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Lubrication of Titanium
"State of the Art"

Assignment 81 142
NSRDC R&D Report 138/67
May 1967

By
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ABSTRACT

The advantages of using titanium in marine machinery are outlined, and the difficulty in lubricating machinery constructed of titanium is reviewed. A number of suggestions are given for possible research which might lead to the successful lubrication of titanium machinery components in a marine environment.

ADMINISTRATIVE INFORMATION

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I. INTRODUCTION

Titantium is useful in a marine environment primarily because it is corrosion resistant, and has an excellent strength-to-weight ratio (up to 1.7 times that of steels (1)). In addition to resisting general corrosion, titanium has good resistance to crevice corrosion, and the highest resistance to corrosion fatigue of any structural metal. It resists impingement attack and cavitation. While the cost per pound of titanium is high, the U.S. Navy is interested in it because its high strength-to-weight ratio makes its actual application cost less than that of Hastelloy C, and competitive with monel. Moreover, the cost per pound of titanium is decreasing continually with increasing commerical use, so that, even on a first-cost basis, titanium is becoming more nearly competitive with such metals as stainless steels. The cost advantage is further increased by an anticipated longer life of titanium parts in many applications.

Furthermore, the possibility of building deep submersibles depends on the ability to use machinery outside the hull to increase buoyancy and decrease the number of hull penetrations. Titanium, with its exceedingly good corrosion resistance and high strength-to-weight ratio, may, in some instances, be the only practical material for outboard machinery of deep submersibles. In addition, the probability of sea water ingress into machinery in any part of a submerged vehicle increases with increasing depth of submergence in the ocean. Therefore, the availability of an alloy that is inherently resistant to sea-water corrosion, such as a titanium alloy, would provide the basis for greater capabilities and reliability.

II. PROBLEM AREAS

Titanium is known to exhibit high friction with conventional lubricants, and it is prone to seizing and galling. A solution to this problem must be found before titanium can be used in conventional machinery designs in which titanium is in frictional contact with itself, or with dissimilar materials. Any treatment proposed to improve the lubrication of titanium and its alloys must not seriously impair either the corrosion resistance or the mechanical properties of the metal or its alloys.

It would seem that titanium would work successfully with hydrodynamic lubrication in a sliding contact situation. This has been found to be so. (2) However, only in very special designs and applications can the hydrodynamic region of lubrication be constantly maintained. In reciprocating machinery, or in the starting and stopping of any machinery, as well as in slow speed, high load machinery, the region of boundary lubrication must be considered. It is this boundary lubrication of titanium that is so difficult.

Analysis of Problem

A study of boundary lubrication should include both chemical and physical phenomena. Chemical phenomena will affect the adherence of a boundary lubricant to the metal (or metal oxide) surface. Physical phenomena will affect the deformation properties of the surface, and may determine whether metal-to-metal contact (through cracks in an oxide surface film, for instance) occurs.

Before a systematic program can be established to improve the lubrication of titanium, the reason for the inherently poor lubricating properties of this metal must be determined. It has been suggested that the fundamental difficulty is chemical in nature. (3) The ineffectiveness of normal lubricant additives (designed to react chemically with the metal surface) bears this out. Titanium (Ti) is a highly reactive metal which rapidly forms a thin oxide film. This oxide film is resistant to most chemicals, corroding appreciably only in strong acids or hot alkalis. Thus, in order to form a chemically bound lubricating layer, the lubricant must either react directly with the oxide, or remove the oxide layer to react with the underlying metal.

It is likely that metal-to-metal contact (Ti-Ti), formed on breaking of the oxide film during frictional deformation of the surface, is responsible for the high friction of titanium. On the other hand, it would seem possible that the friction is, at least partially, due to contact between the titanium and titanium oxide (TiO_2) since the oxide layer adheres well to its metal substrate. An experiment with Ti and TiO_2 (rutile) in sliding contact should give some indication of the degree of this adhesion. In fact such an experiment (4) indicated that the Ti-TiO_2 coefficient of friction (maximum value in stick-slip cycle $\mu \approx 0.40$) is less than the Ti-Ti coefficient of friction ($\mu \approx 0.67$).

It is not generally useful to comment on the mechanical properties of alloys without specifying carefully both composition and heat treatment. Nevertheless, it may be noted that titanium alloys in many cases combine a high strength with considerable ductility. This combination is very useful in metal forming, but may contribute to the galling tendencies of the metal and its alloys, since ductility would allow growth of metallic junctions and high strength would prevent easy rupture of these junctions. The work that has been done in comparing titanium alloys of different structure (alpha, beta, and alpha-beta) indicates that all are equally difficult to lubricate. (5, 6).

