



AFRL-OSR-VA-TR-2015-0166

---

**Atomic-Scale Tuning of Layered Binary Metal OxideS**

**ASHLIE MARTINI  
UNIVERSITY OF CALIFORNIA MERCED**

---

**06/01/2015  
Final Report**

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory  
AF Office Of Scientific Research (AFOSR)/ RTD  
Arlington, Virginia 22203  
Air Force Materiel Command

<b>REPORT DOCUMENTATION PAGE</b>				<i>Form Approved</i> OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services, Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p><b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</b></p>					
<b>1. REPORT DATE (DD-MM-YYYY)</b> 14-07-2015		<b>2. REPORT TYPE</b> Final Performance		<b>3. DATES COVERED (From - To)</b> 01-05-2012 to 30-04-2015	
<b>4. TITLE AND SUBTITLE</b> Atomic-Scale Tuning of Layered Binary Metal Oxides for High Temperature Moving Assemblies				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b> FA9550-12-1-0221	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> ASHLIE MARTINI				<b>5d. PROJECT NUMBER</b>	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> UNIVERSITY OF CALIFORNIA MERCED 5200 N LAKE RD MERCED, CA 95343-5001 US				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b> AFOSR	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>	
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> A DISTRIBUTION UNLIMITED: PB Public Release					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> The objective of this research was to understand, at an atomic level, the material properties that influence the thermal, mechanical and tribological behavior of intrinsically layered binary metal oxides at high temperatures. The initial focus was silver tantalate, which is a relatively simple system that could be accurately modeled but also has significant potential as a multi-functional material for high temperature applications. Investigations were performed through a tightly integrated experimental and modeling approach in which atomistic simulations are validated by experimental observations and then fundamental mechanisms underlying the experimental observations are explained by the simulations. The following is a summary of our key accomplishments through this project that brought us from the initial work of developing experimental and simulation capabilities for studying high temperature coating materials to investigating fundamental mechanisms to explain observed friction and wear behavior and finally to using that understanding to extend the research beyond its initial focus on AgTaO3 to other materials and future materials-based coating design.					
<b>15. SUBJECT TERMS</b> Atomic-Scale, friction coefficient, layered structure materials, Boron Nitride, Molybdenum disulfide, tribology, oxide materials					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b> ASHLIE MARTINI
<b>a. REPORT</b>	<b>b. ABSTRACT</b>	<b>c. THIS PAGE</b>			
U	U	U	UU		

				<b>19b. TELEPHONE NUMBER</b> <i>(Include area code)</i> (209) 228-2354
--	--	--	--	---

## Ashlie Martini and Samir Aouadi

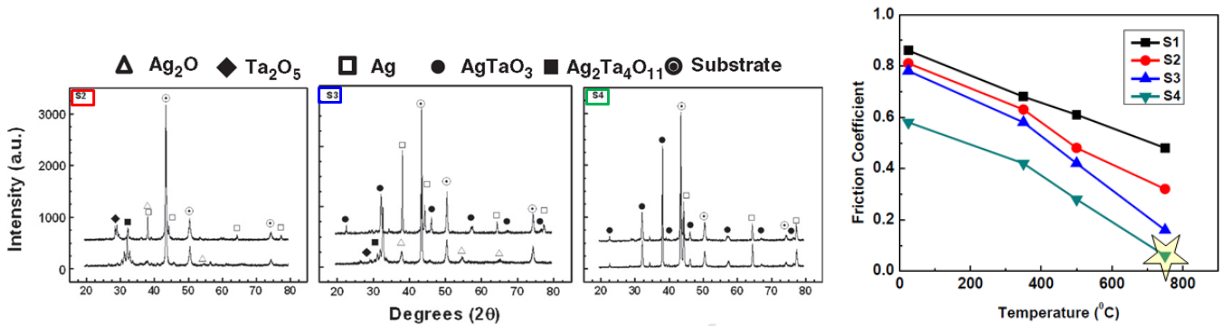
Grant # FA9550-12-1-0221

Final Report Submitted May 2015

The following is a summary of our accomplishments through this project that brought us from the initial work of developing experimental and simulation capabilities for studying high temperature coating materials to investigating fundamental mechanisms to explain observed friction and wear behavior and finally to using that understanding to extend the research beyond its initial focus on  $\text{AgTaO}_3$  to other materials and future materials-based coating design.

