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Tungsten oxide with different oxygen contents: Sliding properties

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Abstract

In this study, tungsten oxide coatings with 13 and 75 at% of oxygen were prepared by DC reactive magnetron sputtering from a pure W target in an $Ar+O_2$ atmosphere. The coating hardness (H) decreased with increasing oxygen content from 25 to 7.7 GPa. The values of H/E ratio were 0.08 and 0.07 for $W_{87}O_{13}$ and $W_{25}O_{75}$, respectively.

The tribological measurements were carried out on a pin-on-disc tribometer at room temperature, with a load of 5 N and steel 100Cr6, ceramic Si_3N_4 and Al_2O_3 balls as sliding partners. The wear track and wear debris were visualised by scanning electron microscopy and the chemical composition of the later was estimated by energy-dispersive X-ray analysis. The friction coefficient was rather high in case of the $W_{87}O_{13}$ coating reaching values in the range from 0.7 to 0.75 for both counterpart materials, and slightly lower for $W_{25}O_{75}$ (~0.50). The coating wear rate decreased with increasing oxygen content with the Al_2O_3 ball, while using Si_3N_4 ball as a counterpart showed an opposite trend. The coating with low oxygen content was more resistant to abrasive wear.

Keywords: Tungsten oxide; Reactive sputtering; Mechanical properties; Tribology

1. Introduction

The development of thin films for wear and abrasive protection was mainly connected with materials based on nitride and carbides of transition metals. However, these materials exhibit a significant drawback, a low oxidation resistance. Consequently, oxide materials have become more interesting for tribological applications due to their expected "oxidation stability" and their low tribo-oxidation sensitivity [1]. There are few research works dealing with tungsten oxide with different oxygen contents focused mainly on electrical and optical properties [2]. Only recently, the structural and the mechanical properties of the $W_{100-x}O_x$, with x from 0 to 75 at%, have been studied in an author's work [3]. Moreover, the tribological properties of tungsten oxides remain almost unknown. Lugscheider et al. [4] studied the tribological behaviour of the tungsten oxide with low oxygen content showing their good tribological properties. Greenwood et al. [5] studied the influence of the morphology of WO_3 coatings deposited by electron beam evaporation on the sliding properties concluding that the amorphous coatings exhibited higher friction coefficient and wear rate than the epitaxial ones.

The present study is focused on the tribological properties (friction coefficient and wear rate) of tungsten oxides. Two coatings were deposited by DC reactive magnetron sputtering, low ($W_{87}O_{13}$) and high ($W_{25}O_{75}$) oxygen contents, which represent two different tungsten oxide systems.

2. Experimental details

Tungsten oxide coatings were deposited by DC reactive magnetron sputtering from a tungsten target in an $Ar+O_2$ atmosphere onto high-speed steel AISI M2 substrates heat treated to have a hardness close to 9 GPa. The deposition runs were performed keeping constant the following parameters: total working pressure (0.3 Pa), target current density (10 mA/cm^2), substrate at floating potential, no substrate rotation, inter-electrode distance (65 mm) and substrate temperature (<350 °C, with no external heating). Thus, the only variable was the O_2 partial pressure, 0.03 and 0.15 Pa. Before deposition, an ultimate vacuum

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pressure better than 5×10^{-4} Pa was reached and the substrates surface was ion cleaned with an ion gun.

The chemical composition and structure were determined by a Cameca SX-50 electron probe microanalysis apparatus (EPMA) and an X-Pert Philips X-ray diffractometer (XRD), respectively. The mechanical properties of the coatings were evaluated by depth-sensing indentation technique using a Fischer Instruments—Fischerscope, with a maximum load of 50 mN. The adhesion/cohesion of the coatings was evaluated by scratch-testing technique using a Revetest, CSM Instruments. The load was increased linearly from 0 to 50 N, using a Rockwell C 200 μm radius indenter tip, loading rate of 100 N/min, and scratching speed of 10 mm/min.

Wear testing was done using a pin-on-disc tribometer (CSEM Instruments). Three different materials were used as counter-parts: 100Cr6 bearing steel, Si_3N_4 and Al_2O_3 balls with a diameter of 6 mm. All measurements were provided with a load of 5 N and a linear speed of 0.05 m/s, relative humidity of air was kept constant at $25 \pm 5\%$. The maximum static Hertzian pressure for an elastic contact between the ball and the coating was about 1.5 GPa (Al_2O_3) and 1.25 GPa (Si_3N_4).

