Tribology International 112 (2017) 103–107

Contents lists available at ScienceDirect

Tribology International

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

Short Communication

Local chemo-mechanical insights into the efficacy of ZDDP additives from *in situ* single asperity growth and mechanical testing

Xuying Liu[a], Ching-Yen Tang[a], Rui Hao[a], Kathleen Walsh[b], Chunliang Zhou[c], Shen J. Dillon[a,b,*]

[a] Department of Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana, IL, USA
[b] Materials Research Laboratory, University of Illinois Urbana-Champaign, Urbana, IL, USA
[c] School of Power and Nuclear Energy Engineering, Harbin Engineering University, Harbin, 150001 Heilongjiang, PR China

ARTICLE INFO

Keywords:
ZDDP
Mechanical properties
Chemistry
TEM

ABSTRACT

This work combines nanoscale tribological wear methods, used to prepare zinc dialkyldithiophosphate (ZDDP) tribofilms under conditions of controlled loading, with site specific nanopillar compression testing to derive a relationship between the ZDDP growth conditions and resultant mechanical properties. The key finding is that ZDDP films grown at higher loads exhibit lower yield strengths, which correlate with differences in tribofilm chemistry. We hypothesize that the load sensitivity of tribofilm properties may underlie the efficacy of ZDDP in suppressing wear by functioning as a hard coating at low loads while exhibiting enhanced lubricity at high loads.

1. Introduction

Engineering optimized lubricant additives underlies the efficient function of engines and mechanical systems. Antiwear additives improve system lifetime and have become increasingly important in engines functioning in ever more extreme environments [1]. The most successful and prolific antiwear additive, zinc dialkyldithiophosphate (ZDDP), has been an important lubricant component since the 1940's [2–4]. The removal of lead from automotive fuels placed ZDDP amongst the most important antiwear additives for automotive applications. However, phosphorous and sulfur tend to poison metal nanoparticle catalysts present in catalytic converters [5]. This fact motivates significant efforts in the last two decades to reduce or replace ZDDP. Suitable complete replacements have evaded discovery partially owing to our limited understanding of the deformation mechanisms of ZDDP during wear and the fundamental properties underpinning its efficacy [6].

Elucidating the fundamental constitutive properties of ZDDP underlying its antiwear efficacy presents challenges due to both the chemomechanical complexity of wear and the chemical heterogeneity of ZDDP tribofilms [3,7–12]. ZDDP films typically contain glassy phosphates, zinc polyphosphates, zinc sulphides, and when grown on metallic substrates the films also contain other metal sulphides and oxides [3,13,14]. The chemical distribution in tribofilms exhibit spatial heterogeneity on the micron and nanoscale both laterally and out of plane [15–17]. This distribution may result in part from the thermo-mechanical nature of ZDDP tribofilm formation, where they can grow via a thermally activated decomposition at elevated temperatures, stress dependent mechanically activated contact sliding at lower temperatures, or a synergistic combination of the two effects [6,12]. Tribological stress during sliding wear inherently localizes at micro-scale and nanoscale asperities, which likely induces the chemical heterogeneity observed in tribofilms. Kinetic growth models for ZDDP tribofilm formation as a function of stress and temperature were recently established based on single asperity contact growth studies using diamond coated atomic force microscope tips [6]. The growth rate was given by,

$$\Gamma = \Gamma_o exp\left(-\frac{\Delta U - \sigma \Delta V}{kT}\right)$$

where U is the internal activation energy, V is the activation volume, σ is applied stress, kT is the thermal energy. While the data could be fit well to a single activation energy (ΔU≈0.8 eV) and activation volume (ΔV≈3.8 Å^3), it remains to be determined whether the properties of the tribofilm that forms under different conditions are also nominally determined by a single descriptor. A number of nanoindentation based hardness values have been reported in the literature and range from 1 to 10 GPa with significant variations observed even within individual samples [8,16,18–25]. The discrepancies in the data suggest that the mechanical properties may in fact be sensitive to the local growth conditions and are inherently spatially heterogeneous. While efforts have been made in prior studies to correlated hardness and chemistry, the local growth conditions are not well known for bulk tribolayer formation. Indentation hardness measurements are not ideal for

* Corresponding author at: Department of Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana, IL, USA.
E-mail address: sdillon@illinois.edu (S.J. Dillon).

http://dx.doi.org/10.1016/j.triboint.2017.03.035
Received 3 January 2017; Received in revised form 16 February 2017; Accepted 31 March 2017
Available online 05 April 2017
0301-679X/

spatially heterogeneous materials because they sample volumes much larger than the indent size. They may also be subject to substrate induced artifacts, particularly in films of unknown local thickness. However, the prior observations motivate the two primary questions being investigated here: i) are the properties of ZDDP tribofilms sensitive to growth load and, if so, ii) what are the correlations between growth conditions, chemistry, and film properties?

The emergence of single asperity ZDDP growth techniques and site-specific nanopillar mechanical properties characterization provide an unprecedented opportunity to correlate tribofilm growth conditions and their associated properties [6,26–28]. In this effort, we induce localized tribofilm growth from 1% ZDDP polyalpha olefin solutions onto silicon wafers under contact sliding of a 2.5 μm diameter cono-spherical diamond tip under different applied loads at 80 °C. Si serves as a model substrate to characterize the inherent properties of the ZDDP free of artifacts associated with chemical reactions with the substrate. We characterize the chemistry of the deposited tribofilms via energy dispersive spectroscopy (EDS) and auger electron spectroscopy (AES), and quantify their mechanical properties through in-situ transmission electron microscopy based nanopillar compression. The experimental approach allows us to directly correlate the relationship between single-asperity growth conditions and the resultant materials properties, providing new insights into the factors governing the performance of ZDDP tribolayers.

