Surface & Coatings Technology 278 (2015) 87–91

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Characterization of TiAlSiON coatings deposited by plasma enhanced magnetron sputtering: XRD, XPS, and DFT studies

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ARTICLE INFO

Article history:
Received 7 May 2015
Revised 5 August 2015
Accepted in revised form 6 August 2015
Available online 9 August 2015

Keywords:
TiAlON coatings
Magnetron sputtering
X-ray photoelectron spectra
Density functional theory
Electronic structure

ABSTRACT

The results of characterization of TiAlSiON hard coatings deposited on ferric-chromium AISI 430 stainless steel by plasma enhanced magnetron sputtering are presented. The coating with maximum hardness (of 43 GPa) was obtained at the following optimal values of elemental concentrations: Si ~5 at.%, Al ~15 at.%, and Ti ~27 at.%. The value of gaseous mixture (Ar–N_2) pressure was of 0.13 Pa and the value of partial pressure of oxygen (O_2) was $1.3 \cdot 10^{-3}$ Pa. The X-ray diffraction (XRD) measurements showed the presence of Ti(Al)N. High-energy resolved XPS spectra of core levels revealed the formation of Ti–N, Ti–O–N, Si–N and Al–O–N bonds. Comparison of XPS valence band spectra with specially performed density functional theory calculations for disordered $Ti_{0.5}Al_{0.5}N_{1-x}O_x$ ($0 \le x \le 0.3$) phases demonstrated that a $Ti(Al)O_xN_y$ phase is formed on the surface of AISI430 steel upon the plasma enhanced magnetron sputtering, which can provide a good combination of high hardness and additional oxidation resistance of this material.

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1. Introduction

Despite a comparatively low oxidation resistance (the oxidation onset is reported at 500 °C [1]), titanium nitride (TiN) coating is used widely in cutting tool applications to increase lifetime and to improve performances of cutting tools. It has been found that adding such elements as Al and Si leads to the formation of TiAlSiN composites, which are characterized by high hardness (>40 GPa) and great oxidation resistance (up to 800 °C) [2]. To explain the oxidation resistance of TiAlSiN coatings, the several mechanisms have been suggested. A dense Al_2O_3 layer has been reported to be formed on the surface, which serves as a barrier against oxygen internal diffusion [3]. It has also been found that a-Si_3N_4-boundary phase in TiAlSiN coatings prevents the diffusion of oxygen along the grain boundaries [4]. To date, a great body of research of TiAlSiN coatings has been focused mostly on the development of various deposition methods and on studying their microstructure, mechanical properties, and oxidation resistance [5–8].

In principle, the another way to enhance the corrosion resistance of hard coatings can be suggested, which involves the formation of metal oxynitride phase of Me(N,O) [9]. In this regard, in the present paper we have studied whether it is possible to form the Ti(Al) oxynitride phase by applying a standard technique for preparing hard TiAlSiN coatings, using plasma enhanced magnetron sputtering under an partial pressure of oxygen at $1.3 \cdot 10^{-3}$ Pa. It is shown in our paper that the measurements of XPS valence band spectra in combination with the density functional theory (DFT) calculations for disordered phases provide a very useful information about the formation of chemical bonds and electronic structure in such multicomponent systems; and the formation of Ti(Al) oxynitride phase is found in TiAlSiN coatings, which can enhance their oxidation resistance.

2. Experimental part and calculations

2.1. Coating preparation

The TiAlSiON films were deposited on AISI 430 stainless steel and T15K6 hard metal by reactive DC magnetron sputtering in N_2–Ar–O_2 gas mixture (Ar — 99,998%, N_2 — 99,999. The deposition system was a cylindrical reactor with four flat magnetrons with the targets of 70 mm in diameter: two titanium (Ti), one aluminum (Al) and one silicon (Si) targets of high purity (Ti — 99,7%, Al — 99,5%, Si — 99,999%). The magnetrons were positioned on the lateral face of the reactor with an internal diameter of 340 mm. Ion assistance with an adjustable density of the ion current was provided by ionizing the gaseous mixture with a wide (50 cm^2) electron beam [10]. For this purpose, a low-energy (~100 eV) electron source with a grid plasma cathode [11] was used, which was positioned on the overhead cover of the reactor. The electron

