TRIBOLOGICAL PROPERTIES OF Ag AND Cu DOPED TRANSITION METAL OXIDE COATINGS

W. GULBINSKI, T. SUSZKO, W. SIENICKI, B. WARCHOLINSKI
Technical University of Koszalin, Raclawicka 15-17, 75-620 Koszalin, POLAND; e-mail: gulbinsk@tu.koszalin.pl

SUMMARY

Results of ball on disc friction measurements carried out in air at temperatures from the range 100 to 700 °C for alumina substrates coated with pure molybdenum oxide MoO3 and vanadium oxide V2O5 are presented. Furthermore, copper and silver doped oxide coatings containing phases belonging to: Ag2O-MoO3; Cu-V2O5 and Ag-V2O5 systems have been deposited and studied.

Keywords: reactive magnetron sputtering, oxide coatings, high temperature friction

1 INTRODUCTION

High temperature friction in the presence of air and humidity is a process where oxidation plays an important role and is rather impossible to avoid. Oxides formed during this process are products of tribocatalytic reactions activated by the temperature of tribosystem and the energy dissipated in it. Their composition depends on structural or coating material used. Oxidation of molybdenum and vanadium containing hard coatings (Mo2N, Mo2C, VN, VC) leads finally to creation of stable oxides possessing easy shear lamellar structures (MoO3, V2O5) [1] and considered as potentially applicable as solid lubricants [2-3]. However, in pure state they are not useful for tribological applications and need to be modified. Several derivatives of these oxides are known but they have not been extensively studied yet in the context of their tribological properties. Among them, there are molybdates of selected metals (Ag, Pb) [4, 5] and vanadium oxide bronzes [6].

The aim of reported research was to elaborate deposition methods of these oxides and oxide derivative phases, to characterise the phase composition of deposits and to study their tribological behaviour at elevated temperatures during friction in air. We analyse transformation processes of coatings during high temperature tests and relate friction behaviour to phase changes which occur in them.

2 SAMPLE PREPARATION AND CHARACTERISATION METHODS

Pure oxide films were deposited on polished (Ra ≅ 0.1 µm.) alumina substrates using pulse-mode reactive magnetron sputtering, from metallic targets. More detail description of this deposition method was presented elsewhere [7]. Pure oxide coatings of about 2µm of total thickness were deposited as not preferentially oriented or as highly (0k0) or (00l) oriented for MoO3 and V2O5, respectively. For Cu and Ag doped coatings, the multilayer deposition procedure was used. It consisted in subsequent deposition of oxide (MoO3, V2O5) and metal (Cu, Ag) layer by layer. Deposition rates of components were estimated from profilometric thickness measurements. Two to twelve sublayers creating the coating were deposited alternatively from two magnetron sources. Thickness ratio of individual sublayers was calculated, assuming bulk density of components, to obtain required stoichiometry of the coating. The substrate temperature during deposition was equal to 450 °C and the same for all samples. Dependent on deposited coating this temperature was high enough or to low to activate a synthesis reaction. In the second case a post treatment in the chamber under Argon or air atmosphere was necessary.

The structural and phase identification of coatings was carried out by means of x-ray diffractometry for Co-Kα radiation. For supplementary phase identification, especially within a wear track, micro-Raman spectroscopy was applied. Exciting laser radiation wavelength was 488 nm. This identification was supported by reference Raman spectra of phases expected in coatings under study. These data originate from measurements on phases synthesised for this purpose in powder form by means of solid state reactions for Cu-V2O5, Ag-V2O5 systems and wet method for Ag2O-MoO3 one. Literature references concerning details of these syntheses can be found elsewhere [4, 6]. For all the phases synthesised in powder form, DTA-TGA measurements in air atmosphere were carried out to verify their oxidation sensitivity and to identify possible phase transformations as sublimation, melting or decomposition. Chemical composition of studied coatings was randomly checked by EDS method giving results remaining in good accordance with the composition estimated from sublayer thickness ratio.