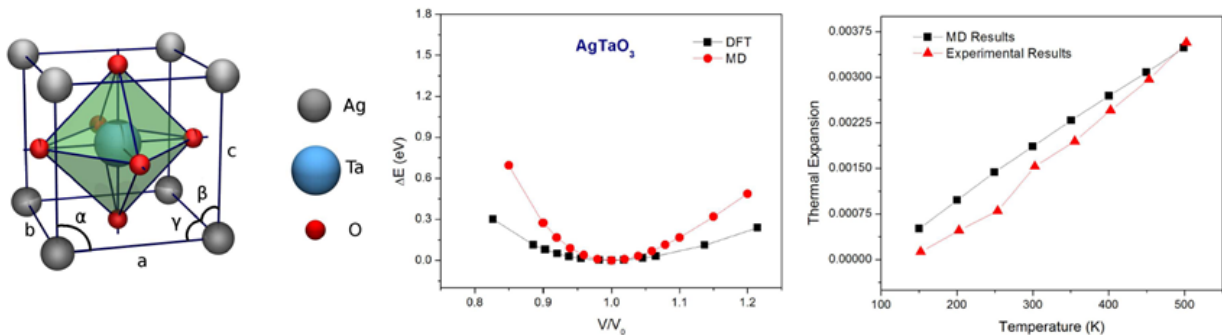
### Material synthesis and characterization

We optimized the process of synthesis via magnetron sputtering to produce thermally stable silver tantalate films. X-ray diffraction confirmed the material was indeed silver tantalate and remained in that phase at high temperature. We then measured friction on these coatings from room temperature to 750 °C and observed an extremely low friction coefficient of 0.06 at 750 °C; this is the lowest friction reported at this temperature for any material to-date.



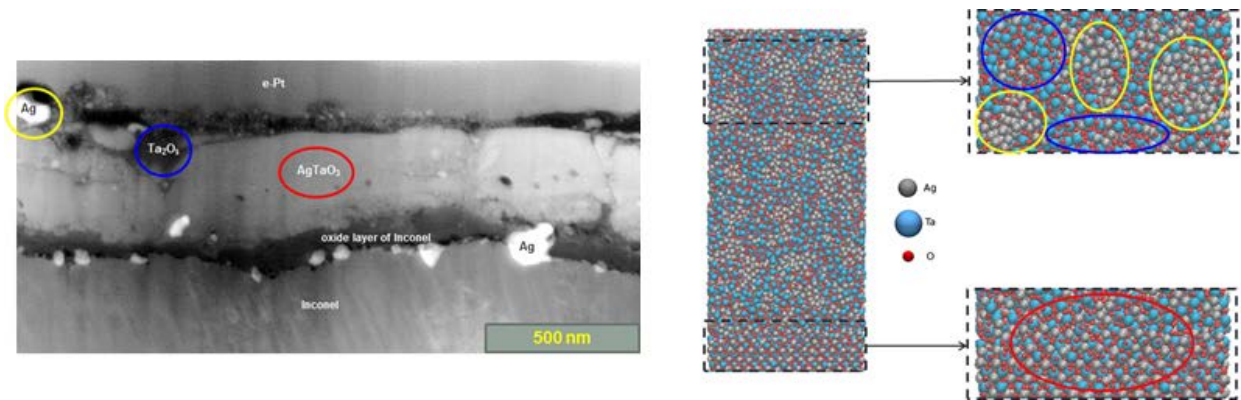
### Modeling methods development

We developed an empirical model to describe the interatomic interactions in silver tantalate and validated the model's ability to reproduce structural, energetic and thermal properties of the material. Density functional theory calculations were performed to provide the energetics and previous experimental measurements were used as a reference for the structure of the material and its evolution with temperature.



