Tribology International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Tribology International

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

Friction behavior of ferritic stainless steel in a strongly diluted alcohol solution of alkylphosphonic acid

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ARTICLE INFO

Keywords:
Stainless steel
Forming
Low friction
Phosphonic acids

ABSTRACT

The present study investigates the potential for using this more environmentally friendly lubrication at an industrial scale forming of stainless steel. Against this background we analyze the characteristics of the tribofilm formed on a stainless steel surface during sliding experiments performed in solutions containing alkylphosphonic acids, under various contact conditions.

Specific tribological tests were designed to analyze the dynamics of the lubricating mechanism. It was found that both the grafting of molecules and the transformation of these into an efficient tribofilm are quick processes, irrespective of substrate roughness or contact pressure, systematically leading to low friction coefficient.

1. Introduction

Stainless steels are common metallic substrates daily used in a large number of applications, mainly due to their excellent corrosion properties (kitchen sinks, cutlery, watches, washing machines, automobile components, medical and chemical apparatus, etc….). Complex forming operations are in most cases required to carry out such technical parts. In addition to the intrinsic mechanical properties of the selected grade which are directly correlated to the composition and the resulting microstructure (austenitic, ferritic,…depending on mechanical specifications and part design), the use of an efficient and adapted lubricant is vital to avoid well-known issues of adhesion or transfer of work material to the tools during the forming processes [1,2]. Today, mineral lubricants, containing different friction modifiers and/or extreme pressure additives such as sulfur, chlorine or phosphorous, are the most efficient industrial solutions available on the market. It is particularly true concerning chlorinated paraffin CPs, whatever the carbon chain length, and the forming operations of stainless steel grades for which mechanical loads, friction and thermal conditions lead to the chemical activation of these additives. Indeed, these extreme pressure compounds (CPs) are designed to react chemically (in appropriate conditions) with the metal surfaces forming easily sheared layers of chlorides, acting as a protection of the surface [3].

However, CPs are facing to environmental restrictions (REACH, EPA), current or future, potentially limiting their use for forming operations because of their inherent eco-toxicity, their poor biodegradability and the carcinogenic risk represented by these compounds. Develop alternative solutions is so absolutely necessary to secure the sector's future by offering efficient and eco-friendly lubricant for the forming operations of stainless steels.

One way to avoid the use of a classical lubricant is to modify metallic surfaces by using organic molecular assemblies [4,5]. For example, Ulman [6] showed that ultrathin organic films are a remarkable and powerful way to tailor surface properties, due to their simplicity, adaptability and reproducibility. More recently, it has been proven that alkylphosphonic acids could be used to produce an easily sheared tribofilm during sliding [7,8]. The effect of alkylphosphonic acid molecules on wear resistance was recently demonstrated in alcohol, however most of the studies have been devoted to perfect copper substrates, ultrasonically cleaned, with a pretreatment leading to well-known appropriate states of oxidized copper [7,9,10]. In a very interesting review, Tang [11] included phosphorus compounds as friction modifiers, in the form of phosphates or phosphonates but never in the form of simple alkyl phosphonic acids.

In the present study, the frictional properties of non-pretreated ferritic stainless steels, with different surface states, were tested in

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http://dx.doi.org/10.1016/j.triboint.2017.04.027
Received 24 August 2016; Received in revised form 13 April 2017; Accepted 18 April 2017

lubricated sliding conditions against ball bearing steel balls, either in rotational ball-on-disk setup or in a linear unidirectional scratch tester. During testing, both substrates and balls were immersed in an alcoholic solution containing a given concentration of alkylphosphonic acid.

Friction measurements, surface analyses after tests and also experiments with special operating modes proved alkylphosphonic acids to be highly efficient as an additive, quickly forming an easily sheared tribofilm from grafted molecules after their transformation during sliding. These experiments also highlighted the importance of mechanochemistry to the behavior of lubricant additives in general well-known in the bibliography [12].

2. Experimental

2.1. Chemicals

De-ionized water (Milli-Q, resistivity 18 MΩ cm) was distilled twice before use. 1-bromoalkanes (ALFA AESAR, > 98%), hydrochloric acid (SIGMA ALDRICH, 37%, 7647-01-0), triethylphosphite (ALFA AESAR, 98%, 122-52-1), 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) and sodium sulfate (SIGMA ALDRICH, 99+%, 7727-73-3) were used as received.

2.2. Synthesis of alkylphosphonic acid compounds (we will use the abbreviation CP)

The Arbuzov reaction was performed in a distillation apparatus fitted with a 5–10 cm Vigreux column. Triethylphosphite (35 mL, 0.2 mol) was added dropwise during 2 h at 190–200 °C to the appropriate 1-bromoalkane (0.2 mol) while stirring. Distillate temperature was kept below 45 °C. After further reaction (30 min), the mixture was cooled and the crude phosphonate used without purification for the subsequent hydrolysis in alkylphosphonic acid.

