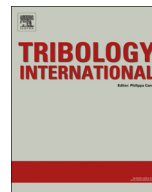




ELSEVIER

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Insights into sliding wear and friction behavior of copper in ethanol containing alkylphosphonic acid molecules



X. Roizard^{a,*}, J. Heinrichs^b, A. Et Taouil^c, S. Jacobson^b, M. Olsson^{b,d}, J.M. Melot^c,
F. Lallemand^c

^a Institut FEMTO-ST, DMA, UMR 6174, CNRS UFC ENSMM UTBM, F-25000 Besançon, France

^b Tribomaterials Group, The Ångström Laboratory, Uppsala University, SE-751 21 Uppsala, Sweden

^c Institut UTINAM, UMR 6213 CNRS, Université de Franche-Comté, F-25009 Besançon cedex, France

^d Materials Science, Dalarna University, SE-791 88 Falun, Sweden

ARTICLE INFO

Article history:

Received 6 October 2015

Received in revised form

15 December 2015

Accepted 26 December 2015

Available online 2 January 2016

Keywords:

Lubricated

Additives

Low friction

Phosphonic acids

ABSTRACT

In this work, the friction and wear behavior of bare copper was investigated for the first time under lubricated sliding conditions in diluted ethanol solutions of butylphosphonic (C4P), octylphosphonic (C8P), dodecylphosphonic (C12P), and hexadecylphosphonic (C16P) acids. The technique aims towards a more environmentally friendly lubrication to be used in shaping of copper sheets. Bare copper samples were subjected to unidirectional sliding using a tribometer with ball-on-disk contact geometry. Copper substrates (20 mm² × 1 mm) were run against 100Cr6 Ø10 mm ball bearing counterbodies. All tests were conducted using the same sliding conditions with a normal load of 10 N, tangential velocity of 0.01 m/s, at room temperature of 20 °C. Worn surfaces were analyzed by Scanning Electron Microscopy, Optical Microscopy and White Light Interference Profilometry. When comparing to sliding tests in the pure ethanol solvent, significant decreases in terms of wear track dimensions, transferred material on the ball and friction coefficients are observed when active molecules are present in the solution. These form protective tribofilms exhibiting lubricating and anti-wear properties.

Deeper studies on the tribological behavior of copper in C4P solution show that both low friction and low transfer of work material to the ball prevail in a specific range of low molecule concentration (5 × 10⁻⁴ M; 25 × 10⁻⁴ M). Even if the molecules are introduced during the test, after a few cycles, the tribological behavior improves, regardless of both friction level and copper surface degradation. Finally, specific friction tests were performed to further investigate the mechanisms. It was found that two mechanisms are involved; firstly molecules grafting onto the surface directly reduces friction, and secondly transformation of these grafted molecules into a tribofilm during the first mechanical contact cycles reduces it even further.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Copper is commonly used for various industrial applications primarily related to its excellent thermal and electrical conductivity. Metal forming processes of copper sheets, such as rolling, stamping and embossing, are widely used in the electronics industry. During the shaping operations, the mechanical stresses between the tool and the shaped metal sheet are very high. Therefore the sliding between these two parts need to be facilitated. In a lubricated tribological contact, friction and surface damage can be reduced by the use of anti-wear additives. Such additives are typically sulfur-, chlorine- and phosphorous-containing compounds designed to

react chemically with the metal surfaces, forming easily sheared layers of sulfides, chlorides or phosphides. These layers separate the two bodies and thereby promote low friction and prevent severe wear and seizure [1].

The application of inorganic nanoparticles has been the focus of particular research attention for some 30 years. The tribological properties of LaF₃ [2], graphite [3], polytetrafluoroethylene (PTFE) [4], MoS₂ [5], TiO₂ [6–8], La(OH)₃ [9], PbS [10], lanthanum borate [11], titanium borate [12], zinc borate [13], ferric oxide [14], ferrous borate [15], Ni [16], CaCO₃ [17] and ZnO [18] nanoparticles used as oil additives have all been investigated during this time. Results show that they can deposit on the rubbing surface and improve the tribological properties of the base oil.

Metallic surfaces can also be modified by using organic molecular assemblies [19,20]. This has proven to be a remarkable and powerful method to tailor surface properties, due to its simplicity,

* Corresponding author.

E-mail address: xavier.roizard@univ-fcomte.fr (X. Roizard).

adaptability and reproducibility [21]. Particularly, one of the most studied approaches used for substrates like copper is a self-assembly process of compounds like organothiols [22,23] or organoselenols derivatives [24]. Such compounds indeed chemically adsorb on Cu surfaces with a significant reduction of the initial oxide layer. This results in the formation of ordered and organized so-called “Self-Assembled Monolayers” (SAMs) [25]. However, in most cases, copper surfaces are covered with a natural oxide layer. In these cases, phosphonic acids, a class of important and widely studied molecules, could be useful. Indeed, they are known to spontaneously self-assemble on oxides [26]. Particularly, they have been reported to form strong metal O–P bonds on oxidized metals such as copper [27,28]. A large number of studies describe alkylphosphonic behavior in the form of well-organized SAMs. They are obtained through dipping substrates into a bath containing the active molecules dissolved in a solvent (mostly absolute ethanol), during a relatively long time (12–24 h), then dried and cleaned in order to remove the solvent and all the excess molecules that were not chemically adsorbed on the surface [27–30].

The novelty of this study is to use these organic molecules as nano-size liquid base lubrication additives ($< 1 \mu\text{m}$), with the purpose to form wear-protective low-friction films (=tribofilms).