### Comparison of experimental and simulation results

We used the new model to perform atomistic simulations of sliding friction from room temperature to 750 °C and observed the same trend as in experiments, i.e. decreasing friction with increasing temperature where the lowest friction is observed at 750C. Results could not be quantitatively compared due to the size scale difference between the experimental (mm) and simulation (nm) contact areas. However, we analyzed the evolution in the model material during sliding and used high resolution transmission electron microscopy to characterize a cross section of the experimentally-measured material before and after sliding; both revealed segregation of the silver near the contact and the persistence of silver tantalate away from the sliding surface.

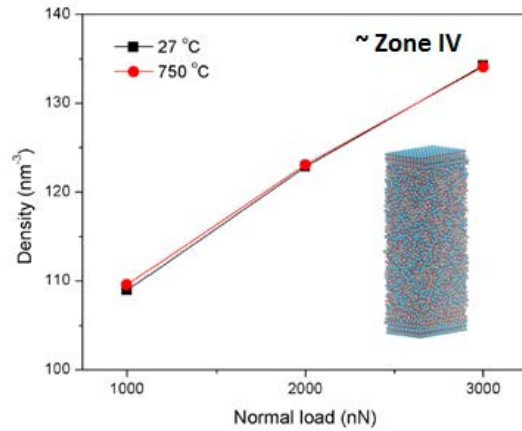
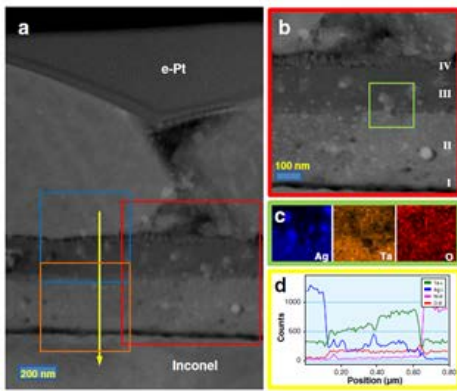


### Proposed sliding mechanisms

Using the experimental measurements and observations from simulation, we identified temperature- and sliding-induced silver segregation as a key mechanism enabling low friction at high temperature. All evidence we have gathered during this project suggests that the silver tantalate acts as a reservoir continually feeding the near-surface combination of silver and tantalum oxide, where the former provides a low shear lubricious phase and the latter is very hard thereby offering reasonable wear resistance.