Approach

The problem of the boundary lubrication of titanium may be attacked from several angles -- liquid lubricants, solid lubricants, treatment of the titanium surface, proper choice of bearing surface, and combinations of any of these. Liquid lubricants would be useful in inboard machinery and encapsulated outboard machinery, but they should be compatible with sea water as a major or minor (impurity) constituent. Ideally, a good liquid lubricant should have boundary-lubricating properties for start and stop conditions, and should also take advantage of hydrodynamic lubrication at high speeds. Solid lubricants, not having an intrinsic self-healing nature unless continuous feed designs are developed, would be most useful in contacts where sliding is intermittent, and the number of cycles is relatively small, e.g. an opening and closing mechanism, as opposed to continuously rotating machinery. Plastic bearing materials would be used against titanium in relatively lightly loaded, low temperature situations, i.e., either at slow speed, or under conditions where effective cooling is provided by a liquid lubricant. A surface treatment giving titanium a hard coating would be particularly beneficial where the titanium might be in sliding contact with a non-metallic (plastic) bearing with water as a lubricant as in outboard machinery. Titanium has been known to serve in such a system, but abrasive particles (sand, etc.) which are likely to be present may cut the titanium surface. Titanium wear particles thus formed could embed in the bearing material and lead to the possibility of Ti-Ti contact. A hard coating on the original titanium surface would minimize such cutting by abrasives, and the resultant formation of metallic wear particles.

III. SUMMARY OF THE LITERATURE

Several reviews of the literature have been written, (5, 7, 8). This report will simply summarize the areas which have been investigated with the purpose of determining what further work would be most fruitful.

Dry Friction

It is curious, but not very useful, to note that the coefficient of friction for unlubricated sliding in air of a metal against itself (speed = 1 cm/sec, load = 1000 gm on 1/4" hemispherical rider, repeated sliding over same track) is lower for titanium ($\mu = 0.49$) (3) than it is for any other metal. This phenomenon may be attributed to the rapidly re-forming oxide film.

It has also been found that alloys with tin (Sn) and aluminum (Al) with fifteen to twenty percent of the alloying element show a surprisingly low coefficient of friction ($\mu = 0.35$ to 0.5) in a vacuum. This has been attributed to a change in deformation mechanisms (prismatic slip in pure hexagonal Ti going to basal slip in these hexagonal alloys)(9). It may, however, be due to the hardening and embrittling effect of the alloying elements, since alloys of high aluminum content are considered to be virtually unworkable (10) . It should be noted that while the coefficients of friction found in these experiments are low for such experiments, they are still not within the useful range. The problem of a boundary lubricant must still be solved.

Liquid Lubricants

As mentioned above, conventional lubricants with conventional additives do not appreciably change the coefficient of friction of Ti vs Ti from its dry friction value of 0.49. (Ti sliding on any other metal rapidly transfers a layer of Ti onto that metal, unless the bearing metal has a hardness less than one-sixth that of the Ti alloy under consideration.(11))

Methylene iodide and chlorofluorohydrocarbons are found to be most effective as liquid lubricants for titanium ($\mu = 0.2$) (3). Polyethylene glycol 1000 (Carbowax) was nearly as effective ($\mu = 0.25$) (3). Generally, the coefficient of friction, using Carbowaxes as lubricants, decreased with increasing viscosity (increasing molecular weight). Other lubricants having the same viscosities, however, did not show such good lubricating properties (3). These results may simply indicate a difference in the pressure coefficient of viscosity (ability to be squeezed out under load) for the different types of lubricants. On the other hand, the results may indicate chemical adsorption of the Carbowaxes on the titanium surface, or formation of crystallites of Carbowaxes of high molecular weight in the adsorbed layer.

Roberts and Owens (12) at General Electric Company report that nine percent iodine (by weight) in n-butyl benzene gives a coefficient of friction of 0.25 to 0.38 when used as a liquid lubricant for titanium. They found that iodine in pure mineral oil was not so effective ($\mu = 0.36$ to 0.68). They interpreted their results as indicating that the formation of a complex of iodine with n-butyl benzene is necessary to the lubricating properties of the system. The iodine complex, in their opinion, then reacts with the Ti surface to form a layer of titanium diiodide (TiI_2), which has a lamellar structure and acts as a solid lubricant. However, subsequent work on various iodine containing organic lubricants used with aluminum and glass bearing surfaces suggests that neither the formation of an iodine complex, nor the formation of a lamellar structure is necessary for some extraordinary properties of iodine as a lubricant additive (13).