The worn volume of the balls was evaluated by optical microscopy. The morphology of the coating surface, ball scars, wear tracks and wear debris was examined by scanning electron microscopy (SEM); the chemical analysis of the wear tracks and the wear debris was obtained by energy-dispersive X-ray analysis (EDX). The profiles of the wear tracks were measured by a mechanical profilometer. The wear rates of the ball and coating were calculated according to [6] as the worn material volume per sliding distance and normal load. The average value of five profiles measured on one wear track was used to calculate the coating wear rate.

3. Results and discussion

3.1. Chemical composition, structure and mechanical properties

The detailed description of the chemical composition, structure and mechanical properties of W–O coatings deposited by a DC reactive magnetron sputtering has been presented elsewhere [3]. Therefore, only a brief summary of the results for the two analysed coatings is presented here. The two tungsten oxide coatings, $W_{87}O_{13}$ and $W_{25}O_{75}$, were deposited with an oxygen pressure of 0.03 and 0.15 Pa, respectively. The coating $W_{87}O_{13}$ exhibits a mixture of α-W and β-W (or β-W_3O) structure, while the structure of $W_{25}O_{75}$ coating can be described as quasi-amorphous. Generally, the hardness of the tungsten oxide decreases monotonically with the increase in the oxygen content from ≈23 GPa for the pure W down to ≈7 GPa for WO_3 films [3]. A similar tendency is observed for the Young's modulus, which varied from 450 to 150 GPa. The loading/unloading curves of the coatings studied in the present work together with the corresponding values of the hardness and the Young's modulus are shown in Fig. 1. In contrast to the hardness values, the "plasticity index" represented by (H/E) is similar, 0.08 and 0.07 for $W_{87}O_{13}$ and $W_{25}O_{75}$ coatings, respectively. However, as will be shown later, neither hardness nor H/E ratio can be considered as a dominant parameter influencing tribological properties of studied tungsten nitrides. The adhesion/cohesion properties of the coatings were evaluated through the critical loads determined by scratching testing, which were defined as the loads for which the first cohesive and adhesive failures were observed. The tungsten oxides showed that the adhesion and the cohesion failures occurred simultaneously. Thus, only one value is presented as a critical load: 35 and 15 N for $W_{87}O_{13}$ and $W_{25}O_{75}$, respectively.

3.2. Tribological characterisation

The main feature of the sliding tests with 100Cr6 ball was the strong transfer of ball material to the coating surface during the first couple of laps. The adhered layer consisting, particularly, of iron oxides protected the coatings from the wear. Consequently, the friction coefficient dramatically increased to a value ~0.95, which corresponds to steel-to-steel sliding. The volume of worn material of the coating was negligible and, thus, it can be concluded that sliding against 100Cr6 balls under the conditions referred above causes no harm to the tungsten oxide coatings. The excellent coating wear resistance corresponds to the results published in [4]; however, no ball material transfer was observed in that study and the friction coefficient was as low as 0.2.

The average friction coefficients and the wear rates of the coatings sliding against the ceramic balls are summarised in Table 1, while the evolution of the friction coefficient with the number of laps is depicted in Fig. 2 (the friction curves for sliding against Si_3N_4 balls were almost identical). The friction coefficient was lower for the coating with the

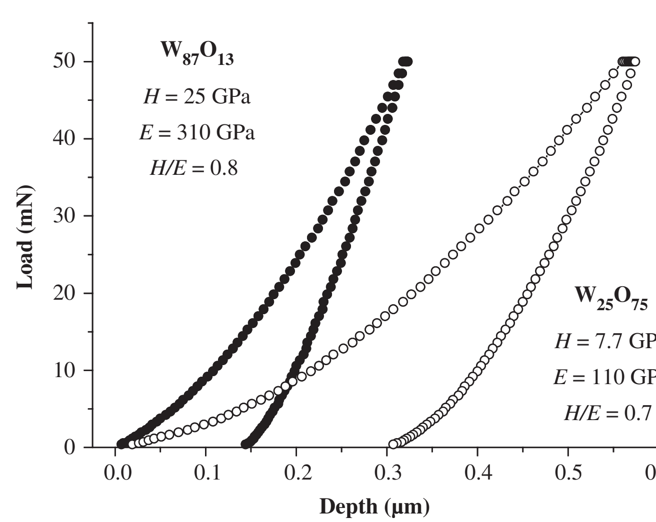

Fig. 1. Loading and unloading curves of tungsten oxide coatings.