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http://dx.doi.org/10.1016/j.surfcoat.2015.08.007
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emitting plasma in the electron source was generated by a discharge system with a hollow self-heated cathode, which functioned in a combined mode with direct discharge current of up to 7 A and superimposed dc-pulsed current (250 Hz, 200 μs) with an amplitude of up to 100 A. An accelerating voltage of 100 V was applied between a mesh electrode of the electron source (grid) and earthed walls of the reactor. The electrons were accelerated in a double layer of a space charge between the plasma of the electron emitter and the beam plasma. A pulsed (50 kHz, 10 μs, 100 V) negative bias voltage was applied between the samples and the reactor walls. The ion current density from the beam-generated plasma was controlled by change of electron beam current and reaches 60 mA/cm^2 in a maximum while average value of ion current density was 4 mA/cm^2. The reactor was pumped out using a turbomolecular pump with a pumping speed of 500 l/s. The gaseous mixture was fed to the reactor through the electron source. At a gas flow of 40 sccm, the total pressure was ~0.13 Pa. The gas flow was constant and the ratio of Ar/N_2 flows was 28/12 in all experiments except for investigation the effect of the N_2 flow on coating hardness in which the ratio changed from 30/10 to 22/18. The substrates were disposed on a manipulator with the planetary gyration. The speed of sample rotation relative to the axis of the reactor was 10 rpm. Prior to deposition, the substrates were sputter-etched for 10 min in an Ar atmosphere with 500 eV Ar ions. A Ti adhesion layer of approximately 100 nm in thickness was deposited onto these samples before coating deposition. The elemental compositions of coatings were controlled by changing the discharge currents for magnetrons with Si (I_{Si}) and Al (I_{Al}) targets and by varying the flow ratio for N_2 (Q_{N2}) and Ar (Q_{Ar}). The partial pressure of O_2 was maintained constant ($1.3 \cdot 10^{-3}$ Pa). The discharge current of each of the two magnetrons with Ti targets was constant and equal to 2 A. The coatings were of 1.5–2 μm in thickness. The temperature of samples at all stages of coating deposition did not exceed 300 °C.

2.2. Coating characterization

The hardness of the coatings was measured by nano–indentation using an ultra micro indentation system DUH-211/211S (Shimadzu) and the hardness value was obtained by Oliver–Pharr method [12]. The hardness tests were performed using Berkovich diamond indenter at load range of 20–100 mN. Each hardness value was an average of at least 10 measurements. The concentration of Ti, Al, Si in coatings was estimated by EDX (Energy Dispersive X-ray analysis) using nitrogen free Aztec X-MAX80 system (Oxford Instruments). XPS method was used for more detail analysis of coating composition (concentration of O and N). For structural analysis, the X-ray diffraction (XRD) measurements were carried out using a Shimadzu XRD 7000 diffractometer using Cu Kα radiation and a graphite monochromator. XRD patterns were processed by the method of integral analysis using XPert High Score Plus software. The average size of the coherent scattering regions was estimated by Scherrer method. The values of microstrain were estimated with the help of full profile Rietveld analysis of XRD patterns.

The XPS core-level and valence-band spectra measurements were made using PHI XPS Versaprobe 5000 spectrometer (ULVAC-Physical Electronics, USA). The Versaprobe 5000 is based on the classic X-ray optic scheme with a hemispherical quartz monochromator and an energy analyzer working in the range of binding energies from 0 to 1500 eV. The greatest advantage of this XPS system is electrostatic focusing and magnetic screening. As a result, the achieved energy resolution is $\Delta E \leq 0.5$ eV for Al *Kα* excitation (1486.6 eV). The vacuum circuit of Analytical Chamber uses oil-free rotary pump which allows obtaining and keeping the pressure not less than 10^{-7} Pa. The dual-channel neutralizer (ULVAC-PHI patent) was applied in order to compensate the local charging of the sample under study due to the loss of photoelectrons during XPS measurements. All samples under study were previously kept in the Intro Chamber within 24 h under rotary pumping. After that the sample was introduced into the Analytical Chamber and controlled with the help of "Chemical State Mapping" mode in order to detect micro impurities. If the micro impurities were detected then the sample was replaced from the reserved batch. The XPS spectra of core-levels and valence band were recorded in Al *Kα* 100 μm spot mode with x-ray power load of the sample less than 25 W. Typical signal-to-noise ratio values in this case were not less than 10,000/3. The spectra were processed using ULVAC-PHI MultiPak Software 9.3.

