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Structural and tribological characterization of tungsten nitride coatings at elevated temperature

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Abstract

Transition metal nitrides exhibit excellent mechanical properties (hardness and Young's modulus), high melting point, good chemical stability and high electrical conductivity. However, tungsten nitrides still stand aside of the main attention. In our previous study, tungsten nitride coatings with different nitrogen content showed excellent wear resistance at room temperature. Nevertheless, many engineering applications require good tribological properties at elevated temperature. Thus, the present study is focused on the tribological behaviour (friction coefficient and wear rate) of tungsten nitride coatings at temperature up to 600 °C.

The structure, hardness, friction and wear of tungsten nitride coatings with nitrogen content in the range 30–58 at.% prepared by dc reactive magnetron sputtering were investigated. The tribological tests were performed on a pin-on-disc tribometer in terrestrial atmosphere with Al_2O_3 balls as sliding partner. The coating wear rate was negligible up to 200 °C exhibiting a decreasing tendency; however, the wear dramatically increased at higher temperatures. The coating peeled off after the test at 600 °C, which is connected with the oxidation of the coating.

Keywords: Tungsten nitride; Sliding wear; Oxidation; Elevated temperature

1. Introduction

Hard coatings have proven to be an excellent solution to improve the wear resistance of mechanical components. Tungsten nitride coatings exhibiting hardness higher than 40 GPa are therefore potential candidates for protective coatings. Surprisingly, their friction and wear properties were not tested as intensively as other transition metal nitrides, such as TiN or CrN. Nevertheless, previous studies have shown that tungsten nitride coatings exhibit excellent mechanical (adhesion, hardness) and tribological (wear resistance) properties [1]. The addition of further elements such as silicon or titanium could further improve the functional properties [1,2].

Recently, a series of tungsten nitride coatings with different nitrogen content (0–55 at.%) was prepared and analyzed [4–6]. In general, the hardness was improved with increasing nitrogen content, in case of α-W and β-W structures typical of low nitrogen contents, whereas the inverse occurred for β-W_2N phase. Concerning the adhesion, the critical load values, as determined by scratch-testing, dropped progressively with increasing nitrogen content while an opposite behaviour was observed for the wear resistance as a consequence of the formation of a protective third-body consisting almost exclusively of tungsten oxide.

Many engineering components are subjected to elevated temperature in tribological conditions during service. High contact surface temperatures also arise due to the generation of friction heating, particularly for large sliding speeds and contact loads. Under these extreme environments, the wear resistance strongly diminishes, which may lead to the rapid failure of the coating. Thus, it starts to be a priority to know the tribological behaviour of hard coatings with temperature. In this work, sliding tests were carried out at elevated temperature to study the friction and wear properties of the tungsten nitride coatings. This study was performed on those W–N coatings which showed previously the most promising mechanical and tribological properties at room temperature [5,6].

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2. Experimental details

The coatings were deposited by reactive magnetron sputtering from a pure tungsten target (99.99% purity) onto steel substrates (DIN X210CrW12) with hardness 62 HRC (about 9 GPa). The substrates were mirror polished to reach a roughness Ra ≤30 nm. The deposition parameters were as follows: target current density of 6 mA cm^{-2}, substrate at floating potential, slow substrate rotation at 20 rpm, inter-electrode distance of 65 mm and no external heating with a substrate temperature lower than 350 °C. Before deposition, an ultimate vacuum pressure better than 2×10^{-4} Pa was reached and the substrates surface was ion cleaned with an ion gun, as described elsewhere [4]. The total pressure, i.e. sum of partial pressures of argon and nitrogen, was kept constant at 0.3 Pa, and Ar/N_2 partial pressure ratio was varied in the range [0.25–1.5]. Two different pumping speeds were used (100 and 200 l s^{-1}), as described below in Section 3.2. The sputtering time was selected in order to obtain coatings with thickness about 3 μm.

A Cameca SX-50 electron probe microanalysis apparatus (EPMA) was used for determining the chemical composition of the coatings. The structure of the films was analyzed by X-ray diffraction (XRD) using a Philips diffractometer with Co Kα radiation (λ = 0.178897 nm) in Bragg–Brentano configuration. The hardness (*H*) and Young's modulus (*E*) of the coatings were evaluated by depth-sensing indentation technique using a Fischer Instruments-Fischerscope H100, with a maximum indentation load of 50 mN. The testing procedure includes a correction of the experimental results for geometrical defects of the indenter tip, the thermal drift of the equipment and the uncertainty in the initial contact, as described in detail elsewhere [7]. The Poisson ratio used for the calculation of the Young's modulus was 0.29.