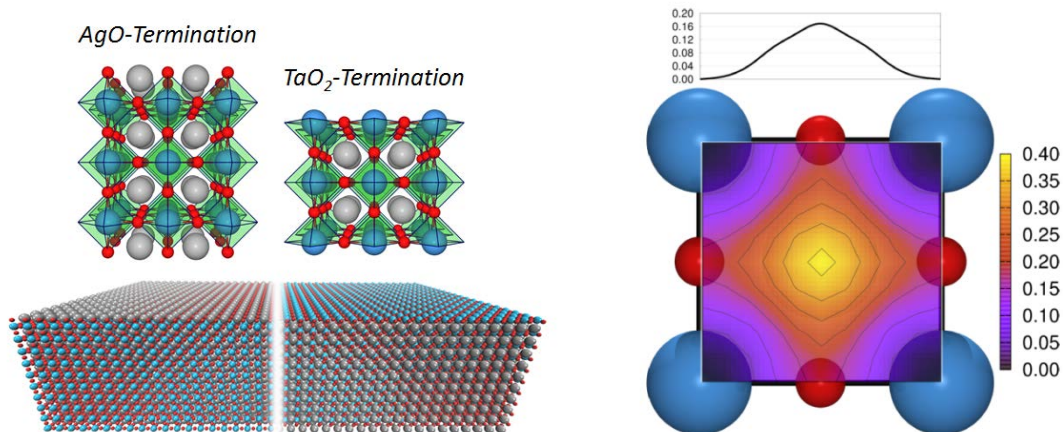
### Exploring the effect of load

Load is well known to affect both the magnitude of friction and wear and the mechanisms by which sliding occurs on solid surface. To explore this effect for AgTaO<sub>3</sub>, we characterized the load-dependence of its friction and wear at 750° using experiments and complementary simulations. These studies revealed the following: (a) friction monotonically increased with load, (b) increasing load decreased the amount of Ag on the surface of the wear track and decreased the thickness of the mechanically mixed layer that forms as a result of the reconstruction of AgTaO<sub>3</sub> into Ta<sub>2</sub>O<sub>5</sub> and Ag, and (c) the silver segregation and clustering (previously shown to be directly correlated to temperature dependence of the material) can also lead to porosity in the tribofilm, and the increase of friction with load is due to the joint contributions of decreasing Ag near the surface and the associated decreased porosity of the tribofilm.



### First principles-based justification of Ag-segregation mechanism

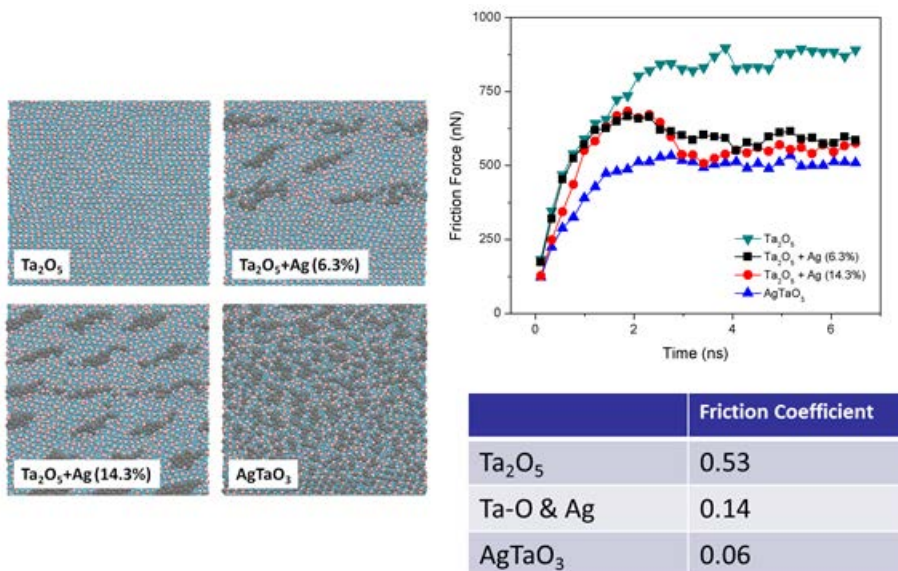
Our previous simulation and experimental results strongly suggested that Ag clustering is the key to the good performance of  $\text{AgTaO}_3$  at high temperatures. We now are able to provide quantitative, atomic-scale support for this argument based combined molecular dynamics and density-functional theory simulations of surfaces and their energetics. Specifically, we showed that silver aggregation on the surface is enabled by the low energy barriers associated with silver migration. Two different surface terminations ( $\text{AgO}$  and  $\text{TaO}_2$ ) were studied and we showed that the migration barrier on the  $\text{AgO}$  surface is smaller, favoring silver aggregation and ultimately giving a lower friction force. Regardless of the termination, the formation of soft silver clusters dominates the sliding behavior when enough energy (mechanical or thermal) is imparted to the surface.



