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SUPERLUBRICITY OF STEEL SURFACES IN PRESENCE OF POLYHYDRIC ALCOHOLS

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ABSTRACT

Anomalous low friction of hydrogen-free tetrahedral hybridized carbon (ta-C) coated surfaces lubricated by pure glycerol was observed at 80°C. In the presence of glycerol, the friction coefficient is below 0.01 at steady state, corresponding to so-called superlubricity regime. This new mechanism of superlow friction is attributed to easy glide on tribo-formed OH-terminated surfaces. In addition to the formation of OH-terminated surfaces but at a lower temperature, we show here some evidence that superlow friction of polyhydric alcohols could also be associated with tribo-induced degradation of glycerol, producing a nanometer-thick film containing organic acids and water.

Second, we show novel outstanding superlubricity of steel surfaces directly lubricated by a solution of myo-inositol in glycerol at ambient temperature (25°C). For the first time, under boundary lubrication at high contact pressure, friction of steel is below 0.01 in the absence of any long chain polar molecules. Mechanism is still unknown but could be associated with friction-induced dissociation of glycerol and interaction with steel surface.

INTRODUCTION

Superlubricity experiments in ultrahigh vacuum have already been reported in the literature by some of us, first in 1993 using stoichiometric MoS₂ coatings [1] in 1996 using hydrogenated carbon films a-C:H [2] and recently in 2007 using ta-C carbon films and glycerol [3]. However, superlubricity has never yet been approached using lubrication of steel surfaces in practical situations. Friction coefficients below 0.05 under boundary lubrication of steel samples have never been reported in the literature.

In this paper, we are most interested in the use of polyhydric alcohols (or polyols) to lubricate different material combinations used in practical situations including silicon and steel. Polyols have been widely used to synthesize the

corresponding esters as lubricant base oils. However, no attempt has been made to evaluate the intrinsic tribological properties of such polyhydric alcohols. Here we will focus on glycerol and myo-inositol that is classified as a member of the vitamin B complex. The chemical formula of myo-inositol is C₆H₁₂O₆. All the polyol molecules (including glycerol) are relatively small and do not contain aliphatic chains like most of amphiphilic molecules used in traditional lubricants. In this paper we show and discuss results obtained with glycerol and myo-inositol on steel and DLC surfaces.

EXPERIMENTAL PART

The sliding tests were conducted in the liquid phase using a reciprocating pin-on-flat tribometer. The hemispherical pin, 10 mm long presents a radius of curvature of 8 mm and was made of hardened bearing steel (AISI 52100) and polished to a surface roughness of Ra 0.05 micron. The flat measured 10×8×2 mm³ was also made of AISI 52100 steel. The contact pressure at the sliding interfaces was varied from 330 MPa to 830 MPa. The sliding speed was constant at 0.003 m.s⁻¹. Lubrication was provided by an oil bath at room temperature.

The ta-C DLC coating was applied to the polished hardened bearing steel (AISI 52100) discs and pins to a thickness of 0.5 micron from a graphite target by arc-ion plating, a physical vapor deposition (PVD) process. It did not contain hydrogen as shown by previous SIMS profiling experiments performed in the bulk of the ta-C coating and reported elsewhere [4, 5]. The sp³ sites percentage in the ta-C coating is about 90% as estimated from XANES experiments which is consistent with the high values of mechanical properties measured by nano-indentation, about 65 GPa for hardness and 650 GPa for Young modulus [5].

The glycerol used in this study is a commercial product from Carlo Erba. Its purity is estimated at 99.5% and its density is 1.257 at 25°C. The commercial myo-inositol is provided in the

form of white powder by Acros Organics Company. Its purity is estimated at more than 98%. To perform the tribological tests, myo-inositol is diluted in glycerol with a concentration of 1% in mass.

