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Improved properties of TiAlN coatings through the multilayer structure ☆

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ABSTRACT

TiAlN/AlN multilayers are attracting great interest for the possibility to modulate their mechanical and tribological properties through the variation of multilayer design. In this work TiAlN single layer, TiAlN/AlN intermixed-multilayer and nano-multilayer were prepared using a reactive magnetron sputtering system starting from targets of TiAl and Al. The aim is to analyze how the multilayer design affects the thermal and tribological properties of the coatings. The microstructure of as-deposited and annealed films has been studied using X-ray diffraction. The chemical composition has been deduced by XPS analyses. Thermal behavior was assessed by means of differential thermal analysis (DTA) and thermogravimetric analysis (TGA), while mechanical properties have been investigated by wear tests.

1. Introduction

Surface coating on tools can confer them a high wear resistance, an increased surface hardness at high temperatures and create a chemical barrier for diffusion or reaction between the tool and the workingpiece, thus reducing tool wear [1,2]. Therefore, the demand to develop new wear resistant hard coatings with good thermal stability has become crucial to enhance tool life as machining speed increases [3]. The first coating successfully used in steel machining industry and still employed for its attractive bright gold color, is titanium nitride (TiN). However, its use at elevated temperature is restricted due to its poor chemical stability and it has been replaced by TiAlN in several applications [4]. It has been shown that the mechanical properties of TiAlN material are strongly dependent on its chemical composition [5,6]. A coating with a composition of $Ti_{0.35}Al_{0.65}N$ shows a slightly higher oxidation resistance than $Ti_{0.62}Al_{0.38}N$. On the other hand, an increase of Al amount in the TiAlN coating, such as in $Ti_{0.19}Al_{0.81}N$, revealed a worse oxidation resistance, similar to that found for AlN [7]. Then, improvements of TiAlN coating properties can be obtained optimizing the Al content, the microstructure and the crystal orientation. Multilayer coatings and superlattices are the most widely employed to provide a better alternative to single layer structures [8,9]. These systems allow to suitably combine different materials, selected to ensure that the properties of the resulting coating are optimized for the specific application required [10–12]. Then, once selected the proper materials, an accurate engineering of the coating structure is necessary to identify the powerful system with the best functional properties. In this work TiAlN and AlN were chosen as basic materials and combined under different architectures, namely, nano-multilayer, intermixed-multilayer and single layer structures. All coatings were deposited by magnetron sputtering. Afterwards, microstructure, chemical composition, thermal stability and mechanical properties of the single layer and the multilayers were investigated by using a combination of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermal analysis TGA (thermogravimetric analysis) and DTA (differential thermal analysis) and tests of wear and friction. Finally, the worn surfaces of these coatings were analyzed by means of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

2. Experimental details

TiAlN and TiAlN/AlN multilayered coatings were deposited on silicon and WC–6%Co using a multi-cathode reactive RF magnetron sputtering system.

TiAl (99.95%) and Al (99.9%) targets were sputtered in high purity plasma of Ar (99.999%) and N_2 (99.999%). The composition of the TiAl target was approximately 50:50 in atomic percentage. For all the experiments, the power densities were approximately 3.88 and 1.94 W/cm^2 for the TiAl and Al targets, respectively.

The coatings were deposited under a base pressure of 2.0×10^{-5} Pa and a working total pressure of Ar + N_2 gas equal to 4.0 Pa. The flow rates of N_2 and Ar were separately controlled by two mass flow controllers. The flow rate ratio of N_2 and Ar + N_2 was fixed at 5%.

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The substrates were cleaned in acetone and isopropyl alcohol by ultrasonic cleaning. The substrates were subsequently etched in situ by Ar^+ ion bombardment for 45 min, obtained by applying a RF bias of −20 V to the substrate at an argon pressure of 6.0×10^{-1} Pa. The coatings were deposited at a substrate temperature of 150 °C.

A Ti interlayer was deposited on the WC–6%Co substrates to improve the adhesion of the coatings. Coatings with controlled layer thicknesses were deposited using a stepper motor connected to the substrate holder through a rotary feed. The substrate was moved in circular motion between the two sputtering targets using the stepper motor. The substrate was kept underneath each target for a well predetermined time to achieve the required multilayer thickness.

The multilayers were realized with two different methods of alternation of TiAlN and AlN layers, i.e. continuously deposited with both targets (TiAl and Al) turned on and the substrate rotating and passing under each of the target (TiAlN/AlN-i, where "i" stands for "intermixed") or, alternatively, deposited with only one target turned on and with the power switching between the two targets at each cycle (TiAlN/AlN-n, where "n" stands for "nano-multilayer"). Look at Fig. 1 which shows schematically in the deposition system the relative position of the sputtering sources and the substrate table. In this way, it is easier to understand how the deposition was carried out for samples TiAlN/AlN-i and TiAlN/AlN-n.

The multilayer period is about 4.5 nm. Coatings deposited on silicon substrates with thickness of about 40 nm (corresponding to 9 periods in multilayered films) were used for structural, chemical and thermal stability studies, while coatings deposited on WC–6%Co substrates with thickness of approximately 2.2 μm (corresponding to 500 periods in multilayered films) were used for wear tests.