Wear testing was done using a high temperature pin-on-disc tribometer (CSEM Instruments); the sliding partner was Al_2O_3 balls with a diameter of 6 mm and a load of 5 N giving a maximum static Hertzian pressure for an elastic contact between the ball and the coating of about 1.5 GPa. The morphology of the coating surface, ball scars, wear tracks and wear debris were 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 (EDS). The profiles of the wear tracks were measured with a mechanical profilometer (Tencor Alpha Step 500). The wear rates of the ball and coating were calculated as the worn material volume per sliding distance and normal load. The average value of three profiles measured in each wear track was used to calculate the coating wear rate.

3. Results and discussion

3.1. Selection of appropriate candidates for high temperature sliding tests

In our recent study [6], the tribological properties of tungsten nitrides with nitrogen content 0–55 at.% were analyzed at room temperature. In general, the coatings could be divided into two groups with different dominant wear mechanisms. The coatings with low nitrogen content (up to 15 at.%) exhibited higher values of friction coefficient and wear rate, since their sliding properties were dominated by abrasive wear and delamination. The high nitrogen content (33–55 at.%) leaded to a typical three-body wear with a thick layer of tungsten trioxide consisting of small round particles. The presence of the third-body protected the coating and significantly decreased the friction; the wear modes could be described as mild and polishing. The hardness and the wear rate of tungsten nitrides are shown in Fig. 1. Three chemical compositions from the later group were selected for the tribological tests at elevated temperatures. The reasons for such a selection can be summarized as follows:

- coatings with high nitrogen content exhibited lower wear;
- the high wear resistance of these coatings is caused by the formation of a third-body between the surfaces in contact and the adhered layer of tungsten trioxide. The elevated temperature should promote the formation of such layer;
- the selected compositions cover coatings with either the highest hardness or the lowest friction and wear.

3.2. Chemical composition and structure at room temperature

Two chemical compositions were obtained using 10 and 20 sccm of nitrogen flow: $W_{70}N_{30}$ and $W_{53}N_{47}$, respectively. Since 20 sccm was the limit of the flowmeter, the pumping speed was reduced from 200 to 100 l s^{-1} in order to increase the nitrogen content in the coating up to 58 at.%. It should be pointed out that the deposition process is not fully identical with the previous study [4,5], since substrate rotation was applied compared to the stationary substrate position used before.

The coating $W_{70}N_{30}$ clearly exhibited the f.c.c. NaCl-type β-W_2N structure with a strong (1 1 1) orientation (Fig. 2). The shift of the β-W_2N peak position in relation to the ICDD database position (ICDD card nr. 25–1257) can be correlated with the high

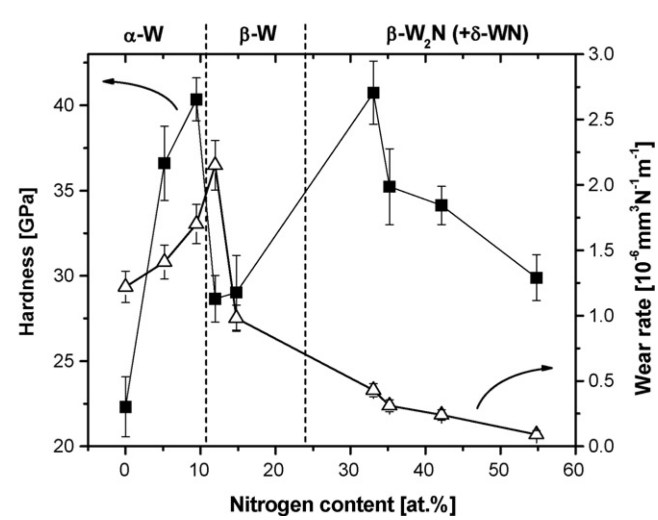

Fig. 1. Hardness and wear rate of tungsten nitride as a function of the nitrogen content [6].