Friction measurements were carried out in ball on disc configuration. These friction studies were material oriented, thus low loads and sliding speeds were chosen to extract as much as possible information about the coating before its destruction. The square samples, 20×20×0.7 mm3, were mounted at the rotating and resistively heated table. The temperature sweep was 10 °C/min in the temperature range 100 - 700 °C. The lower limit of temperature range was chosen to restrict effects of water adsorption-desorption at the sample surface. The measurements were carried out under normal load of 1 N and with constant speed 1 cm/s. Alumina balls, 8mm in diameter, polished to Rₐ less than
70 nm were used. The data were collected continuously by computer acquisition system (DASY-Lab) with the sampling frequency 5 Hz. The measurements for selected track were done during heating and subsequent cooling cycle, to illustrate reproducibility of observed behaviour and/or accompanying hysteresis effects. For reference, series of friction tests was done, in whole temperature range, for uncoated alumina.

3 RESULTS AND DISCUSSION

3.1 Uncoated alumina
Friction tests for uncoated alumina gave reproducible results collected at Fig.1.

As shown at Fig.1, in the experiment conditions, friction coefficient values change from 0.45 to 0.55 for temperatures in the studied range and are lower than reported in the literature [8]. Such a discrepancy of friction coefficient values is rather common because they depend on experimental conditions. Observed hysteresis is a result of irreversible changes, which occur at rubbing surfaces. However, the shape of the hysteresis loop is reproducible, within experimental error, for subsequent measurements. Thus, it means that observed changes of μ versus temperature are really temperature induced and are not a result of run in processes.

3.2 Ag-MoO₃ coatings
Coatings containing phases from this system were deposited as multilayers of oxide and silver. Independent on number of sublayers, final coatings were, according to XRD analysis, fully reacted already in as-deposited state. Thickness ratio of sublayers was changed to obtain final molar ratio of oxides in the range from 0 for pure MoO₃ to 1 for Ag₂MoO₄. According to the phase diagram of this system [4], three double oxide phases were found in the coatings. With increasing silver content that are: Ag₂Mo₄O₁₃, Ag₂Mo₂O₇ and Ag₂MoO₄.

At Figures 2 and 3, x-ray diffraction results and Raman spectra for selected coatings are compared with reference data for powders.

In the context of tribological studies it is interesting to mention that melting temperature, which is about 800 °C for MoO₃ drops quickly to about 530 °C for 18 mol% Ag₂O and than to 480 °C when Ag₂O content reaches 40 mol%. Figure 4 shows results of friction test for stoichiometric MoO₃ and Ag₂MoO₄ coatings.

Here, decrease of friction coefficient μ with temperature can be, in the first stage (200 – 430 °C), attributed to good known effect of oxides softening. For higher temperatures (above 450 °C), the melting of silver molybdate results in increase of μ. Above 600 °C, sublimation of MoO₃ begins and causes a distinct drop of μ for pure molybdenum oxide coating. For studied coatings, temperature hysteresis of μ is also observed. The
loop is wider in the case of MoO$_3$ coating for which the measurement temperature crossed the sublimation treshold.

### 3.3 Ag-V$_2$O$_5$ coatings

Besides the testing of tribological behaviour of pure vanadium oxide coatings, the aim of studies in this system was to synthesise, in thin film form, vanadium oxide bronze $\beta$-Ag$_{0.33}$V$_2$O$_5$, to test its thermal and oxidation stability and to perform friction tests for such a coating. The films of this bronze were produced by means of the same multilayer technique. Because of low reactivity of silver, the coatings were heated during 1 hour at 600 $^\circ$C in Argon atmosphere under normal pressure, directly in the deposition chamber. According to the literature data [6] confirmed by our DTA-TGA studies, this black, electrically conducting $\beta$-bronze which melts without decomposition above 650 $^\circ$C, is the most stable one in its whole existence range which extends from $x = 0.26$ to 0.48. It often coexists with two, isostructural phases with silver content responding to $x = 0.26$ and 0.40.