### Tuning composition for optimized performance

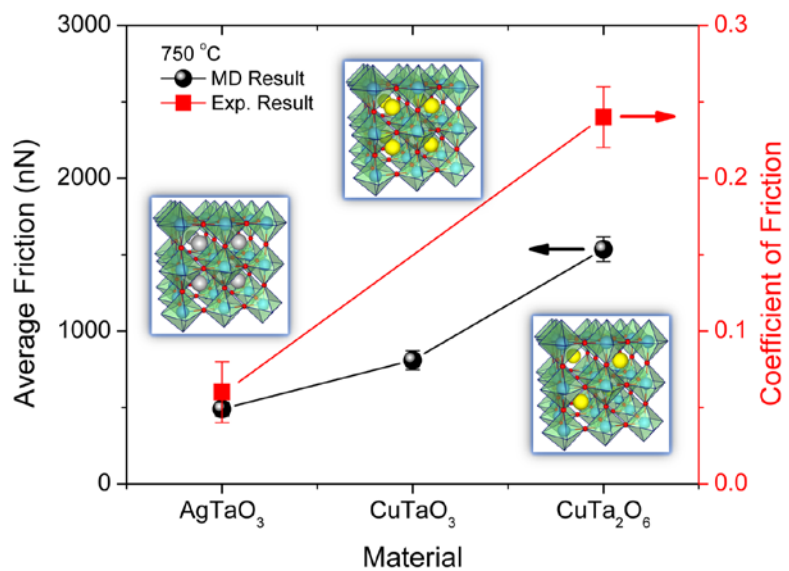
Based on the observation that  $\text{AgTaO}_3$  decomposes during sliding and the supposition that the products of this decomposition enable low friction and wear, it is possible that performance may be tuned by identifying an optimal combination of the elements in the material before sliding. To explore this possibility, we used experiments and complementary simulations to study coatings of tantalum oxide

with a small content of Ag embedded in it. Both the experimental characterization and the theoretical modeling indicated that silver migrated to the surface leaving a porous  $\text{Ta}_2\text{O}_5$  structure underneath. In addition, this migration resulted in the formation of  $\text{AgTaO}_3$  in selected regions of the coatings. The observed time-dependent surface reconstruction, which is associated with a continuous change in film structure and chemistry, resulted in a decrease in values of the friction coefficient. This study not only supports the previously-suggestion mechanisms in both Ag (soft low shear phase) and  $\text{Ta}_2\text{O}_5$  (hard phase resisting compression) play important roles, but that the composition can in fact be tuned to modulate friction under different conditions.



### Extension to other ternary oxides

Given the relatively poor wear performance of  $\text{AgTaO}_3$  and the issues associated with Ag particle migration, we have been exploring alternatives to obtain both low friction and high wear resistance. We have exploring Cu-Ta-O as a potential replacement. Specifically, we used experiments, density functional theory and molecular dynamics simulation to study  $\text{CuTaO}_3$  and  $\text{CuTa}_2\text{O}_6$ , and contrast their performance with that of  $\text{AgTaO}_3$ . Results show that the MD-predicted friction force follows the trend  $\text{AgTaO}_3 < \text{CuTaO}_3 < \text{CuTa}_2\text{O}_6$ , which is consistent with the experimentally-measured coefficients of friction. The wear performance from both MD and experiment exhibits the opposite trend, with  $\text{CuTa}_2\text{O}_6$  providing the best resistance to wear. The sliding mechanisms were investigated using experimental characterization of the film composition after sliding, quantification of Ag or Cu cluster formation at the interface during the evolution of the film, and DFT energy barriers for atom migration on the material surface. All analyses support the hypothesis that the formation of metal (or metal oxide) clusters on the surface are responsible for the friction and wear behavior of these materials.



1.

**1. Report Type**

Final Report

**Primary Contact E-mail**

Contact email if there is a problem with the report.

amartini@ucmerced.edu

**Primary Contact Phone Number**

Contact phone number if there is a problem with the report

209-228-2354

**Organization / Institution name**

University of California Merced

**Grant/Contract Title**

The full title of the funded effort.

Atomic-scale Tuning of Layered Binary Metal Oxides for High Temperature Moving Assemblies

**Grant/Contract Number**

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-12-1-0221

**Principal Investigator Name**

The full name of the principal investigator on the grant or contract.

