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14. ABSTRACT
Double oxide phases that combine a transition metal and a noble metal have very recently become a subject of investigation as potential lubricious materials for high temperature tribological applications. In this award, silver molybdates and tungstates were produced in thin film and powder forms. The lowest frictional properties of these materials were measured at 600 °C to be 0.1 and 0.4 for the Ag2Mo2O7 and Ag2WO4 phases, respectively. The frictional performance of these materials was correlated to changes in their structural and chemical properties using

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Double oxide phases that combine a transition metal and a noble metal have recently become a subject of investigation as potential lubricious materials for high temperature tribological applications. Two selected double metal oxide phases, namely silver molybdates and tungstates, were produced in thin film and powder forms using magnetron sputtering and hydrothermal methods, respectively. The lowest frictional properties of these materials were measured at 600 °C to be 0.1 and 0.4 for the $\text{Ag}_2\text{Mo}_2\text{O}_7$ and $\alpha$-$\text{Ag}_2\text{WO}_4$ phases, respectively. Changes in the chemistry and crystal structure of these materials were investigated with increasing the temperature up to 600 °C using in-situ Raman spectroscopy, X-Ray diffraction and a differential scanning calorimeter. These tools revealed that the coatings went through a phase transition accompanied by a phase segregation of silver. Simulations performed to investigate the structural and thermal properties of these materials using ab-initio molecular dynamics (AIMD) method were in agreement with the experimental results. The structural and chemical information obtained using computational and experimental studies was correlated to their high temperature tribological performance. Moreover, a new double metal oxide based on the Ag-V-O system was created and tested at very high temperatures. This system was found to be lubricious (friction coefficient of 0.1) at temperatures as high as 1000 °C. This is a significant result given that this is the first solid lubricant that was found to perform well at these extreme temperatures. This finding will enable the design of new military machinery that operates at these high temperatures. Potential applications include solid lubrication for small caliber barrel and weapon action components, EM Gun rail materials, and helicopter engines.

INTRODUCTION
The use of solid lubricants (SLs) to reduce friction and wear between rubbing surfaces is the only alternative solution when service conditions are extreme such as the ones encountered in the aerospace, tooling, materials forming, automotive, and nuclear power industries [1-6]. Extreme operating conditions include high vacuums, high or cryogenic temperatures, radiation, dust, and corrosive environments [2]. However, SLs have their own shortcomings: they have a limited application range in terms of their lubricity with the working environment and are too soft making them less than adequate for wear reduction [4-6]. For example, graphite and molybdenum disulfide ($\text{MoS}_2$) are the most widely used SLs at room temperature. Graphite cannot provide lubrication in vacuum whereas $\text{MoS}_2$ degrades rather quickly in moist air. Both of these materials are not lubricious at high temperatures and lack the hardness that would make them resistant to wear in any environment. The shortcomings of using the traditional monolithic single phase SL overlayer are resolved by creating a chameleon coating that combines hard and lubricious phases. This chameleon coating literally adapts its “skin” to the working environment to reduce both the wear rate and the friction coefficient [5].
High temperatures are the harshest conditions for most tribological applications. The most commonly used SLs at high temperatures include soft metals (Ag, Cu, Au, In, Pb, Zn) and a few oxides (PbO and B$_2$O$_3$) or fluorides (CaF$_2$ and BaF$_2$) [2,7]. Unlike the commonly used SLs at room temperature referred to above, the coefficient of friction (CoF) provided by these materials is relatively high and ranges from 0.3 to 0.5. Very recently, new lubricious double metal oxides were found to exhibit very low CoFs at high temperatures (0.1-0.3) [8-11]. Most of the work concentrated on silver molybdates (AgMo$_x$O$_y$) because of their relatively low CoF ($\mu = 0.1$) but two other compounds in the same class of materials were investigated, namely silver vanadate and copper molybdate (AgV$_x$O$_y$ and CuMo$_x$O$_y$) [12]. Although the latter materials were not investigated systematically as a function of elemental composition, they performed satisfactorily ($\mu = 0.2$). Recently, our group created silver molybdate surfaces by investigating the tribological properties of Mo$_2$N/MoS$_2$/Ag nanocomposite adaptive coatings at high temperatures (600 °C) [10,11]. The performance of these coatings surpassed that of any other material reported in the literature with a CoF that was maintained at 0.1 for 300,000 cycles using a 1 N load. The test was stopped without coating failure. Optical profilometry measurements showed very little material build up in the wear track [11]. Raman spectroscopy and X-Ray diffraction (XRD) revealed the formation of lubricious Ag$_2$Mo$_2$O$_7$ in the wear track [11]. Sulfur was found to act as a catalyst for the formation of this compound [13].

We will perform computational and experimental studies to understand and correlate the structural, thermal, chemical, and frictional properties of selected double metal oxides, namely Ag$_2$Mo$_2$O$_7$ and Ag$_2$WO$_4$. These two compounds were selected for this first study on this class of materials hoping to create computational tools that will provide the theoretical foundation to enable the future design of new lubricious compounds of the form MeTM$_x$O$_y$ (Me = noble metal and TM = transition metal). We will show experimentally that only silver molybdates undergo a phase transition below 600 °C. Ab initio molecular dynamics (AIMD) calculations support the experimental data and provide an insight on the various changes that happen to both structures as a function of temperature.