![Figure 5: XRD results for V$_2$O$_5$ and Ag$_{0.33}$V$_2$O$_5$ coatings compared with powder standards.](image)

For further studies, pure vanadium oxide V$_2$O$_5$ and $\beta$ bronze Ag$_{0.33}$V$_2$O$_5$ coatings were prepared and tested by x-ray diffraction – Figure 5, and Raman spectroscopy – Figure 6. As shown at Fig. 5, studied films are before tribo-tests single-phase in diffraction.

![Figure 6: Raman spectra for vanadium oxide and silver vanadium bronze coatings compared with powder data.](image)

Pure V$_2$O$_5$ remains unchanged also after the tribo-test. For bronze coating however, beside the main component ($\beta$-bronze) traces of another phase appear. They can be identified as $\delta$-Ag$_{0.68}$V$_2$O$_5$ and another $\beta$-phases Ag$_x$V$_2$O$_5$ where $x = 0.26$ or 0.40. Because of electron conductivity of $\beta$ bronzes, their Raman response is noisy. Nevertheless, the characteristic features can be found in powder and coating spectra. Also Raman analysis shows the change in the wear track but its clear interpretation is not possible yet.

![Figure 7: Dependence of friction coefficient on temperature for V$_2$O$_5$ and Ag$_{0.33}$V$_2$O$_5$ coatings.](image)

Results of friction test shown at Fig. 7 confirm stability of vanadium oxide coating resulting in good reproducibility of $\mu$ vs. $T$ curve. Above 200 $^\circ$C softening effects are observed. For temperatures higher than 660 $^\circ$C oxide melting results in an increase of friction.

Reproducibility of friction test results for $\beta$-Ag$_{0.33}$V$_2$O$_5$ coating is satisfactory. Interpretation of effects appearing between 200 and 600 $^\circ$C requires however further studies. Above 650 $^\circ$C typical, melting induced effect is observed.

### 3.4 Cu-V$_2$O$_5$ coatings

Using the same procedure as for silver containing vanadium bronze, coatings of its copper analogue were deposited. Even though Cu to V$_2$O$_5$ molar ratio was carefully controlled during the deposition, the final coatings were multi-phase and contained, beside an expected phase, several $\beta$-bronze phases differing in copper content ($0.26 \leq x \leq 0.40$). It is worth to mention here that this copper $\beta$-bronze is much less stable from silver containing one. According to literature data and our DTA-TGA measurements on powders, it begins to oxidise in air above 400 $^\circ$C to CuV$_2$O$_6$. We have to confess also that preparation of pure $\beta$-Cu$_{0.33}$V$_2$O$_5$ phase, free of V$_2$O$_5$ and other related phases is extremely difficult. The solid state synthesis of reference material was followed by several recrystallisation cycles under Argon atmosphere. The structure of reference powder and deposited coatings was studied in diffraction and shown at Fig. 8.

Raman spectra of studied coatings clearly confirm coexistence of $\beta$-Cu$_{0.33}$V$_2$O$_5$ phase and V$_2$O$_5$ in them. As shown at Fig. 9, especially in a wear track, signal originating from vanadium oxide becomes very distinct.
high temperature friction in air. For both materials, friction coefficient decreases from high values (0.7 - 0.8) at 100 °C to about 0.4 at 500 °C and then, while sublimation or melting begins, to about 0.3. In conditions of the experiment, no correlation was found between preferential orientation of MoO3 and V2O5 films and their behaviour in friction. We studied also properties of coatings consisting of phases created by doping of these oxides with copper and silver. The most interesting results were obtained for phases belonging to the Ag2O-MoO3 and Ag-β-V2O5 systems. High temperature friction coefficient for silver molybdate Ag2MoO4 and silver containing vanadium oxide bronze β−Ag0.33V2O5 reached 0.2 at 450 and 600 °C, respectively. These phases are stable and don’t decompose during melting. Furthermore, silver molybdate and other phases from this system are easily formed in air at temperatures above 500 °C, already for low concentrations of silver in MoO3. It results in significant lowering of melting temperature of the reaction product. We believe, that formation of such a phase, as a result of tribocatalytic processes, at the surface of hard coating (Mo2N, Mo2C) containing silver as dopant, can lead to decrease of friction.

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6 REFERENCES