Table 1
The mechanical and tribological properties of tungsten oxide coatings

Sample	Thickness (μm)	Hardness (GPa)	Young's modulus (GPa)	Friction coefficient		Wear rate ($\times 10^{-6} mm^3/N m$)	
				Al_2O_3	Si_3N_4	Al_2O_3	Si_3N_4
$W_{87}O_{13}$	2.5	25.0	310	0.73	0.69	4.40	0.96
$W_{25}O_{75}$	6.0	7.7	110	0.49	0.66	2.90	9.33

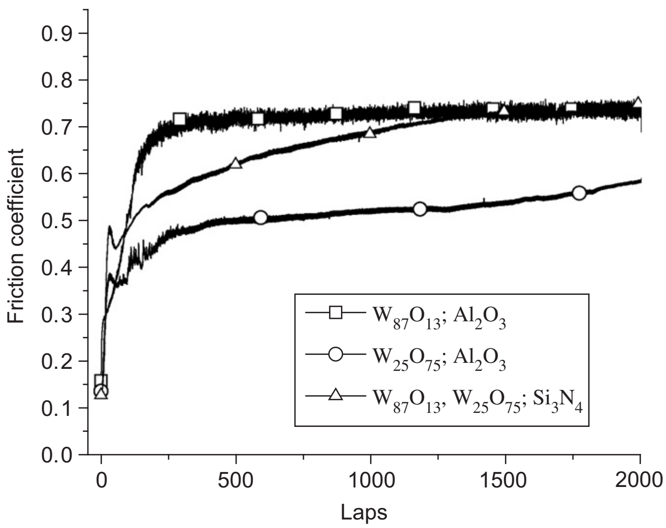

Fig. 2. Evolution of friction coefficient with number of laps.

higher oxygen content; however, for the wear the behaviour is different: (i) the $W_{87}O_{13}$ coating showed higher wear rates than $W_{25}O_{75}$ when sliding against Al_2O_3 and (ii) the sliding with Si_3N_4 balls worn significantly tungsten trioxide coating while the wear rate of $W_{87}O_{13}$ was negligible. The Al_2O_3 balls wear scars were negligible after the tests, while the wear of Si_3N_4 balls was significantly higher, as will be shown hereinafter.

To understand the friction and the wear behaviours, the analysis of the wear tracks and the ball scars by optical and scanning electron microscopies was carried out.

Fig. 3 shows the SEM micrographs of the wear tracks of the coatings when sliding against Al_2O_3 and Si_3N_4 balls. The presence of a third body with large cracks is obvious in the case of the $W_{25}O_{75}$ coating (Fig. 3c, d). However, it should be pointed out that the cracks in the adhered layer could not interfere the wear process, since they were induced after the pin-on-disc tests due to an ageing effect, as shown in our previous work [7]. In fact, a very dense and almost featureless third-body adhered to the coating surface was observed by optical microscope immediately after the sliding. Therefore, the cracks observed by SEM did not intervene during the sliding process. The results of the wear analysis can be summarised as follows:

1. $W_{87}O_{13}$ vs. Al_2O_3: The worn oxidised material only partially covers the coating surface (see Fig. 3a). Very shallow scratches in the wear track are visible.
2. $W_{25}O_{75}$ vs. Al_2O_3: A homogeneous and compact adhered layer of debris covering the wear track influences the wear by protecting the coating (Fig. 3b). Moreover, vestiges of a tungsten oxide layer transferred to the ball surface can be observed. The wear mechanism is typical of an almost exclusive third-body wear. The sliding of tungsten oxide against itself prevails after the rapid formation of the third-body leading to lower friction coefficients.
3. $W_{87}O_{13}$ vs. Si_3N_4: The wear rate of the coating is negligible; the sliding process only gives rise to a reduced surface roughness in the area of the contact. Conversely, the ball underwent a very high wear ($K = 760 \times 10^{-6} mm^3/N m$) being characterised as polishing wear.
4. $W_{25}O_{75}$ vs. Si_3N_4: Despite the presence of a large amount of wear debris in the wear track, this case is fundamentally different compared to the sliding against an Al_2O_3 ball. Fig. 3c clearly documents that there are large areas of the wear track not covered with the adhered layer. The ball wear rate is still very high, $K = 380 \times 10^{-6} mm^3/N m$ and the wear scar is very rough with sharp and deep scratches. Thus, it seems that the dominant wear mechanism influencing the tribological behaviour is a mixture of abrasive wear with third-body abrasive wear. The hard particles worn from the ball are embedded into the relatively soft layer formed by the wear debris of tungsten oxide causing further abrasion damage to both surfaces in the contact. Consequently, the rapid change in the surface morphologies induces the instability of the transferred layer, which is spalled off from one place and moved to another one. This is confirmed by the observation of the scratches in the worn track, which are overlapped by an adhered layer of wear debris, as documented in Fig. 3d showing in detail the SEM micrograph of the wear track.