The X-ray diffraction and reflectivity experiments were carried out by using an X-ray diffractometer in parallel beam geometry (Philips MPD PW1880, 3 kW generator) optimized for small-angle scattering measurements. For all the measurements $Cu_{K\alpha}$-radiation ($\lambda_{CuK\alpha}$ = 0.154186 nm) was used. The X-ray diffraction measurements (XRD) were performed at glancing incidence angle (with fixed incidence angle $\omega_i = 1.0°$) in a range between 5° and 85°. Specular (ω, 2θ) scans (XSR) were acquired at the grazing angle of incidence of the X-rays equal to the exit angle 2θ measured in the range between 0° and 9° with a step size of 0.01°.

For X-ray photoelectron spectroscopy (XPS) studies, samples were analyzed by AXIS Ultra DLD KRATOS using an Al Kα monochromatic X-ray source at 600 W. Survey scans were acquired at a pass energy of the analyzer equal to 160 eV, while narrow scans were acquired with a pass energy of 20 eV. All spectra were recorded from an analysis area of 700×300 μm^2, while depth profiling was performed all along the films' thickness using a coronene ($C_{24}H_{12}^+$) organic source as sputtering source [13]. The energy of the $C_{24}H_{12}^+$ gun was 8 keV, sputtering the samples at 65° respect to the surface normal. The use of this organic source ensures the absence of alteration of the chemical composition and bonds along the specimen thickness, unlike conventional Ar^+ sources. In the depth profiles, a normalization respect to the C1s signal has been operated, because the C1s signal detected inside the films was due to the implanted carbon from coronene. During spectrum acquisition the charge neutralizer was always on. "CasaXPS" software [14] was used both for quantitative peak fitting on narrow spectra of Ti 2p, Al 2p, N1s and O 1s regions and on survey spectra to built up the depth profiling.

Differential thermal analysis (DTA) with thermogravimetry (TGA) was performed in a calibrated Netzsch-STA 409C from room temperature (RT) up to 1300 °C with a heating rate of 20 °C/min in flowing Ar (99.999% purity, 20 sccm flow rate) and synthetic air (79% N_2, 21% O_2, 20 sccm flow rate) to mimic application conditions. Every DTA curve was corrected using as baseline the second scan performed on the same material. The annealing process of the coatings was performed in vacuum (base pressure below 5 mPa) with heating and cooling rates of 20 °C/min at temperatures of 700, 800, 900, and 1000 °C on silicon substrates. The same coatings have been analyzed by XRD in order to support the DTA results.

A pin-on-disk wear method was used to investigate the wear resistance of the coatings. A bearing steel ball, 5.5 mm in diameter, was adopted as the stationary pin. A normal load of 1 N was applied.

The sliding speed was 0.2 m/s on the circular track, for 500 rotations of the sample. The test temperatures were 30 °C and 400 °C and the relative humidity was kept at 60%. The wear time was 40 min for each test. Three friction tests were conducted for each specimen and for every wear scan five measurements of the total wear volume were performed at different points of the wear path and their average values are reported. The wearing morphology of the films was investigated by scanning electron microscope (SEM) XL40 Philips in plan view and significant areas inside and outside the wear tracks were examined by energy dispersive spectroscopy analyzer (EDS).

3. Results

3.1. Structure of coatings

Fig. 2 presents the X-ray diffractograms of TiAlN, TiAlN/AlN-n and TiAlN/AlN-i coatings. The TiAlN/AlN-n coating (see Fig. 2 in the middle) shows the characteristic peak of the (101) direction of h-AlN s.g. $P6_3mc$ (JCPDS card #87-1054) at $2\theta = 38.29°$. Two broad peaks, centered at ~35° and ~40.2°, not expected, can be attributed to the hexagonal phase of Ti_2AlN (JCPDS card #18-0070). In addition there are two peaks related to the (111) and (200) directions of the cubic phase of TiAlN. Experimental investigations show that $Ti_{1-x}Al_xN$

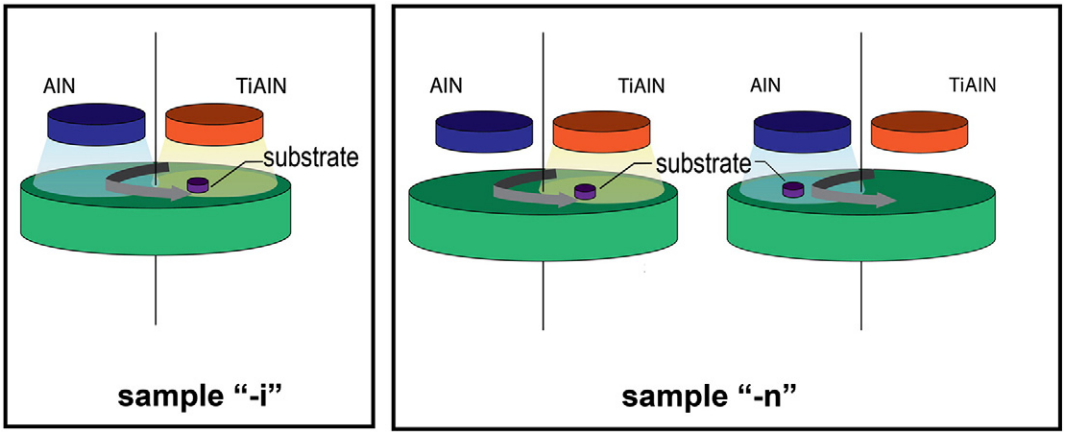

Fig. 1. Diagram of the deposition system and the relative positions of the target and the substrate. In this way it is easier to understand how the deposition was carried out for samples TiAlN/AlN-i and TiAlN/AlN-n.