Ashlie Martini

**Program Manager**

The AFOSR Program Manager currently assigned to the award

Ali Sayir

**Reporting Period Start Date**

05/01/2012

**Reporting Period End Date**

04/30/2015

**Abstract**

The objective of this research was to understand, at an atomic level, the material properties that influence the thermal, mechanical and tribological behavior of intrinsically layered binary metal oxides at high temperatures. The initial focus was silver tantalate, which is a relatively simple system that could be accurately modeled but also has significant potential as a multi-functional material for high temperature applications. Investigations were performed through a tightly integrated experimental and modeling approach in which atomistic simulations are validated by experimental observations and then fundamental mechanisms underlying the experimental observations are explained by the simulations. The following is a summary of our key accomplishments through this project that brought us from the initial work of developing experimental and simulation capabilities for studying high temperature coating materials to investigating fundamental mechanisms to explain observed friction and wear behavior and finally to using that understanding to extend the research beyond its initial focus on AgTaO<sub>3</sub> to other materials and future materials-based coating design.

First, we optimized the process of synthesis via magnetron sputtering to produce thermally stable silver tantalate films. X-ray diffraction confirmed the material was indeed silver tantalate and remained in that phase at high temperature. We then measured friction on these coatings from room temperature to 750 °C

and observed an extremely low friction coefficient of 0.06 at 750 °C; this is the lowest friction reported at this temperature for any material to-date. We then developed an empirical model to describe the interatomic interactions in silver tantalate and validated the model's ability to reproduce structural, energetic and thermal properties of the material. Density functional theory calculations were performed to provide the energetics and previous experimental measurements were used as a reference for the structure of the material and its evolution with temperature. We used the new model to perform atomistic simulations of sliding friction from room temperature to 750 °C and observed the same trend as in experiments, i.e. decreasing friction with increasing temperature where the lowest friction is observed at 750 °C. Both simulations and experiments revealed segregation of the silver near the contact and the persistence of silver tantalate away from the sliding surface. This observation suggested that low friction is possible because the silver tantalate acts as a reservoir continually feeding the near-surface combination of silver and tantalum oxide, where the former provides a low shear lubricious phase and the latter is very hard thereby offering reasonable wear resistance. Further investigation revealed that friction on AgTaO<sub>3</sub> increases with load, and that this trend is attributable both to the silver segregation mechanisms we first identified and the associated porosity in the tribofilm. These studies were complemented by combined molecular dynamics and density-functional theory simulations of AgTaO<sub>3</sub> surfaces (AgO and TaO<sub>2</sub> terminated surfaces) and their energetics through which we showed that silver aggregation on the surface is enabled by the low energy barriers associated with silver migration. Based on the observation that AgTaO<sub>3</sub> decomposes during sliding and the supposition that the products of this decomposition enable low friction and wear, we explored the possibility that performance may be tuned by identifying an optimal combination of the elements in the material before sliding. For this, we used experiments and complementary simulations to study coatings of tantalum oxide with a small content of Ag embedded in it. Both the experimental characterization and the theoretical modeling indicated that silver migrated to the surface leaving a porous Ta<sub>2</sub>O<sub>5</sub> structure underneath. In addition, this migration resulted in the formation of AgTaO<sub>3</sub> in selected regions of the coatings. The last major research focus of this project was extension to other materials, motivated by the relatively poor wear performance of AgTaO<sub>3</sub> and issues associated with Ag particle migration in components. Specifically, we studied Cu-Ta-O compounds and contrasted their performance with that of AgTaO<sub>3</sub>. Simulations and experiments showed that friction force follows the trend AgTaO<sub>3</sub> < CuTaO<sub>3</sub> < CuTa<sub>2</sub>O<sub>6</sub>. However, the wear performance was found exhibits the opposite trend, with CuTa<sub>2</sub>O<sub>6</sub> providing the best resistance to wear. The sliding mechanisms were investigated using experimental characterization of the film composition after sliding, quantification of Ag or Cu cluster formation at the interface during the evolution of the film, and DFT energy barriers for atom migration on the material surface. All analyses supported the hypothesis that the formation of metal (or metal oxide) clusters on the surface are responsible for the friction and wear behavior of these materials.

#### **Distribution Statement**

This is block 12 on the SF298 form.

Distribution A - Approved for Public Release

#### **Explanation for Distribution Statement**

If this is not approved for public release, please provide a short explanation. E.g., contains proprietary information.

#### **SF298 Form**

Please attach your SF298 form. A blank SF298 can be found [here](#). Please do not password protect or secure the PDF. The maximum file size for an SF298 is 50MB.