The friction curves presented in Fig. 2 correspond to the wear behaviour of the tungsten oxide coatings described above. The running-in is about 200 laps for all the tested coatings. The friction coefficient is then stabilised, representing a steady-state wear regime when sliding against Al_2O_3 balls, while it progressively increases for Si_3N_4 counterparts. In this last case, the increase in μ should be connected with the high wear observed in the ball, since the sharp hard wear particles worn from the balls provoke a polishing or a polishing/abrasive wear causing the

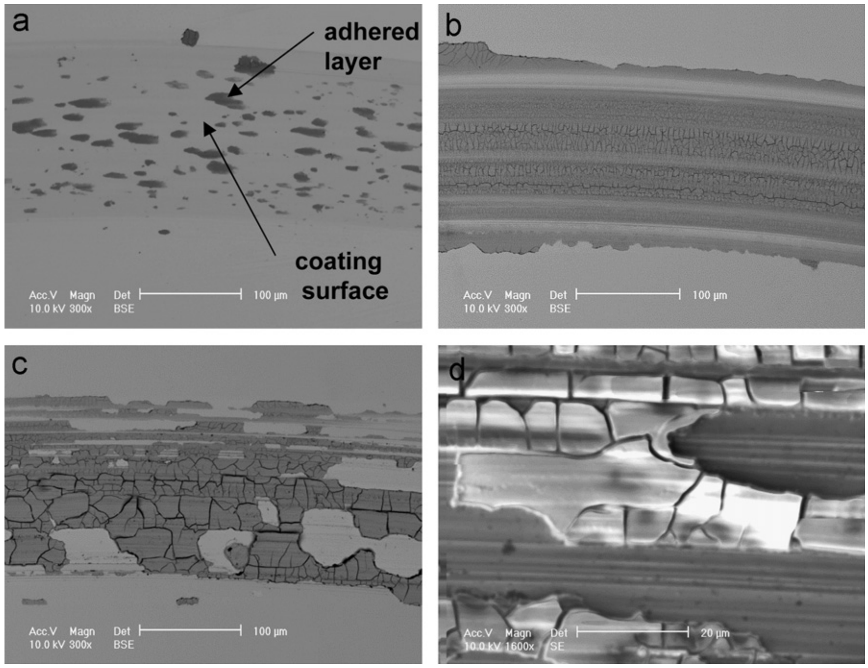

Fig. 3. SEM micrographs of the wear track produced by sliding: (a) $W_{87}O_{13}$ vs. Al_2O_3, (b) $W_{25}O_{75}$ vs. Al_2O_3, (c) $W_{25}O_{75}$ vs. Si_3N_4 and (d) details of the adhered layer.

permanent increase of the friction. The higher hardness of the $W_{87}O_{13}$ coating prevents the significant damage of the coating and the wear is exclusively limited to the ball. The ball wear rate is then much higher than that of the sliding couple with softer $W_{25}O_{75}$ coating. Thus, the wear resistance against the abrasive wear is much higher in the case of the low oxygen coating.

4. Conclusions

Tungsten oxide coatings were deposited by reactive DC magnetron sputtering. The coating with low oxygen content exhibited a mixture of α-W and β-W (or β-W_3O) structure, while the structure of the $W_{25}O_{75}$ film can be described as quasi-amorphous. The hardness decreased from 25 GPa for the low oxygen content coating to 7.7 GPa for $W_{25}O_{75}$. The H/E ratio was 0.08 and 0.07 for $W_{87}O_{13}$ and $W_{25}O_{75}$, respectively. The sliding tests with 100Cr6 steel balls showed a strong transfer of the ball material to the coating surface causing a high friction coefficient. Nevertheless, the coating wear was negligible. The sliding process with ceramic balls was mainly influenced by the presence of the wear debris layer adhered either to the ball or to the coated sample. The friction coefficient of the coatings against Si_3N_4 was close to 0.7 for both coatings. However, the wear rate was 10 times higher in the case of the $W_{25}O_{75}$ coating. The $W_{87}O_{13}$ coating showed a higher friction (~0.73) and wear rate than $W_{25}O_{75}$ when sliding with Si_3N_4 balls. In general, the coating with low oxygen content was more resistant to abrasive wear.

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References

[1] Woydt M, Skopp A, Dörfel I, Witke K. Wear 1998;218:84.
[2] Yamamoto A, Abe Y, Kawamura M, Sasaki K. Vacuum 2002;66:269.
[3] Parreira NMG, Carvalho NJM, Cavaleiro A. Thin Solid Films 2006;510:191.
[4] Lugscheider E, Knotek O, Bobzin K, Bärwulf S. Surf Coat Technol 2000;133–134:362.
[5] Greenwood OD, Moulzolf SC, Blau PJ, Lad RJ. Wear 1999;232:84.
[6] Holmberg K, Matthews A. Coating tribology. Amsterdam: Elsevier; 1994.
[7] Polcar T, Parreira NMG, Cavaleiro A. Wear 2007;262:655.