Reconstruction mechanisms of tantalum oxide coatings with low concentrations of silver for high temperature tribological applications

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(Received 28 August 2014; accepted 30 October 2014; published online 12 November 2014)

Silver tantalate (AgTaO_3) coatings have been found to exhibit outstanding tribological properties at elevated temperatures. To understand the mechanisms involved in the tribological behavior of the Ag-Ta-O system, tantalum oxide coatings with a small content of silver were produced to investigate the metastable nature of this self-lubricating material. The coatings were produced by unbalanced magnetron sputtering, ball-on-disk wear tested at 750 °C, and subsequently characterized by X-ray diffraction, Scanning Auger Nanoprobe, cross-sectional Scanning Electron Microscopy, and Transmission Electron Microscopy. Complementary molecular dynamic simulations were carried out to investigate changes in the chemical and structural properties at the interface due to sliding for films with varying silver content. Both the experimental characterization and the theoretical modeling showed that silver content affects friction and wear, through the role of silver in film reconstruction during sliding. The results suggest that the relative amount of silver may be used to tune film performance for a given application. © 2014 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4901817>]

It is well established that high temperature working environments are still a major challenge for the tribology community. Oxidation of the commonly-used solid lubricants, such as MoS_2 and graphite, has hampered their use at elevated temperatures due to the degradation of material properties.¹ Solid lubricants that have been reported in the literature as well as used in industry when the temperature exceeds ~300 °C include noble metals, alkaline halides, Magnéli phases, and ternary oxides (also termed binary metal oxides).² These systems usually exhibit friction coefficients in the range of 0.1–0.4, depending on the selected material, working temperature, and load. For more detailed information on the properties of these materials as high temperature solid lubricants, the reader is encouraged to refer to the following review articles.^{3–6}

Very recently, silver tantalate (AgTaO_3) was reported to be a promising lubricant material at elevated temperatures.^{7,8} The measured coefficient of friction (CoF) at 750 °C was found to be as low as 0.04–0.06 in two recent studies conducted by our group. Additionally, transmission electron microscopy (TEM) revealed that the AgTaO_3 phase produced clusters of silver surrounded by Ta_2O_5 near the surface, where the applied stress was presumed to attain its maximum values. These features were reproduced in molecular dynamics (MD) simulations,^{8,9} and results indicated that the lubricious nature of AgTaO_3 at high temperatures was enabled by the joint contributions of the hard Ta_2O_5 phase and lubricious silver clusters in the shear- and temperature-induced surface layer. Theoretical and experimental cross-sectional images of the coatings in the wear track revealed that the

presence of Ta_2O_5 and silver increased dramatically closer to the interface whereas the remainder of the coating consisted primarily of AgTaO_3 with a very small amount of finely dispersed silver. Reconstruction of AgTaO_3 from the silver and Ta_2O_5 phases from mechanical mixing during wear testing has also been hypothesized.⁷ With increased normal force during testing, the diffusion and plowing of the silver from the surface increased, causing the coating to decrease in density and increase in porosity. MD modeling complemented the experimental results and supported the hypothesis that friction increased with load due to changes in the silver distribution and near-surface density.⁸ In the present study, we further investigate the suggestion that low friction in AgTaO_3 is enabled by the reconstruction of the material into silver and Ta_2O_5 by studying the tribological properties of Ag/ Ta_2O_5 nanocomposite coatings using experimental tools in tandem with MD simulations.

To execute this study, Ta_2O_5 with 14 at. % silver coatings were produced by unbalanced magnetron sputtering utilizing a ATC 1500 system (AJA International, North Scituate, MA) employing elemental targets of tantalum and silver (Power settings of 200 and 10 W, respectively), which were co-sputtered in a mixed atmosphere of Ar and O_2 (partial pressure 5.0 and 2.3 mTorr, respectively) for deposition on mechanically polished Inconel 718 substrates. Coatings with silver content in the 3 to 18 at. % range were also produced but will not be the focus of the current article since the conclusions from the experimental investigation were very similar (the same reconstruction mechanism was observed for all of them) and the coating with 14 at. % content displayed the best overall performance in terms of its friction coefficient and wear rates. Optical profilometry showed a coating thickness of $2.0 \pm 0.3 \mu\text{m}$. X-Ray

