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Characteristics of arc plasma deposited TiAlZrCN coatings

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Abstract

TiAlZrCN superhard coatings, in which Ti and Al were additions to ZrCN base compound, were prepared by the cathodic arc method. The films were deposited on Si, plain carbon steel and high-speed steel substrates in a mixture of N_2 and CH_4 gases. Elemental and phase composition, chemical bondings, texture, surface roughness, hardness, adhesion, tribological characteristics and erosive–corrosive resistance were investigates as a function of gas composition and total gas flow rate, using XPS, GDOES and XRD techniques, surface profilometry, microhardness and scratch adhesion measurements, tribological and erosive tests. It was shown that the properties and performance of the coatings were strongly dependent on the $CH_4/(CH_4+N_2)$ flow rate and also on the total gas flow. The tribological and anti-erosive characteristics of the TiAlZrCN coatings were found to be superior to those of reference films (ZrN, ZrC, ZrCN, and TiAlCN). Maximum hardness values (42–45 GPa) were obtained for the films prepared at $CH_4/(CH_4+N_2)$ ratios ranging from 0.2 to 0.4.

Keywords: TiAlZrCN coatings; Cathodic arc deposition; Microstructural and mechanical properties; Wear; Erosion and corrosion resistance

1. Introduction

The earlier developed ternary hard coatings for tribological applications and dry machining have been produced as a result of studies aimed at improving the performance of TiN films, which are the most commonly used protective coatings. Holleck [1] has shown that the formation of solid solutions in an equilibrium state exhibit good levels of hardness and performance in various applications. These solid solutions can be obtained by replacing metal or metalloid atoms in a binary system. Over the last decade, the addition of different amounts of certain elements (Cr, Zr, V, Nb, Hf, W, Y, Si, and B) has become a common method to modify the properties of binary and ternary Ti-based nitrides. Adding Cr or Y improves the oxidation resistance, while Zr and V provide better wear resistance, Nb and W increases hardness, B improves the resistance against abrasion, Hf improves the wear behavior of cutting tools, Si enhances hardness, thermal stability and resistance to oxidation [2–8].

The carbonitrides of transition metals have been used for many years instead of conventional TiN or TiC coatings in numerous applications. The microhardness of carbonitride systems is correlated with the type of bonding in the compound and a maximum value occurs at a valence electron concentration of about 8.4 [9]. This optimum value of the electron concentration can be achieved by properly adjusting the C/N ratio in the film composition.

The most known ternary carbonitrides coatings are TiCN and ZrCN [10–14], but more complex systems such as TiVCN, TiZrCN or TiAlCN films were also investigated [9,15–18]. Of quaternary systems, TiAlCN were the most extensively analyzed for chemical structure, mechanical and tribological properties.

The aim of this work was to study the characteristics of TiAlZrCN coatings, in which Al and Ti atoms were substitutes for Zr atoms. The addition of Al and Ti in the fcc structure of ZrCN was expected to improve the characteristics of ZrCN coatings concerning film morphology and microstructure (reduction of grain size in a more equiaxed structure), microhardness, thermal stability, resistance to oxidation, toughness, and adhesion. It is interesting to note that Yao et al. [19] reported an improvement of hardness and wear performance of ZrCN films with Ti and

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W addition. ZrCN was chosen as base-compound because preliminary experiments showed ZrCN coatings to exhibit superior microhardness as compared with Ti-based binary or ternary systems (TiN, TiCN or TiAlN) deposited under similar conditions (gas flow rate and substrate bias). Besides, Zr-based coatings were found to be superior to Ti-based ones in some other aspects, especially their chemical resistance to some relevant environments (e.g. H_2O_2) [20]. Examples of applications which need resistance to H_2O_2 environment are vessels or pipes containing disinfectants or cleaning liquids.

The investigations were focused on mechanical, tribological and anti-erosive properties of the coatings deposited under various conditions (different gas compositions and total gas flow rates).

The cathodic arc method was selected as a deposition technique because it is a versatile, efficient, highly productive method and the high ionization plasma it produced is beneficial for the deposition of hard coatings [21]. The films were also characterized in terms of their elemental and phase composition, crystallographic structure and surface roughness. The coating characteristics were assessed in comparison to ZrN, ZrC, ZrCN and TiAlCN films (reference coatings).