RESULTS AND DISCUSSION

Anomalous low friction of ta-C coating in presence of glycerol

Figure 1 shows the friction coefficient obtained for ta-C/ta-C material combination in presence of liquid pure glycerol and in presence of glycerol + 1 weight per cent of myo-inositol. As can be seen, we obtained an ultra-low friction coefficient ($\mu \approx 0.02$) for the ta-C/ta-C combination under boundary lubrication conditions with pure glycerol at room temperature. This anomalous low friction behavior of ta-C material in presence of glycerol, including even superlubricity ($\mu \leq 0.01$), has also been obtained with other tribometers under boundary lubrication conditions [3-5]. It involves the interaction between the ta-C coating material and the alcohol groups contained in the glycerol molecule. As a result, a very thin and low-shear-strength tribofilm is formed on the ta-C sliding surface [3-6]. It appears that superlubricity is directly related to the tri-alcohol chemical functions (-OH) of the glycerol molecule. However, as shown in figure 1, in the case of ta-C at room temperature, the addition of myo-inositol does not improve significantly the friction level.

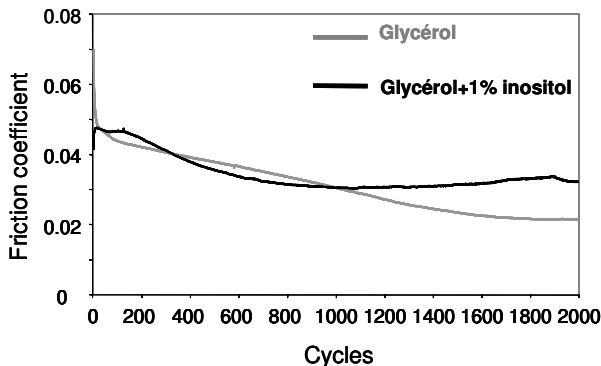


Fig. 1: Evolution of friction coefficients vs. the number of cycles for ta-C/ta-C friction pair material lubricated with pure glycerol and glycerol+1wt.% myo-inositol. Initial Hertzian contact pressure was 735 MPa.

Friction of steel in presence of glycerol and myo-inositol

Unfortunately glycerol alone is not able to durably lubricate the uncoated steel/steel friction pairs in a wide contact pressure range. Fig. 2 shows friction curves of steel pairs lubricated by glycerol at different contact pressures and at ambient temperature. It is interesting to notice that the highest contact pressure, about 830 MPa, gives the better friction reduction. The friction reduction mechanism is pressure-dependent for glycerol lubricated steel systems. A high

contact pressure seems necessary to activate the tribochemical reaction. However, the low friction regime, which starts immediately, does not last for a long time and friction generally increases up to 0.1 after a few hundreds of cycles.

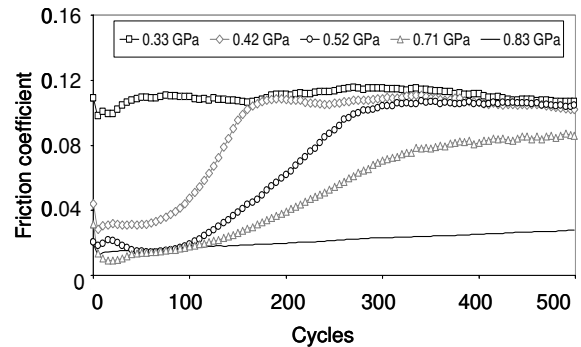


Fig. 2: Evolution of friction coefficient vs. the number of cycles for polished steel/steel friction pairs lubricated with glycerol at ambient temperature and for different contact pressures [7].

This fact suggests a tribochemical reaction between the iron oxide layer and the alcohol. We stopped a similar experiment after 100 cycles without releasing the load and keeping the static contact conditions for about two hours. After this, we were surprised to observe by SEM a mark in the contact area (corresponding to the Hertzian diameter) that displays a typical corrosion pattern on the surface (Fig. 3) with revelation of the chromium carbide grains in the steel structure (evidenced by XES analysis in the SEM but not shown here).

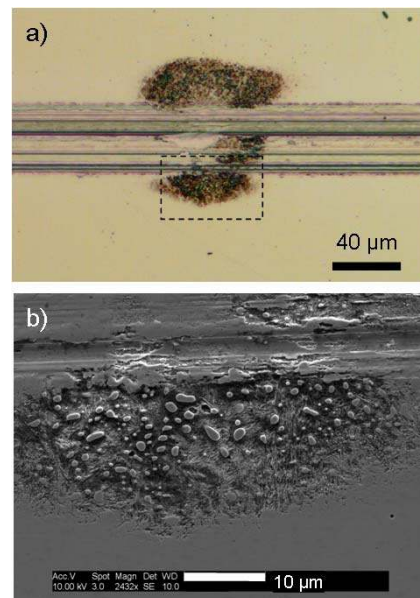


Fig. 3: Wear track observed on the flat after a friction test of 100 cycles with pure glycerol. A mark was observed on the flat where the ball stayed static during the two hours. a) Optical image, b) SEM image [7].