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diffraction (XRD) was performed on the coatings before and after wear testing. Ball-on-disk wear testing was performed (Nanovea, Irving, CA) at 750 °C against a 6 mm Si₃N₄ counterface in atmospheric humidity and air with a normal load of 2 N for 10 000 cycles. After the 750 °C sliding test, Auger electron spectroscopy mapping of the coating surface and wear track was performed and a FEI Nova 200 NanoLab dual-beam, focused ion beam (FIB) coupled with high resolution scanning electron microscopy (SEM), was employed to lift out a site selective cross-sectional TEM specimen from the center of worn regions.

Figure 1(a) shows XRD patterns for the films (i) before and (ii) after wear testing at 750 °C. XRD analysis of the as-deposited coating revealed the presence of Ta₂O₅. No silver-based phase was observed in the XRD pattern. Silver, present in low concentration, is likely to be evenly distributed throughout the film, similar to the study performed by Lee *et al.*¹⁰ on Ag:Ta₂O₅, where the silver concentration was higher than in the current study and they had to anneal the sample at 700 °C for 1 h to induce the formation of silver nanoparticles which were on the order of 5 nm in size. Since the lower silver concentration and the samples are not heat treated in this study, it is reasonable to expect that the silver is not on the order of dimensions observable by XRD. The coating was then subjected to high temperature wear testing at 750 °C. Figure 1(b) shows the frictional behavior of the Ta₂O₅/Ag coating. During the first 1350 cycles of the test, the coefficient of friction was in the 0.33 ± 0.19 range. As the test proceeded, the coefficient of friction steadily dropped to reach a value of 0.14 ± 0.09, which was maintained until the end of the test. Post-test XRD data (Fig. 1(a)) revealed the formation of two new phases, namely AgTaO₃ and silver deficient Ag₂Ta₄O₁₁. We believe that the deposited coating was metastable and that thermo-mechanical and thermo-tribological testing resulted in silver diffusing to the surface, which reacted with the Ta₂O₅ phase to produce AgTaO₃. The time-dependent enhanced lubricity of the coating is hypothesized to be the result of the increased silver content and the formation of the silver tantalate phases. In the steady state, we observed that friction was slightly higher for the Ta₂O₅/Ag system (0.14) than that reported for AgTaO₃ (0.06), but was much lower than that of Ta₂O₅ (0.5). Interestingly, the wear rate was lower for Ta₂O₅/Ag (1 × 10⁻⁷ mm³/N.m) than for the lubricious AgTaO₃ (4 × 10⁻⁷ mm³/N.m), probably due to the combination of the

low CoF and the relatively high hardness (due to the low silver content) of the tantalum oxide phase. The wear rate for Ta₂O₅ was found to be 8 × 10⁻⁶ mm³/N.m.

Figure 2(a) shows Scanning Auger Nanoprobe (SAN) maps acquired after wear testing at 750 °C. These maps demonstrate that silver had diffused to the surface of the coating as a result of the external thermal and mechanical stimuli. Silver was found to be primarily present in the middle and the outside of the wear track. This behavior is different from that observed for AgTaO₃ under the same testing conditions where silver was primarily pushed to the edges of the wear track.⁷ The incomplete coverage of silver in the wear track is likely the cause in the larger CoF on Ta₂O₅/Ag compared to AgTaO₃. This is supported by the observation that Ta₂O₅, which is a much harder phase that does not shear easily, displayed a CoF of ~0.5 under the same testing conditions. Fig. 2(b) shows high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of the wear track after wear testing of the Ta₂O₅/Ag coating at 750 °C. This figure reveals that the tribolayer consisted of two distinct regions, a highly porous top layer and a much denser underlayer. Throughout the dense and porous regions, we observed veins and particles of silver that agglomerated as a result of the sliding process. The highly porous regions are likely due to silver diffusion to the surface.