Solid Lubricants

Solid lubricants, such as graphite and molybdenum disulphide, also adhere poorly to the titanium oxide surface. Resin bonding of the lubricant to the surface sometimes is successful, but the results are erratic. A roughening of the surface (shot-peening, etc.) gives a better keying of solid lubricants to the titanium surface (as well as forming a tough work-hardened surface layer). Some chemical modifications of the titanium surface also give better adhesion of the solid lubricants as will be noted below. A Teflon grease on a porous conversion coating has shown promise as a lubricant for titanium (beta alloy) wire rope.(14)

Anodizing and Chemical Conversion Coatings

A non-metallic coating on titanium may prevent metal-to-metal contact, and if it is porous, may hold a liquid or solid lubricant in the sliding contact region. To have a useful lifetime, the coating must be reasonably thick, adherent, and wear resistant. Since thicker films tend to be less adherent, a compromise is required.

An adherent conversion coating is produced with sodium phosphate, potassium fluoride, and hydrofluoric acid solution. A potassium-titanium-fluoride complex is presumably formed. The hardness and wear resistance of the film is increased with a heat treatment (in air) at 800 F for two to five hours. (15)

Titanium can be anodized in acid, alkali, or neutral salt electrolytes. (16) When the oxide is insoluble in the electrolyte (neutral salts or weak acids) a thin, hard coat is produced. When the anodic film is somewhat soluble, as in strong acids or alkalis, thick, porous films are produced. Both types of films improve the wear resistance of titanium. The porous coatings may be treated with epoxy resins and molybdenum disulphide or graphite. The anodic "hard coat" developed at the Watervliet Arsenal (17) uses an auxiliary cathode of low carbon steel, and achieves a coating which is believed to contain titanium, iron and oxygen.

Oxidizing, Nitriding, and Carbonizing.

Oxygen, nitrogen and carbon all form interstitial solid solutions in titanium, causing solid solution strengthening with very small amounts of alloying element. (10) Thus, a heat treatment of Ti (or its alloys) in an atmosphere of any of these gases (or a mixture of them) produces a hard surface layer. Simply heating in air at 350 C for 17 hours can reduce the coefficient of dry friction to approximately 0.2. (4) Temperature, time at temperature, and partial pressure may all be varied to optimize the coating thickness, hardness, and mechanical properties of the bulk material. Control of reduced pressures is not commercially feasible, but a thick, hardened, adherent oxidized layer has been produced, without embrittlement of the bulk material, by

- oxidation in dry oxygen followed by diffusion treatment in an argon atmosphere, (18)
- oxidation in a molten glass bath (in which the high viscosity of the glass slows the diffusion of oxygen to the interface), (18) and
- oxidation in a fused lithium carbonate bath. (19)

The higher solubility and more rapid diffusion of oxygen in titanium (relative to carbon and nitrogen in titanium) allow a thicker layer of increased hardness to be formed with oxygen than with carbon or nitrogen. (8)

Metallic Coatings

Metallic coatings are of limited utility in a marine environment, since the coating will be less corrosion resistant than the titanium. Since the corrosion resistance of Ti is not thus utilized, the coating might be better applied to a less expensive substrate. However, considerable work has been done on metallic coatings for Ti (primarily for the aircraft industry) and, for completeness, mention will be made of it here.

Metallic coatings may be applied by electroplating, dip coating, flame spraying, cladding and (on a laboratory scale) vapor deposition. Surface pretreatment to remove the oxide layer is indispensable for obtaining an adherent coating. This pretreatment may be either chemical (pickling) or mechanical (abrading). A heat treatment following the application of the metallic coating is also necessary for a good diffusion bond between the coating and the base metal. Electroless nickel coating has been developed specifically for gear applications. (20) Other metals which have been used to coat titanium are chromium, copper, gold, platinum, zinc and brass, cobalt, molybdenum, and various "sandwich" structures.