2. Experimental details

The coatings were deposited in a cathodic arc unit [22] equipped with both a Zr and a Ti+Al cathode. The Ti+Al target consisted of an Al central disc, surrounded by a Ti external ring. Si substrates were used for XPS investigations, while C45 steel for X-ray analysis. Tribological and erosive–corrosive tests were conducted for coatings prepared on C45 steel substrates, taking into account that the most parts for which the investigated coatings could offer an efficient protection against wear, erosion and corrosion are made of plain carbon steel. On the other side, HSS substrates were chosen to evaluate the film microhardness and adhesion because the most data in the literature refer to such measurements carried out on various coatings deposited on this substrate type. The samples were mechanical polished to a roughness of $R_a \approx 0.08$ µm. The base pressure in the deposition chamber was of about 1×10^{-3} Pa. Prior to deposition, the samples were sputtered by Ar ion bombardment (1000 V; 5 min). The reactive atmosphere was a mixture of N_2 and CH_4 gases. Various film compositions were obtained by varying the total gas (CH_4+N_2) flow rate (TFR) and the ratio of CH_4/(CH_4+N_2) flow rates. The total gas flow was ranging from 60 to 140 sccm, while the CH_4/(CH_4+N_2) flow ratio was varied between 0.13 and 0.91. The working pressure was between 5×10^{-2} Pa (for TFR = 60 sccm) and 8×10^{-2} Pa (for TFR = 140 sccm). The currents at the Zr and Ti+Al cathodes were maintained constant at 135 and 90 A, respectively. For all samples, a substrate bias of −100 V was applied. During deposition the substrate temperature was of about 280 °C for the reference coatings and of about 320 °C for TiAlZrCN. The deposition duration was chosen to deposit films with the same thickness (~4.8 µm). The working parameters were selected so that the Ti and Al contents in the film composition to be less than 10%. For reference coatings (ZrN, ZrC, ZrCN, TiAlCN), the arc current and the substrate bias values were the same as those for the TiAlZrCN deposition.

X-ray photoelectron spectroscopy (XPS) method was used to determine the elemental composition of the films and the chemical bonding states. XPS analysis was performed on a VG ESCA 3 MK II spectrometer, calibrated with respect to the C 1 s peak. A 4 keV Ar^+ ion beam was used for sputter etching of the samples (50 min). Chemical composition depth profiles were obtained by GDOES analysis, using SPECTRUMA 750 spectrometer (conditions: 1000 V, 15 mA). Raman spectroscopy was performed to investigate the carbon bonding in the films. The Raman spectra were taken with a LABRAM-HR spectrometer (Horiba Jobin-Yvon), using the 632 nm excitation wavelength of a HeNe laser providing 3 mW at the sample surface. Phase composition and texture were analyzed by X-ray diffraction (CuKα radiation). Film hardness H was measured with a Neophot-2 microhardness tester (0.05 N load). Scratch tests under standard conditions (indenter — 0.2 mm radius diamond tip, load-continuous increase from 0 to 100 N, scratching speed — 10 mm/min, scratching distance — 10 mm) were used to determine the film adhesion (critical load L_c, defined as the load where film flaking starts, was determined by optical examination of the trace). The thickness and roughness of the films were determined using a Dektak 150 surface profiler.

Tribological characteristics of the coatings were investigated using a ball-on-disc system. The tests were performed in a dry atmosphere using a steel counterpart (C45 steel, 19.8 mm in diameter, hardness of 57 HRC at a load of 1 N, and a sliding speed 0.2 m/s). The total sliding distance was 100 m. The wear behavior was evaluated by measuring the sliding friction coefficient and the depth of the worn trace.

Coating resistance against erosion and corrosion was tested by means of a laboratory device (specially designed machine), where the tested samples were moving on a circular trajectory, at a certain distance from the system axis, in a vessel containing an erosive–corrosive solution. The C45 steel samples were rectangular (54 × 12 × 2.5 mm). Three samples were tested in the same run, with a linear speed of 7.1 m/s and a test duration of 60 min. The samples were placed at equal distances between each other but were tilted at different impingement angles to the axis (15°, 30° and 45°). In order to evaluate the performance of TiAlZrCN films as protective coatings in the oil industry, formation water with 3% sand grains was chosen as erosive–corrosive solution. The chemical composition of the solution was: 70.4 g/l NaCl, 10.0 g/l $CaCl_2$, 3.7 g/l $MgCl_2$, 0.6 g/l Ca$(HCO_3)_2$, and 0.2 g/l $CaSO_4$. The hardness of the sand grains was determined to be about 16 GPa with a grain size bellow 125 µm.

3. Results

3.1. Mechanical properties

The main mechanical characteristics (hardness H and critical load L_c) of the TiAlZrCN coatings and their corresponding deposition parameters are given in Table 1. For comparison, the characteristics of reference films are also presented.