RESULTS

Stoichiometric films of Ag$_2$Mo$_2$O$_7$ and Ag$_2$WO$_4$ were grown on inconel 718 discs (2.50 mm in diameter x 6.25 mm thick) with a reactive sputtering technique described in detail in [10]. Two different recipes were used for the creation of these films by sputtering: (1) by co-sputtering from a Ag and a Mo or W targets in an oxygen environment and (2) by co-sputtering from a Ag and a MoS$_2$ or WS$_2$ with no reactive gas and subsequently annealing the produced coatings in air at 700 °C for one hour. Hydrothermal methods described in [14,15] were also used to produce these materials in powder form to facilitate the investigation of its intrinsic thermal properties.

X-Ray Diffraction was used to determine the phase composition of the fabricated materials. Only samples that consisted of pure Ag$_2$Mo$_2$O$_7$ or Ag$_2$WO$_4$ phases were used for further evaluation. The friction coefficients ($\mu$) for the deposited coatings were measured at 600 °C against Si$_3$N$_4$ balls using a load of 1 N and were found to be 0.1 and 0.4 for Ag$_2$Mo$_2$O$_7$ and Ag$_2$W$_2$O$_7$, respectively. Gulbinski et al. [8] reported on the formation of relatively small amounts of silver molybdate compounds on the tribo-surface of Mo$_2$N/Ag coatings. They argued that the lubricious nature of this material is the result
of its softening or micro-melting within the tribo-contact at these temperatures. The phase diagram of silver molybdates were actually reported by Wenda [16]. According to this phase diagram, $\text{Ag}_2\text{Mo}_2\text{O}_7$ has a melting point at $T_m = 516^\circ\text{C}$. There are, however, no reports on the thermal and tribological properties of silver tungstates in the literature. Erdemir [17] formulated a crystal chemical model that stipulates that the larger difference in electronegativity values of oxide pairs the lower the CoF. Based on this assumption, the frictional properties of $\text{MoO}_3 - \text{Ag}_2\text{O}_3$ and $\text{WO}_3 - \text{Ag}_2\text{O}_3$ should have been very similar since the electronegativity of $\text{MoO}_3$ and $\text{WO}_3$ are almost the same (8.8 and 8.9, respectively) [17].

Raman scattering was utilized to investigate the crystal structure and phase transition of both compounds in the temperature range from 25 to 700 °C. Shown in Fig. 1 are the Raman spectra for both compounds as a function of temperature. The peaks at 912, 884, and 837 cm$^{-1}$ are due to stretching modes of $\text{MoO}_4$ units whereas the one at 663 cm$^{-1}$ is
due to bridging Mo-O-Ag bonds [18,19]. The peaks in the 200-400 cm$^{-1}$ range correspond bending modes [19]. The Raman scattering peaks became broader while their intensity decreased. The evolution of the peak intensities in Fig. 1 suggests that the signature of the bridging bonds (663 cm$^{-1}$) start to disappear before the stretching modes that correspond to MoO$_4$ indicating that they rupture first. At 550 °C, all of the peaks Raman peaks disappeared for the Ag$_2$Mo$_2$O$_7$ system confirming that the onset of a phase transition. The Raman peaks for the Ag$_2$WO$_4$ system did not disappear up to 600 °C suggesting that these materials did not melt. The occurrence of a phase transition at 509±1 °C was confirmed using a Perkin Elmer DSC7 differential scanning calorimeter (DSC) on Ag$_2$Mo$_2$O$_7$ powders (ΔH = 162.4±2 J/g). No phase transitions were observed for the Ag$_2$WO$_4$ system when tested up to 600 °C. Similar results were obtained using X-Ray diffraction that included a heating stage (Fig. 2). The diffraction peaks corresponding to silver molybdate disappeared at T > 500 °C and new peaks that correspond to silver emerged suggesting the occurrence of phase segregation.

The electronic structure for both double metal oxides was calculated using the projector augmented wave implementation of the density functional theory (DFT) using the Vienna ab initio simulation package (VASP) [20]. For the exchange correlation potential, the PW91 functional [21] was used in the generalized gradient approximation (GGA) calculations. A plane-wave cut-off of 600 eV was used. The ab initio molecular dynamics (AIMD) simulation at constant volume was carried out using 112 atoms for both double metal oxides. Fig. 3 shows diagrams of the crystal structure of silver molybdates at 800 °K as a function of time. The structure was found to become more disordered accompanied by a silver segregation. This disorder was found to be due to the weaker bond between the silver and oxygen atoms. In addition, silver molybdates have a layered structure that may shear easily at high temperatures because of these weak Ag-O bonds.

![Fig. 3: Ab initio MD simulations for Ag$_2$Mo$_2$O$_7$ at 800 °K at (a) 0 and (b) 63 metadynamics steps.](image)

Silver vanadates seem to have a similar structure and was therefore selected as a material to be investigated as a potential high temperature tribological material. These materials were produced as coatings and were tested at temperatures as high as 1000 °C and were found to have a coefficient of friction in the 0.1 to 0.2 range depending on their stoichiometry. These results are very encouraging since there is no known solid lubricant in the literature that has performed this well under these conditions.
References