IV. SUMMARY AND RECOMMENDATIONS

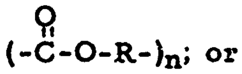
All of the friction and wear tests suggested below should be performed on commercially available titanium alloys of each type (alpha, beta, and alpha-beta) to see whether the crystal structure of the alloy plays any role in its ability to be lubricated. It is possible that the different alloys have oxide surface layers differing in structure, mechanical properties, and adherence to the substrate metal, all of which would affect the lubrication process. It is also possible that frictional deformation and heating cause phase changes, e.g. from metastable beta to alpha. The structure of the metal immediately adjacent to the surface both before and after a friction test is thus of interest.

Liquid Lubricants

There is still controversy about the mechanism of lubrication by iodine as an addition in organic solvents, i.e., whether it is necessary to have a complex-forming solvent and whether a lamellar structure is formed and is essential to the good lubrication of this system. For example, the lubrication may instead be due to the formation of "friction polymer" by the polymerization of the organic solvent at the temperature generated at frictional contacts. Furey (13) found a resinous deposit on surfaces lubricated by organic solvents containing iodine. The lubricant for titanium suggested by General Electric (12) (n-butyl benzene + iodine) should be investigated in a friction and wear study on titanium in which load and speed are variables.

The effect of atmosphere (active or inert) and the presence of water in the atmosphere, or as an impurity in the lubricant, should also be investigated. The compound, TiI_2, reacts rapidly with water, and if TiI_2 is indeed formed, such iodine containing lubricants would be of limited utility in a marine environment. Similar investigations should be made of I_2 with other complex-forming and non-complex-forming solvents.

The Carbowaxes $(-CH_2-CH_2-O-)_n$ should also be investigated for their lubricating ability as a function of load and speed. To determine whether chemical adsorption is taking place, related polymers should be studied in friction and wear tests on titanium, e.g., $(CH_2-O-)_n$; ketonic types,

 $(-\overset{O}{\overset{\|}{C}}-R-)_n$; ester types,  $(-\overset{O}{\overset{\|}{C}}-O-R-)_n$; or thio ethers $(CH_2-S-CH_2-R-)_n$

where R is an inactive group such as a hydrocarbon group. To determine whether polymer crystallites formed on the surface are contributing to the lubrication, a friction and wear study with titanium should be made of polymers which cannot crystallize, i.e., branched polymers, as well as crystallizable polymers which have different chain conformations in the crystalline phase, i.e., zig-zag chains, helical chains, and cyclic polymers.

Oxidation.

Those anodizing treatments which have been reported to increase the wear resistance of titanium in different wear situations should be rated for their wear resistance under identical conditions. An attempt should be made to characterize the most successful coatings as to their chemical nature, their crystal structure, orientation and morphology, and their mechanical properties, with the object of optimizing their utility.

The three beneficial oxidation treatments mentioned above (18, 19) should be investigated and the procedures optimized. Again, close identification of the coating formed is considered to be the most direct means of finding the optimum treatment conditions.

Anodized, oxidized and untreated samples of titanium should be tested in sliding contact with similarly treated specimens as well as with nonmetallics, i.e., plastic bearing materials. The effect of abrasive particles on surface treated titanium specimens bearing against plastics should also be investigated.

Plastic Bearing Materials

Titanium sliding against plastic materials is not significantly different from other metals in a similar situation. Of concern, however, is the possibility of transfer of titanium to the plastic bearing, and resultant Ti-Ti contact. It has been indicated (21) that some plastics may cause more metal transfer than others. This point should be further investigated with particular reference to titanium. The ability of plastics to imbed abrasive particles, and thus protect a titanium bearing surface from them should also be investigated.

It is apparent, therefore, that several promising avenues of approach to the problem of the lubrication of titanium exist. Solution of this problem could lead to the use of titanium in existing designs for machinery with longer life, or in new designs for machinery that could not be constructed from commonly used metals.

V. FUTURE WORK

Recommendations for extension of the art have as a general goal removal of the limitations to the use of titanium and its alloys in rubbing situations and extension of the application of these metals in machinery.

It is planned to proceed as follows:

- Continue to collect new information on titanium and titanium alloys in the lubrication process.

- Evaluate friction and wear characteristics of commercially available and newly developed titanium alloys--establishing relationships of crystal structure, mechanical properties and wear phenomena. Environments will be air and sea water.

- Consider overcoming the deficiencies or problems disclosed by adopting or extending the approaches described in this report.

From the above studies it is expected to establish the types of equipment, such as gearing and bearings, that could benefit from the use of titanium and titanium alloy components.

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