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Influence of oxide phase formation on the tribological behaviour of Ti–Al–V–N coatings

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Abstract

Ti–Al–V–N coatings are potential candidates for dry machining applications due to the combination of superior mechanical properties of the $Ti_{1-x}Al_xN$ phase and the lubricating effects of vanadium oxides formed between 500 and 700 °C. The aim of this work was to prepare Ti–Al–V–N coatings with a high V content (25 at.% V in the Ti–Al–V target) to evaluate the influence of the oxides formed, on the friction behaviour during tribological tests up to 700 °C. The coatings were deposited by DC magnetron sputtering of a powder-metallurgically produced Ti–Al–V target in an $Ar+N_2$ discharge. High temperature ball-on-disc tests were used to investigate the tribological properties against alumina balls. Up to temperatures of 500 °C only minor changes in tribological properties compared to $Ti_{1-x}Al_xN$ coatings could be observed. Increasing the testing temperature to 600, 650, and 700 °C yields a continuous reduction of the friction coefficient from around 1 to 0.27, respectively. However, during the experiment at 700 °C the friction coefficient increases to a constant value of 0.45. Thus, main emphasis was laid on the examination of the formed oxide phases to elucidate their relation to the changing friction coefficients. Scanning electron microscopy investigations, X-ray diffraction and Raman spectroscopy shows that first a V_2O_5 phase is formed which is responsible for the reduction of the friction coefficient. The further oxidation to form TiO_2 and $AlVO_4$ on the surface and especially in the wear track (due to the higher local flash temperatures) controls the ongoing oxidation.

Keywords: Ti–Al–V–N coatings; Lubricious oxides; Friction; Raman

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1. Introduction

In the last decades $Ti_{1-x}Al_xN$ coatings have become the standard choice for many applications. Their high hardness, good wear and oxidation resistance made them interesting especially for high speed and dry cutting operations [1–3]. However, the disadvantage of this coating system is the high friction coefficient of around 0.8–1.1 against steel [4–6]. Therefore, a lot of effort was made in the last years to lower the friction coefficient at room- as well as at higher temperatures [7–10]. Conventional liquid and solid lubricating mechanisms fail at temperatures >500 °C. Thus, a new high temperature low friction concept (based on Magnéli phase oxides, which have easy shearable planes) has been investigated [11–14]. Especially, vanadium containing coatings lead to the formation of Magnéli phase oxides (e.g. V_nO_{3n-1}) in the interesting temperature range between 500 and 700 °C [15]. Thus, $Ti_{1-x}Al_xN$/VN superlattice coatings [16,17] and Ti–Al–V–N supersaturated coatings [18] have already been verified to show a combination of high hardness and low friction coefficients. Furthermore, it has also been shown that an increasing content of V incorporated in the coating leads to a decrease of the friction coefficients at elevated temperatures. Moreover, the friction coefficient changes with longer sliding distances, thus increased exposure times [18,19]. It is assumed that the low friction coefficient results from the

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formation of several V–O phases as well as the melting of the V_2O_5 phase at around 680 °C [19,20]. However, the type of formed oxides and the relation to the changing tribological behaviour are not sufficiently explored.

The purpose of this study is to correlate the formation of specific oxides on the surface and in the wear track of supersaturated Ti–Al–V–N coatings at different temperatures and after different exposure times, with the changing tribological behaviour. Tribological tests at 550, 600, 650, and 700 °C were conducted to evaluate the dependence of the friction coefficient on the temperature. Furthermore, the sliding tests at 700 °C were stopped after 14, 100, and 1000 m to analyse the changing friction coefficients and to correlate them to the changing oxide phases in the wear track with time and sliding distance. Moreover, coatings deposited on Si substrates were oxidized in a conventional heat treatment furnace at 600 °C, 650 °C, and 750 °C for 1.5 h in air to characterize the oxidation behaviour of the coating. Scanning electron microscopy (SEM) micrographs, X-ray diffraction and Raman investigations were conducted to shed light on the oxide formation.