This paper investigates the tribological properties of four alkylphosphonic acids with different chain length [butylphosphonic (C4P), octylphosphonic (C8P), dodecylphosphonic (C12P), and hexadecylphosphonic (C16P) acids] under ethanol-lubricated sliding conditions. First, we discuss the effect of chain length and molecule concentration on the friction behavior and material transfer onto the slider. Next, we present the grafting kinetics and tribofilm formation, and discuss their roles and influence on the friction level.

2. Experimental section

2.1. Chemicals

De-ionized water (Milli-Q, resistivity $18 \text{ M}\Omega \text{ cm}$) was distilled twice before use. 1-Bromobutane (ACROS ORGANIC, 99%, 109-65-9), 1-bromooctane (ALFA AESAR, 98%, 111-83-1), 1-bromododecane (ALFA AESAR, 98%, 143-15-7), hydrochloric acid (SIGMA ALDRICH, 37%, 7647-01-0), triethylphosphite (ALFA AESAR, 98%, 122-52-1), aqueous methanesulfonic acid (ALFA AESAR, 70%, 75-75-2), absolute ethanol (ACROS, pure, 64-17-5), sodium hydroxide (ACROS, 97+%, 1310-73-2), potassium hexacyanoferrate(II) trihydrate (SIGMA ALDRICH, 98.5+%, 14459-95-1), sodium sulfate (SIGMA ALDRICH, 99+%, 7727-73-3) were used as received.

2.2. Synthesis of alkylphosphonic acid compounds

All alkylphosphonate compounds were obtained following the Arbuzov–Michaelis reaction between triethyl phosphite and alkyl halides. For butylphosphonic acid (C4P), triethylphosphite was added dropwise at 190–200 °C into a threefold excess of refluxing 1-bromobutane under 45 min stirring. The distillate temperature was not allowed to exceed 45 °C. After further reaction (6–8 h), the mixture was cooled and excess 1-bromobutane was removed by atmospheric distillation. Diethyl butylphosphonate was then obtained at 102–107 °C (20 mmHg). It was then boiled with 10–12 M aqueous hydrochloric acid for 24 h. The clear homogeneous solution was concentrated *in vacuo* to a solid residue, which was dried at 80 °C for 2 h. Recrystallization in toluene afforded pure 1-butylphosphonic acid (yield: 85%).

Syntheses of octylphosphonic acid (C8P) and dodecylphosphonic acid (C12P) were carried out following a published

procedure [31], using 1-bromooctane and 1-bromododecane as starting compounds, respectively.

Diethyl hexadecanephosphonate was obtained according to the same procedure from 1-bromohexadecane. Acidic hydrolysis to corresponding phosphonic acid (C16P) was different: diethyl hexadecanephosphonate was mixed with 70% aqueous methanesulfonic acid and boiled during 24 h (bath temperature: 180 °C). Water was then added and the mixture was refluxed for additional 24 h. After cooling to 75–80 °C under stirring, technical acetone was added and precipitated hexadecane-1-phosphonic acid was filtered and washed with technical acetone until mother liquors were colorless (yield: 73%).

2.3. Pretreatment of the copper substrate

Copper substrates (CuA1, EN 1412) were used without additional polishing of their rolled surfaces. The surface roughness R_a was between 0.1 μm and 0.5 μm depending on the measurement direction relative to the rolling direction (anisotropic surface roughness). The copper surfaces were ultrasonically cleaned in absolute ethanol and distilled water for 5 min and then electrochemically reduced in 0.5 M aqueous perchloric acid under a current of $-800 \mu\text{A}/\text{cm}^2$ for about 120 s, until metallic copper potential was attained ($< -70 \text{ mV}/\text{SCE}$). The samples were cleaned again in aqueous nitric acid solution ($\text{pH}=1.8$) for 7 min and oxidized by exposure to a 5% aqueous hydrogen peroxide (H_2O_2) solution for 10 min at room temperature. This pretreatment led to three different appropriate states of oxidized copper, CuO , Cu_2O and $\text{Cu}(\text{OH})_2$ at the substrate surface, allowing the best grafting of phosphonic acid groups [25].

2.4. Friction test

The frictional properties of the treated copper substrates were tested in lubricated sliding against ball bearing steel balls (100 Cr6) in a rotational ball-on-disc setup. The balls had a diameter of 10 mm, the normal load was 10 N, and the rotational radius was 3 mm. The normal load used corresponds to a maximum Hertzian contact pressure of 840 MPa, a pressure very close to the Vickers hardness of copper (80 Hv). Three repeated tests were performed for each lubrication condition, all at room temperature. Both substrates and balls were ultrasonically cleaned in ethanol, prior to testing. During testing, both substrates and balls were immersed in the solvent (ethanol at 97%), either in pure form or containing a given concentration of alkylphosphonic acid molecules. The tests were performed with a total duration of 200 cycles, using a sliding speed of 0.01 m/s (about one revolution every two seconds), if no other information is given. However, some tests were interrupted earlier, enabling surface degradation analysis, or in order to introduce molecules into the solution. For detailed studies of the steady-state tribofilm appearance, a longer test of 7200 cycles was performed for the C4P molecule, at the same sliding speed. For each test, worn surfaces were analyzed by Scanning Electron Microscopy, Optical Microscopy and White Light Interference Profilometry.

3. Results and discussion

3.1. Friction behavior

The addition of alkylphosphonic acid molecules in alcoholic solution strongly reduced the friction between the copper disc and steel ball, see Fig. 1. With the selected molecule concentration ([0.001 M]), the friction coefficient stayed below 0.1 and kept stable, for all alkyl chain lengths. This value is similar in magnitude

Download English Version:

<https://daneshyari.com/en/article/614188>

Download Persian Version:

<https://daneshyari.com/article/614188>

[Daneshyari.com](https://daneshyari.com)