To complement the experimental measurements, we carried out MD simulations of a rigid hemispherical probe sliding over a tribofilm consisting of Ta₂O₅, Ta₂O₅/M at % Ag (M = 6.3, 14.3, 20.0, and 26.0), or AgTaO₃. The Ta₂O₅/Ag films were created by embedding ~8 nm³ regions of silver atoms into the Ta₂O₅ film, where the percent silver was adjusted by increasing the number of these silver regions. All films had dimensions of 16.30 nm (in sliding direction) × 11.44 nm × 3.88 nm. To mimic the near-surface reconstruction observed in the experiment, a mechanically-mixed tribofilm was created by first sliding a rigid plate (same cross sectional area as the film) over the material surface. Then the plate was removed and a probe was introduced into the model and slid on the resultant tribofilm. During the simulation, the bottom layer of the tribofilm was held fixed, and the probe with 2.72 nm radius moved laterally at a constant speed of 100 m/s for 1 ns with a timestep of 1 fs. The high sliding speed, which is larger than that in the corresponding experiment, is necessitated by the timescale limitation in MD simulations, particularly for the relatively large number of atoms in this

FIG. 1. (a) XRD of coating before (i) and after (ii) wear testing at 750 °C and (b) coefficient of friction of wear test coating at 750 °C over 10 000 cycles.

FIG. 2. (a) Scanning Auger electron spectroscopy mapping of the coating surface and wear track after wear testing at 750 °C and (b) cross-sectional TEM of the wear track showing elemental mapping along the line highlighted in the TEM image.

model. A normal load of 300 nN was uniformly distributed on the probe. The temperature of the system was maintained at 750 °C throughout the simulation using a Langevin thermostat. Periodic boundary conditions were applied in the sliding plane (otherwise, atoms were confined by the rigid boundaries). The friction force was measured as the average lateral force on the rigid probe during each cycle, where a cycle is defined by the probe crossing the periodic boundary of the simulation cell. Wear depth was defined as a vertical distance between the equilibrated film surface and the bottom of the wear track. To quantify the evolution of the films in response to sliding, as suggested by our previous studies,^{8,9} we identified silver clusters and characterized their size. A silver cluster was identified as a group of silver atoms consisting of at least four atoms with each neighboring distance less than 0.25 nm. In our simulations, the Modified Embedded-Atom Method was used to describe the atomic interactions using potential parameters developed specifically for AgTaO₃,¹¹ and all simulations were carried out using the open source code LAMMPS.¹²

Figure 3(a) shows the friction force for each model film. In general, the friction initially increased (consistent with a run-in process) and then approached a steady state around the fifth cycle. In the steady state, the Ta₂O₅ exhibited the highest friction, and then friction decreased with increasing silver content. This is consistent with trends reported in previous experimental work where adding/increasing silver decreased friction in Mo₂N/MoS₂/Ag¹³ and YSZ-Ag-Mo nanocomposites,¹⁴ as well as other coating materials (such as TiN, CrN, ZrN, DLC, and TaN).^{15,16} This correlation between friction and silver content can be attributed to the fact that silver facilitates sliding over a range of temperatures due to its low shear strength.¹⁷ We also observed that AgTaO₃ exhibited the lowest friction, slightly lower even than that of the Ta₂O₅/Ag film

with similar silver content (i.e., 20%), which is consistent with our experimental results.

The various model films were also characterized in terms of their wear resistance, as shown in Figure 3(b). We observe that the wear rate (slope of the depth vs cycle plot) reached approximately a constant value in steady state. Also, for each cycle, the wear depth increased with increasing silver content, with Ta₂O₅ exhibiting the best wear performance. We also observed less wear on the AgTaO₃ film than the Ta₂O₅/Ag films. This is inconsistent with the experimental result that Ta₂O₅/Ag exhibited less wear than AgTaO₃. However, it has been reported that the effect of incorporating silver into a coating is non-monotonic. Specifically, the wear performance of a coating material improves with a small amount of silver, but may deteriorate as more silver is added.¹⁵ The experimental results are consistent with the former trend while the simulation results reflect the latter. The discrepancy is likely related to relative sizes of the model and experiment. Specifically, in the 14 at. % silver model film, all the silver atoms are localized at the sliding interface, whereas, in the experiment, the silver is likely not distributed evenly within the film and the actual amount of silver in the material at the sliding interface may be less than 14 at.%. The simulation results in Figure 3(c) suggest that the actual percent silver in the interface during experiment is likely less than 6 at. %.