2. Experimental methods

We prepared synthetic base-stock by mixing of 3.3 wt% commercial break-in oil additive (containing 30 wt% Zinc Dialkyldithiophosphate) with 96.7 wt% Dec-1-ene (homopolymer hydrogenated, 100 wt%, INEOS Oligomers, Feluy, Belgium). The base-stock was placed in an aluminum pan and contacted to a heating stage with silver paste. Pre-cleaned Si wafers were immersed in the oil and heated to 80 °C. Tribofilms were grown under a 2.5 μm cono-spherical diamond tip (90°, VR25736, Micro Star Technologies, Huntsville, TX) in a TI-950 TriboIndenter (Hysitron, Inc., Minneapolis, MN). Films were grown at a 3 Hz scan rate and different loads between 175 μN and 700 μN in 5 μm×5 μm squares. Thermal films with similar thickness were grown in the same base stock at 150 °C for 13 h on Si substrates. The films were cleaned by rinsing in hexane (98.5%, Fisher Scientific, Hampton, NH) to remove remaining base-stock and dried in an Ar filled glove box. Auger electron spectroscopy was performed in a PHI 660 scanning Auger microprobe. Raman spectra were obtained on a Horiba confocal Raman using a 532 nm laser source (Fig. S2).

In order to protect the films and provide a contacting plane during nanocompression, 300 nm thick Cr (99.95%, Lesker) layers were deposited on top of the films by Magnetron Sputtering (AJA International INC. N Scituate) under 3 mTorr Ar with a base pressure below 10^{-6} Torr. Nanopillar samples were fabricated through focused

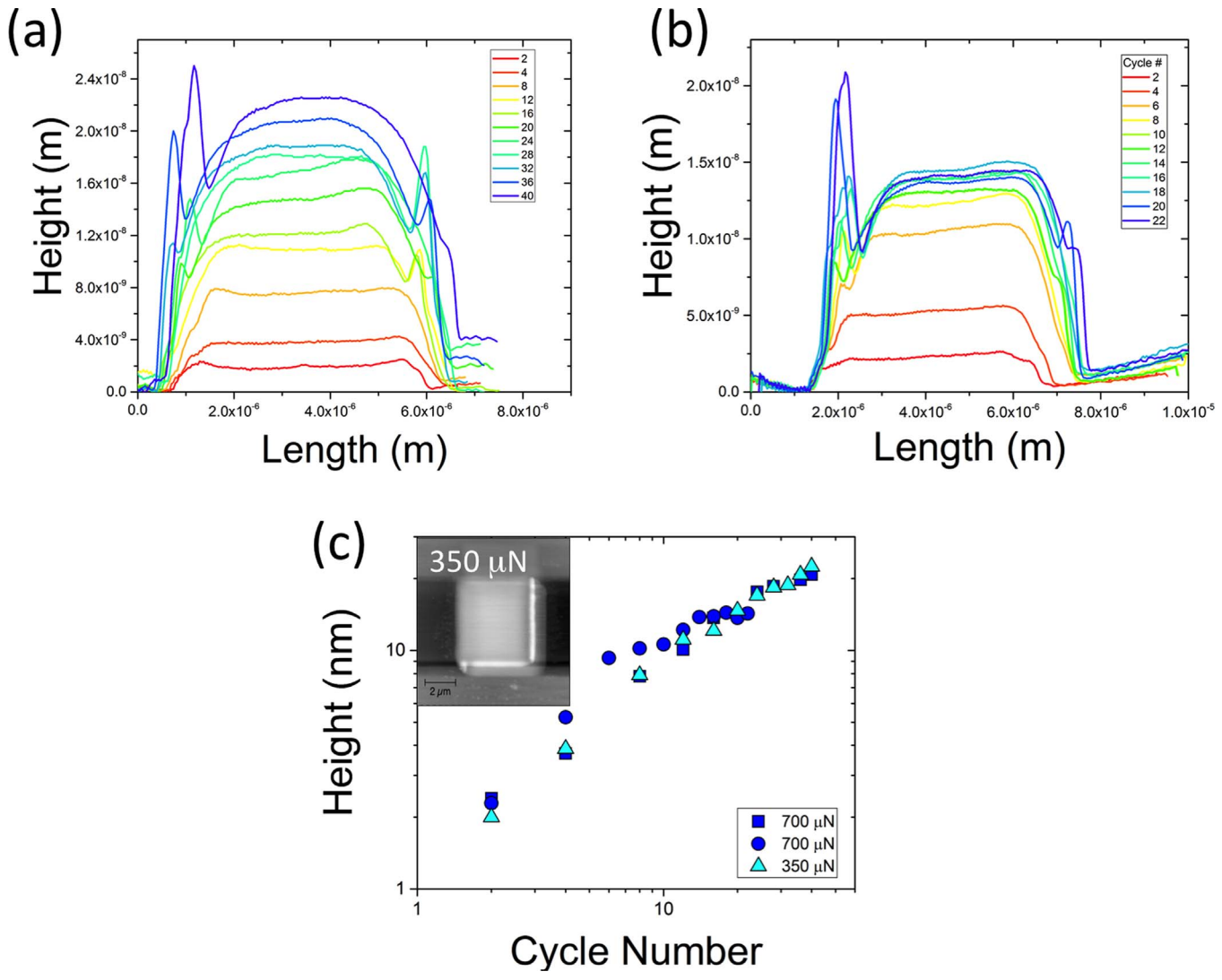

Fig. 1. Height profiles measured in-situ during ZDDP tribolayer growth at (a) 350 μN and (b) 700 μN. The height versus cycle number is plotted in (c) along with an example scan probe topographic of the film obtained in-situ.