[AFD-070820-035.pdf](#)

**Upload the Report Document. File must be a PDF. Please do not password protect or secure the PDF. The maximum file size for the Report Document is 50MB.**

[FinalReport\\_20150518.pdf](#)

**Upload a Report Document, if any. The maximum file size for the Report Document is 50MB.**

#### **Archival Publications (published) during reporting period:**

Gao H, Otero-de-la-Roza A, Gu J, Stone DS, Aouadi SM, Johnson ER and Martini A, "(Ag,Cu)-Ta-O ternaries as high temperature solid lubricants", ACS Applied Materials & Interfaces, Under Review

Stone DS, Gao H, Chantharangsi C, Paksunchai C, Bischof M, Martini A and Aouadi SM (2014) "Reconstruction mechanisms of tantalum oxide coatings with low concentrations of silver for high temperature tribological applications", Applied Physics Letters, 105, 191607.

Aouadi S, Gao H, Martini A, Scharf TW and Muratore C (2014) "Lubricious oxide coatings for extreme temperature applications: A review", Surface and Coatings Technology, 257, 266.

Stone DS, Gao H, Chantharangsi C, Paksunchai C, Bischof M, Jaeger D, Martini A, Scharf TM and Aouadi SM (2014) "Load-dependent high temperature tribological properties of silver tantalate coatings", Surface and Coatings Technology, 244, 37.

Gao H, Otero-de-la-Roza A, Aouadi SM, Martini A and Johnson ER (2014) "Chemical Basis of the Tribological Properties of AgTaO<sub>3</sub> Crystal Surfaces", Journal of Physical Chemistry C, 118, 012125.

Dong Y, Gao H, Martini A and Egberts P (2014) "Reinterpretation of velocity-dependent atomic friction: Influence of the inherent instrumental noise in friction force microscopes", Physical Review E, 90, 012125.

Gao H, Dong Y and Martini A (2014) "Atomistic Study of Lateral Contact Stiffness in Friction Force Microscopy", Tribology International, 74, 57.

Dong Y, Li Q and Martini A (2013) "Molecular dynamics simulation of atomic friction: A review and guide", Journal of Vacuum Science and Technology A, 31, 030801.

Gao H, Otero-de-la-Roza A, Aouadi SM, Johnson ER and Martini A (2013) "An Empirical Model for Silver Tantalate", Modelling and Simulation in Materials Science and Engineering, 21, 055002.

Gao H, Stone DS, Mohseni H, Aouadi SM, Scharf TW and Martini A (2013) "Mechanistic studies of high temperature friction reduction in silver tantalate", Applied Physics Letters, 102, 121603.

D.S. Stone, S. Harbin, H. Mohseni, J.-E. Mogonye, T.W. Scharf, C. Muratore, A.A. Voevodin, A. Martini and S.M. Aouadi (2013) "Lubricious silver tantalate films for extreme temperature applications", Surface and Coatings Technology, 217, 140.

Gao H, Aouadi SM, Scharf TS and Martini A (2013) "High-Temperature Tribological Properties of Silver Tantalate", Tribology and Lubrication Technology, 69, 22.

Dong Y, Perez D, Gao H and Martini A (2012) "Thermal activation in atomic friction: revisiting the theoretical analysis", Journal of Physics: Condensed Matter, 24, 265001.

**Changes in research objectives (if any):**

N/A

**Change in AFOSR Program Manager, if any:**

N/A

**Extensions granted or milestones slipped, if any:**

N/A

**AFOSR LRIR Number**

**LRIR Title**

**Reporting Period**

**Laboratory Task Manager**

**Program Officer**

**Research Objectives**

**Technical Summary**

**Funding Summary by Cost Category (by FY, \$K)**

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

**Report Document**

**Report Document - Text Analysis**

**Report Document - Text Analysis**

**Appendix Documents**

**2. Thank You**

**E-mail user**

May 22, 2015 13:51:38 Success: Email Sent to: amartini@ucmerced.edu