2. Experimental

Grounded and polished substrates of AISI M2 high speed steel discs (DIN 1.3343, Ø30 × 10 mm), which were quenched and tempered to a hardness of 65 HRC (for tribological testing), as well as polished single crystal Si plates exhibiting a (100) orientation (for heat treatment in air) were used as substrates. Prior to deposition, all substrates were ultrasonically pre-cleaned in acetone and ethanol. Single-phase face-centered cubic (fcc) Ti–Al–V–N coatings were deposited via a Ti–Al–V target (powder-metallurgically produced, Ø75 × 6 mm) with an Al/Ti ratio of 2 and a V content of 25 at.%. An unbalanced D.C. magnetron sputtering system with a reactive $Ar+N_2$ discharge was used for deposition. The total working gas pressure $p_{Ar}+p_{N_2}$ was kept constant at 0.2 Pa, the N_2 partial pressure (p_{N_2}) was 30% of the total pressure, the temperature during deposition was set to 400 °C. The discharge current was adjusted to 1 A and the deposition time was 60 min resulting in a film thickness of approximately 4.0 μm.

A CSM high-temperature ball-on-disc tribometer was used for dry sliding experiments at 500, 600, 650, and 700 °C in ambient atmosphere. The relative humidity was between 30% and 40% for all experiments. The coated samples were worn against alumina balls with a diameter of 6 mm. Sliding speed, normal load, and the radius of wear track were kept constant at 0.1 m/s, 5 N, and 7 mm, respectively. The sliding distance was set to 14, 100, 250, and 1000 m, respectively. Wear tracks after ball-on-disc testing were investigated using a 3D profiling system (Wyko NT1000). Heat treatments were conducted in a conventional annealing furnace in ambient air at 600, 650, and 750 °C for 1.5 h.

Oxides on the surface after thermal exposure were characterized using scanning electron microscopy (SEM, Cambridge Instruments Stereoscan 360). The chemical components at different areas of the oxidized surface were determined by energy-dispersive electron probe micro-analysis (EDX) using elemental standards. The crystallographic structure was investigated by X-ray diffraction (XRD, Siemens D500) using Bragg Brentano mode and Cu K_α radiation. A Renishaw 2000 Raman microscope with a Peltier cooled CCD camera recording in extended scanning mode with a laser wavelength of $\lambda = 632.8$ nm (He–Ne Laser, 17 mW) was used for Raman investigations of the wear tracks after high temperature tests.

3. Results and discussion

3.1. Tribological properties

Fig. 1 shows the friction curves of Ti–Al–V–N coatings tested at 500, 600, and 650 °C (see Fig. 1a), and 700 °C (see Fig. 1b). The friction coefficient decreases from 0.95 at 500 °C to 0.7 at 600 °C and 0.55 at 650 °C (see Fig. 1a). At 700 °C, the friction coefficient is approximately 0.27 for a sliding distance of about 70 m (Section 1), an increasing friction coefficient can be seen in the transition zone between 70 and 200 m (Section 2), and afterwards the friction coefficient is constant at around 0.45 (Section 3) for the remaining sliding distance up to 1000 m (see Fig. 1b). Therefore, two more tribological tests were conducted at 700 °C. They were stopped after 14 m (Section 1, low friction coefficient) and 100 m (Section 2, transition zone) to investigate their wear tracks in detail.

3.2. Surface investigations

The formation of different oxides on the coating at specific temperatures has been investigated in order to establish correlations between the formed oxides and the friction coefficient. The coatings were stable in air up to annealing temperatures of 550 °C, no significant oxidation could be observed. Between 600 °C and 700 °C rapid oxidation occurred. Fig. 2 shows XRD patterns of Ti–Al–V–N coatings annealed in air at 600, 650 and 750 °C for 1.5 h. After annealing at 600 °C only two coating peaks at $2\Theta = 36°$ and 43°, identical with the fcc phase in the as-deposited condition, can be detected. A minor peak at $2\Theta \approx 20.5°$, identified as V_2O_5 peak, indicates the onset of oxidation at this temperature. This agrees with observations of other authors [15,21] who have found that oxidation starts between 550 and 600 °C. Increasing the temperature to 650 °C leads to massive oxidation of the coating surface. Mainly V_2O_5 peaks are detected but there are also some indications for an $AlVO_4$ phase. The distinction of these two phases is difficult, due to a number of similar standard peak positions. Nevertheless, also Al_2O_3 and TiO_2 are detected.