Alkane-1-phosphonic acid (other than butane-1-phosphonic acid) was obtained by boiling crude diethyl alkylphosphonate (0.1 mol) in 12 M aqueous HCl (200 mL) for 18–24 h. After slow cooling to room temperature, the crude phosphonic acid was filtered and washed with water to pH > 3.

Recrystallization from cyclohexane afforded pure product in 60–70% yield.

2.3. Material

Ferritic stainless steel substrates (X2CrTiNb18 – 1.4509), were used as received, without additional polishing steps. The trade name K41 will be used thereafter. To investigate the effect from surface roughness on the tribological response in specifically designed tests, two surfaces finishes were used: an industrial finish “2B” and a manually polished substrate. Concerning the 2B roughness, this one was imprinted during the last rolling-step (skin-pass operation), leading to oriented roughness. 12 surfaces (2.84×2.16 mm^2 each) were measured. As the sample is flat enough we have considered that there is no waviness, in such a case no filter is required. The Table 1 combines the results for the two types of surface roughness. Concerning K41 2B surface texture, the kurtosis value is close to the normal distribution (equal to 3); and the distribution is symmetric (0 skewness). The distribution of polished K41 is left-skewed (height distribution is skewed above the mean plane) and is more peaked than a Gaussian distribution.

The Fig. 1 illustrates the “2B” industrial finish state obtained after a final skin-pass operation.

Table 1
Roughness parameters of K41 2B and polished K41.

	(ISO 25178)			
	Sa (arithmetic mean height)	**Sq** (root mean square height)	**Ssk** (Skewness)	**Sku** (Kurtosis)
K41 2B	0.35 µm ± 0.09	0.40 µm ± 0.11	−0.20 ± 0.10	3.50 ± 0.20
K41 – polished	0.08 µm ± 0.02	0.10 µm ± 0.02	−2.40 ± 0.40	7.80 ± 0.50

2.4. Tribological measurements

To explore the friction behavior, tests were performed on different tribometers: a rotational pin-on-disk tribometer (with a circular track of 3 mm radius) and a scratch tester (with a linear track of 10 mm). Since tribofilms are formed through agglomeration and compaction of wear fragments, wear particles generated in a rotating test have a smaller likelihood of existing in the wear track, and fragments pushed in front of the ball will instead be integrated into the tribofilm. We have almost the same phenomena in using scratch tester but some of wear particles can be observed outside the end-point of the wear track, after having been pushed in front of the ball. But the crucial difference is that, in the case of scratch tester, there is a constant sliding direction with the rolling direction.

In both tests, the counter surface was a steel ball (100Cr6) with a diameter of 10 mm applying a normal load of 10 N (leading to a Hertzian mean contact pressure of 680 MPa). However, to investigate the effect of roughness tests were also performed using a Si_3N_4 ball (very smooth in comparison to the steel ball) and different normal loads, up to 50 N, which corresponds to a Hertzian mean contact pressure of 1.28 GPa.

The sliding speed was 0.01 m s^{-1} for rotational pin-on-disk experiments and 0.01 m min^{-1} for the scratch tests. These two sliding velocities are too low to allow hydrodynamic effect. For each lubrication condition (dry sliding and lubricated sliding in pure solvent or containing 0.001 M CP dissolved in solvent), three repeated tests were performed, at room temperature, showing extremely accurate results and an excellent reproducibility. Prior to testing, substrates and balls were ultrasonically cleaned in ethanol. After the sliding tests all balls were analyzed by optical microscopy. The stainless steel sample surfaces were investigated using Scanning Electron Microscopy (SEM). The SEM analysis was performed using a low acceleration voltage of 2 kV to achieve surface sensitive imaging in order to have a better visibility of tribo-layers. Elemental composition was analyzed using Energy Dispersive X-Ray Spectroscopy (EDX).

3. Results and discussion

3.1. Friction behavior

Although galling occurred between the stainless steel disk and the steel ball already before 100 cycles in dry conditions (without any lubricant) the sliding behavior was relatively stable in the pure solvent (see Fig. 2), with µ slowly increasing up to a stable value close to 0.4. The very initial friction was high in both cases, followed by a linear increase with the number of sliding cycles.

Contrastingly, the addition of alkylphosphonic acids in alcoholic solution strongly reduced the friction, as shown in Fig. 2 (green line). With the selected contact conditions (pin on disk, V=0.01 m s^{-1}, P=10 N), the friction coefficient stayed invariably stable below 0.1. This value is similar to previous results obtained on copper substrates, under the same testing conditions but using different solutions containing molecules of several alkyl chain lengths [9]. Moreover, the friction