It is no question that this corrosion has been made glycerol because there is no evidence of corrosion of steel surface outside the contact zone, where the lubricant was also present during a long period. We can suggest that glycerol was present inside the contact area and has certainly been tribochemically transformed into some organic acids compounds. This is corroborated by the fact that no corrosion was observed in the case of a static loaded contact without sliding before. We can also notice that the different chemical reactions show that water molecules are also formed during the transformation of glycerol in acids. It is possible that these water molecules connect with OH groups on the surface by hydrogen bond, maybe sustaining the low friction of the surfaces.

In Figure 4, we compare the friction properties of steel surfaces lubricated by glycerol and glycerol + 1 weight per cent of myo-inositol at ambient temperature. It is remarkable to see the effect of inositol in reducing friction of steel/glycerol system in the superlow regime. No other lubricant is able to reach such a friction value with steel/steel tribological system except in hydrodynamic lubrication. Moreover, no wear track on steel is visible by optical microscopy. For the first time, we were able to decrease friction of steel samples in the superlow regime at ambient temperature and high contact pressures. It is thought that the mechanism of friction reduction of steel by inositol is similar to the case of ta-C with glycerol and that inositol molecules can produce water molecules inside the contact area. MD simulations are currently under consideration. Moreover, we observed that in presence of the solution of inositol, friction increases after a certain time and tends to reach the value of pure glycerol (Fig. 5). If we add another drop of solution in the contact, then friction decreases again in the superlow regime. This strongly suggests that inositol has been consumed by the friction process, possibly in forming water.

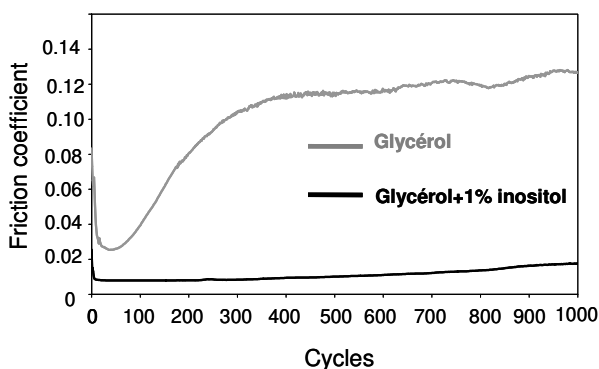


Fig. 4: Evolution of friction coefficients vs. the number of cycles for steel/steel friction pair material lubricated with pure glycerol and glycerol+1wt.% myo-inositol. Initial Hertzian contact pressure was 735 MPa.

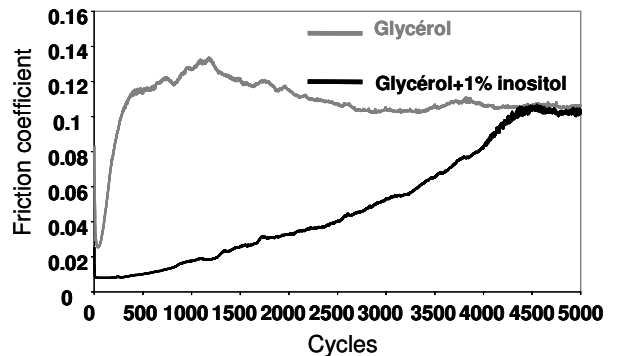


Fig. 5: Evolution of friction coefficients for steel/steel friction pair lubricated with pure glycerol and glycerol+1wt.% myo-inositol during 5000 cycles. Initial Hertzian contact pressure was 735 MPa.

CONCLUSION

A new tribological macro-system which is able to reach superlubricity under practical conditions of boundary lubrication at ambient temperature was presented in this paper. Typically, the use of steel surfaces and/or ta-C coated-steel surfaces lubricated by selected polyhydric alcohols molecules can give unsurpassed low friction values below 0.01, approaching the so-called superlubricity regime.

The mechanism of friction reduction is basically different from the well-known classical long-chain polar molecules model [8]. The proposed new mechanism is based on the existence of a network of H-bond interactions in the confined interface zone.

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