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Tribology International 38 (2005) 1022–1034

TRIBOLOGY INTERNATIONAL

www.elsevier.com/locate/triboint

Boundary lubrication additives for aluminium: A journey from nano to macrotribology

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Abstract

The tribology of two potential additive molecules for aluminium has been studied in the self assembled monolayer state at low loads (10^{-9}–10^{-2} N) and in dispersion state in *n*-hexadecane at high load (60 N). The two additive molecules are 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (FOTS), which has a rigid rod-like helical structure and octadecyltrichlorosilane (OTS), which has a zigzag backbone configuration. The adhesion, friction and wear performance have been investigated. Molecular conformational order and stiffness were found to play major roles in frictional dissipation and wear resistance, recorded in a nanotribometer and a pin-on-disc machine, while for very low load measurements (LFM), adhesion was found to have a significant role on friction along with molecular entropy.

Keywords: Atomic force microscopy; Fourier transform infrared spectroscopy; Macrotribology

1. Introduction

Aluminium and magnesium are likely to make major inroads as engine materials for mass manufactured cars in the next decade or so. A search towards this is therefore, an objective to optimization of engine tribology, will play an important role. A unique combination of optimum microstructure and optimum interfaces, which are protective, efficient in transmission and minimize dissipation losses needs to be evolved. A search for additives, which can generate such interfaces for light metals, normally covered with persistent layers of oxides and hydroxides, has acquired a renewed impetus. We look to a new generation of commercially available additives, presently considered [1–6] for protection of semiconductor silicon surfaces and components in electronic packaging, micro electro-mechanical systems and information storage, for possible use as boundary lubrication additives for aluminium-based components used in moving machinery. These are organosilanes, which adhere to the aluminium substrate through oxygen atoms by self-assembled process [7,8].

Many potential applications of self-assembled monolayers (SAM) have inspired extensive scrutiny of their tribological properties. High temperatures and extreme pressure are likely to remove these monolayers; we thus limit our outlook to relatively mild conditions. Properties of interest are adhesion, friction and wear [9]. Polar functionality of the terminal group, molecular entropy or conformational order influenced by intermolecular Van der Waals forces, lateral polymerization, steric hindrance, structure and stiffness of the backbone and chemical/physical affinity of the head group to the substrate are relevant parameters which may influence tribology. In this the aggregate functionality near the surface is influenced by molecular entropy while external variables such as pressure, temperature and the medium and its polarity intervene through the above parameters to fix the specifities of tribological interaction. Given this generality, what is, however, not clear how relevant is a relevant parameter at a given scale of operation.

It is known that the adhesion and surface energy [10,11] of CF_3 terminated molecules are somewhat less than that of a CH_3 terminated molecules although there appears to be some experimental evidence to the contrary [3,4]. In contrast, lateral force microscopy studies [1,2,5] clearly demonstrate that the friction corresponding to the former is significantly greater than that of the latter.

In moving to the backbone, it now appears established that molecular conformation has a profound effect on

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0301-679X/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.triboint.2005.07.030

tribological performance [9], with higher entropy and diminishing packing density [12,13] promoting higher friction. It is argued that this encourages additional channels of energy dissipation through the excitation of molecular motion [14,15]. A number of structural parameters such as atom size (fluorine is bigger then hydrogen) [1], chain length [14], lateral polymerizability [16], crystalline phase [2] and lattice parameters of the substrate material [17] influence the entropy and density of the molecular assembly. External variables, such as temperature [18] and pressure [19,20,12], influence adhesion and friction through their ability to influence the given structurally-determined entropy, this ability being itself a function of the a, priori structure [21]. In a boundary lubrication regime, as two mating asperities approach and move away from each other in an environment where energy is dissipated through friction, a molecule adsorbed on the substrate is subject to a thermal cycle. If the entropy is irreversible the next contact encounters a disordered assembly. We have concluded [22] on the basis of our studies of alkane thiols with different chain length (C_{18} and C_8) that the potential for entropy change due to change in temperature is dependent on the a, priori defect density in the molecule. We have extended this approach here to two commercially available molecules; octadecyltrichlorosilane (OTS) [8] and 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (FOTS) [7], which are potentially useful as boundary lubricants for aluminium and we have observed that the entropy generation is modest upto a heat treatment peak temperature of 483 K for OTS and 573 K for FOTS. FOTS is thus more thermally stable then OTS in spite of the latter being laterally polymerisable and of longer chain length (18 carbons) than the former (8 carbons). The OTS and FOTS differ not only by the fact that they are hydrogen and fluorine terminated respectively, but also the back bone in OTS has a zigzag configuration while that in FOTS has a helical structure.

In this paper we conduct tribological studies of FOTS and OTS in different regimes of normal load; 0–25 nN, 25–100 mN and 60 N (10 order load range), as a function of heat treatment cycle at different peak temperatures. The study is of immediate practical relevance as the test molecules are serious contenders for additive application in aluminium tribology. The rationale for this large span of test loads is however, not just to look for nano mechanical phenomena which in aggregate can explain macrotribology, but to establish different mechanisms which predominate different experimental scales. Today, practical processes are found at all scales, from nano to macro. The comparative study also provides us with a unique opportunity to observe the complex interplay of three basic, but not totally unrelated parameters, which are known to influence molecular tribology. FOTS adheres less than OTS, and this is known [9] to reduce friction. It has a short chain compared to OTS which is known [22] to promote higher entropy and friction and finally it has a rigid rod like helical structure which may be suggested intuitively to offer greater resistance to sliding motion. We try to delineate each of these effects using a range of techniques; Atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectroscopy, contact angle measurement, Surface enhanced Raman spectroscopy, contact force measurement, nanotribometry and macrotribometry and observe the predominant effects at room temperature and in situations where we control the molecular entropy by changing the heat treatment peak temperatures.

2. Experimental

2.1. Materials

Polycrystalline aluminium containing 97.25% aluminium, 1% silicon, 0.6% magnesium, 0.5% manganese and 0.35% iron is used as substrate. OTS and FOTS were purchased from Lancaster, UK and were used as received. Iso-octane (99.5%, dry) and *n*-hexadecane (99+%, anhydrous) obtained from Sd-fine-chem, India and sigma-Aldrich, USA, respectively were used as organic solvents. Deionised water, obtained by processing of distilled water through a Millipore purification system, was used to hydrolyse the aluminium substrate.

2.2. Sample preparation

Polycrystalline aluminium in strip (30×10×1.5 mm) and disc (10 mm diameter) dimensions were initially polished mechanically (sequentially with 1–3 and 0.25 μm diamond paste) to obtain 8–12 nm RMS (root mean square) roughness and then sonicated with acetone for 15 min to remove all polishing debris. The polished samples were kept in air for 1 h to generate a natural oxide film and then samples were sonicated with Millipore water for 30 min. Finally, the substrate was dried in a stream of dry nitrogen gas for 15 min and preserved in a desiccator. Before SAM deposition, samples were kept in a UV cleaning chamber for 30 min to burn off all carbonaceous contaminations, which would block adsorption sites. The aluminium samples, prepared as above, were immersed in freshly prepared additive solution (1 mM) for 1 h, taken out, rinsed and washed with iso-octane (twice) for 10 min to remove excess and physisorbed silane molecules. Finally the samples were kept in vacuum for 2 h.

2.3. FTIR analysis

All spectra were taken using Infra-Red Reflection Absorption Spectroscopy (IRRAS) on a Perkin Elmer GX