To understand the friction and wear trends, we analyzed the evolution of the silver content during sliding. Since both the number and size of silver clusters may affect friction, the overall contribution was quantified as the integral of the probability distribution of cluster sizes. In this study, we focused on the wear track and the silver clusters in that region. Figure 3(c) shows that silver clustering in all Ta₂O₅/

FIG. 3. Model-predicted (a) friction force, (b) wear depth, and (c) silver clusters for tribofilms with different compositions.

Ag films increased with silver content. This trend can be directly correlated to the decreasing friction with silver shown in Figure 3(a). However, the fact that the friction for the $\text{Ta}_2\text{O}_5/20 \text{ at.}\% \text{ Ag}$ and $\text{Ta}_2\text{O}_5/26 \text{ at.}\% \text{ Ag}$ was similar indicates that there is a limit to the friction reducing effect of silver. That is, once the silver content reaches some critical value ($\sim 20\%$ per the results in this simulation), the friction will no longer decrease with increasing silver content. As suggested by previous experimental results on $\text{WS}_2\text{-Ag}$,¹⁸ this behavior might be attributed to the depth of penetration of the probe, which gradually increases with silver content due to the softness of silver, leading to increased plowing stress in front of the counterface. This affects the wear behavior and is consistent with the wear results shown in Figure 3(b). The trends exhibited by the silver clustering in the AgTaO_3 suggests that the silver that is initially evenly distributed in the film gradually forms silver clusters that continue to provide low shear resistance as sliding progresses. The behavior of silver clusters in AgTaO_3 is further supported by a calculation of the average vertical displacement (upwards towards the surface) of silver during sliding, which we found to be 0.09 nm and 0.24 nm for the AgTaO_3 and $\text{Ta}_2\text{O}_5/20 \text{ at.}\% \text{ Ag}$ films, respectively. This, along with the silver cluster results, indicates that silver clusters form and migrate to the surface more gradually on the AgTaO_3 films than the $\text{Ta}_2\text{O}_5/\text{Ag}$ films, leading to both lower friction and wear.

In summary, $\text{Ta}_2\text{O}_5/\text{Ag}$ coatings with a silver content of 14 at. % were produced by unbalanced magnetron sputtering and were found to possess a surface that adapts over time as a result of the combination of elevated temperatures and sliding. Molecular dynamics simulations were performed to study the tribological properties for the films with different compositions. Both the experiments and simulations showed

that the surface of the coating was changed over time as a result of the migration of silver to the surface. These changes affected friction and wear of the sliding interface. Results from experiments and simulations revealed that friction decreased while wear increased with the increase in silver content in $\text{Ta}_2\text{O}_5/\text{Ag}$ films. However, both methods also showed that the lowest friction was always observed on AgTaO_3 . The lower CoF values for AgTaO_3 are probably due to the even distribution of the silver in this system and the gradual formation and migration of silver clusters to the interface. Interpreting wear performance was less straightforward since the experimentally-measured wear was smaller on the $\text{Ta}_2\text{O}_5/\text{Ag}$ films than the AgTaO_3 , while simulations predicted the opposite trend. This difference was attributed to localization of silver in the interface in a simulation that is unlikely to occur in the experiment. Overall, the results suggest that it may be possible to tune the friction and wear performance of Ag-Ta-O films by controlling the amount of embedded silver for a given set of operating conditions.

This research was supported by the Air Force Office of Scientific Research (Award No. FA9550-12-1-0221). The authors also gratefully acknowledge the Center for Advanced Research and Technology (CART) at the University of North Texas (UNT) for access to the experimental facilities used in this study.

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