2.3. Electronic structure calculations

The electronic structure calculations of disordered Ti(Al)-oxynitrides for different oxygen content were performed with help of the coherent potential approximation (CPA). Both the CPA scheme and home-made codes used in the present investigation are described in [13]. Keeping in mind that the presence of Al in Ti-sublattice and O in N-sublattice influences on the lattice constant value [14–16], we have used the corresponding lattice parameters *a* [16] for CPA calculations of $Ti_{0.5}Al_{0.5}\ N_{1-x}O_x$ (x = 0, 0.1, 0.15, 0.2 and 0.3). For self-consistent calculation of the coherent potential, it is necessary to build a Hamiltonian H_0 of the undoped system (TiN) and to determine parameters ΔV describing the difference between the impurity and the host sites. The Hamiltonian H_0 was calculated in frames of the linearized muffin-tin orbital method in the tight binding approximation (TB LMTO) [17] and projected into Wannier functions basis according to the procedure presented in [18]. This Wannier functions basis included 4 *s*-, 4*p*- and 3*d*-orbitals of Ti atom together with 2 *s*- and 2*p*-orbitals of N atom. Then ΔV parameters for Al and N were calculated within the supercell approach. Finally, the CPA calculations were performed with the inverse temperature value $\beta = 10\ \text{eV}^{-1}$, Matsubara frequencies cut off at 1000 eV. This cycle was repeated for every *x* under consideration due to *a*(*x*) dependence [16].

3. Results and discussion

3.1. Mechanical properties

Fig. 1a displays the hardness of the coatings as a function of I_{Si} (at constant values of $I_{Al} = 2.6$ A and $Q_{N2} = 12$ sccm, I_{Al} ($I_{Si} = 0.7$ A, $Q_{N2} = 12$ sccm) and Q_{N2} ($I_{Si} = 0.75$ A, $I_{Al} = 2.5$ A). As shown in Fig. 1, the Si content, which increases from 3 to ~10 at.% with I_{Si} increasing from 0.5 A to 1.25 A, causes the most essential influence on hardness of the coatings. The hardness reaches its maximum value of 41 GPa at Si content of nearly 5 at.% and decreases sharply as Si content increases further. The variation of Al content in the range of 11–19 at.% with I_{Al} increasing from 2.2 A to 2.8 A is accompanied by changes of the coatings hardness by no more than 4 GPa. The coating with the maximum hardness (41 GPa) was obtained at the following optimal values of elemental contents: Si ~ 5 at.%, Al ~ 15 at.%, Ti ~ 27 at.%; and value of $Q_{N2} = 12$ sccm.

The annealing of the coatings in vacuum at 800 °C during 2 h leads to an increase of hardness by 2–7 GPa. The most essential growth of hardness corresponds to Si contents below the optimal value (~3 at.%). The maximum hardness (43 GPa) was achieved upon annealing.

The coatings deposited at the optimal parameters ($I_{Si} = 0.7$ A, $I_{Al} = 2.6$ A, $Q_{N2} = 12$ sccm) and different amplitudes of electron beam current were investigated in order to evaluate the influence of pulsed ion current density on the coating characteristics. The mean current of electron beam was kept constant (at 7 A). To keep the value of mean electron beam current constant at decreasing pulse current, the direct current was raised. The hardness of the coatings as a function of electron beam current amplitude is shown in Fig. 1b. It was established that as hardness of the coatings increased by 10 GPa with the pulse ion current density increasing from 0 to 60 mA/cm^2 (increasing the amplitude of electron beam current up to 100 A).

An increase in the coatings hardness from 31 to 43 GPa has been observed earlier for the ion/atom ratio fluxes varying from 2.5 to 4 in the DC mode [19]. The enhancement of mechanical properties can be explained by an increase of the species mobility in the growing film thus

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