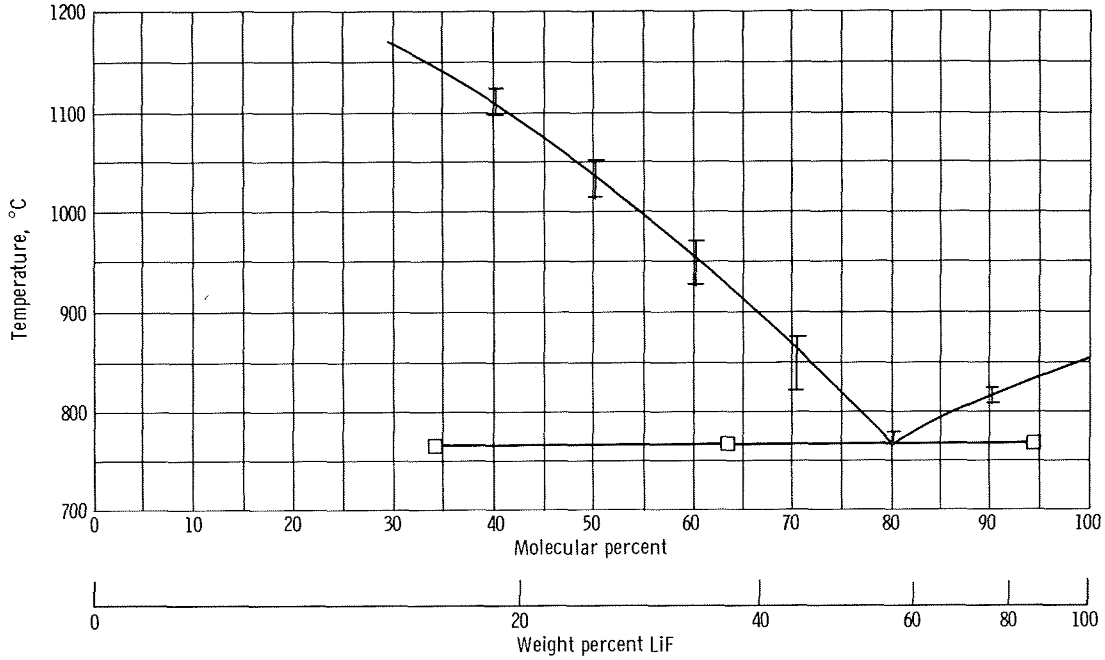

Figure 2. - Phase diagram for CaF_2 - LiF (ref. 4).

The first coatings were fired at 1100° C. Complete melting of the coating took place but the beryllium-nickel alloy was dimensionally unstable when heated to this temperature. At a firing temperature of 900° C, no dimensional instabilities occurred in the alloy, and sufficient melting occurred in the fluoride composition to produce a smooth, strongly bonded coating.

The dimensional changes in nickel-beryllium after the coatings were fired at 1100° C may have been caused by the precipitation of the intermetallic compound Ni-Be. Nickel-beryllium is age-hardenable by the precipitation of the β phase which includes the intermetallic Ni-Be (see phase diagram, fig. 3). The bearing cages were received in the solution-annealed condition with a hardness of Rockwell B-85. The 900° C firing procedure did not significantly change the hardness, but the 1100° C procedure resulted in a hardness increase to Rockwell C-35.

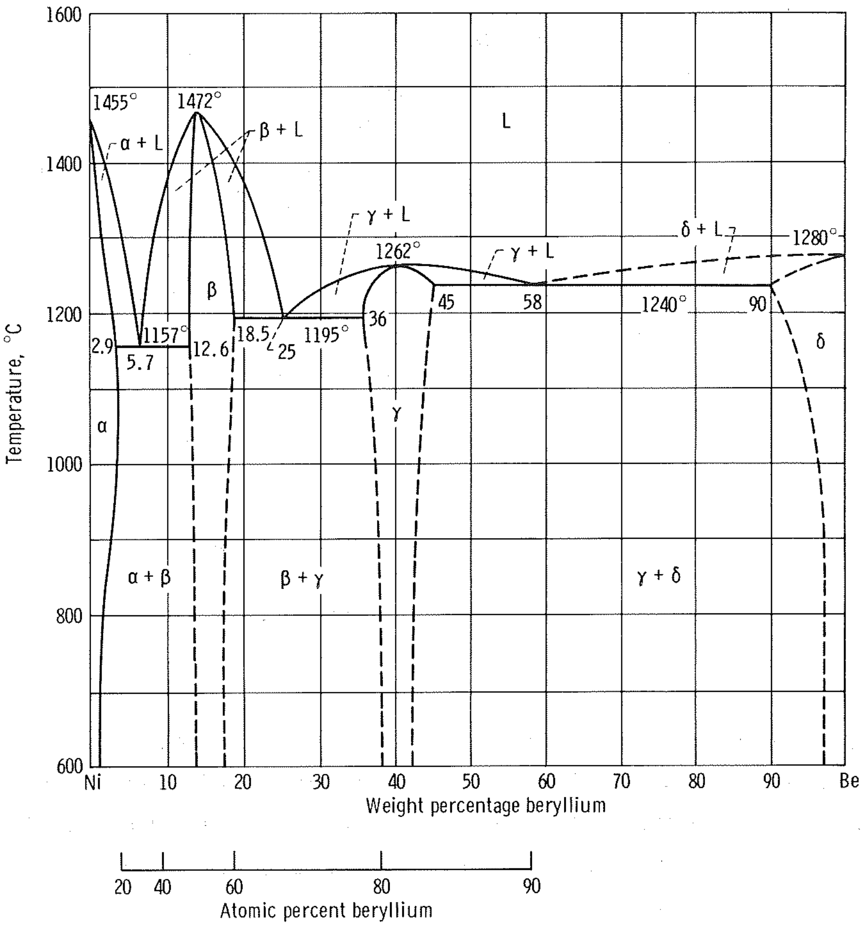

Figure 3. - Phase diagram for beryllium-nickel (from ref. 5).

CONCLUSIONS

1. Adherent, solid lubricant coatings of fused fluorides can be applied to nickel-beryllium alloy. The coating composition used in this work was 77 weight percent calcium fluoride - 23 weight percent lithium fluoride.

2. A satisfactory coating procedure was to spray an aqueous suspension of fluoride powder onto the cage surfaces, then to fuse the coating by heating in a dry hydrogen atmosphere for 10 minutes at 900° C.

3. The maximum firing temperature should not exceed 900° C. (A higher firing temperature (1100° C) caused the alloy to shrink approximately 0.1 percent.)

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 19, 1970,
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