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Microstructural and mechanical properties of graded and multilayered $Al_xTi_{1-x}N/CrN$ coatings synthesized by a cathodic-arc deposition process

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ABSTRACT

Graded and multilayered $Al_xTi_{1-x}N/CrN$ coatings were synthesized by cathodic-arc evaporation (CAE) with plasma enhanced duct equipment. Chromium and AlTi alloy cathodes were used for the deposition of $Al_xTi_{1-x}N/CrN$ coatings. During the coating process of graded $Al_xTi_{1-x}N/CrN$, an $Al_{0.63}Ti_{0.37}N$ top layer was deposited on an interlayer of $Al_{0.63}Ti_{0.37}N/CrN$, which was obtained by regulation of cathode power. With different cathode current ratios ($Al_{0.67}Ti_{0.33}/Cr$) of 0.75, 1.0, and 1.33, the deposited multilayered $Al_{0.63}Ti_{0.37}N/CrN$ coatings possessed different chemical contents and periodic thicknesses. The nanolayer thickness and alloy content of the deposited coating were correlated with the evaporation rate of alloy cathode materials. Periodic thickness and layer thickness ratio of $Al_{0.63}Ti_{0.37}N/CrN$ increased with increasing $I_{[AlTi]}/I_{[Cr]}$ cathode current ratio. High resolution transmission electron microscopy showed that lattice distortion and dislocations are found at the interface between $Al_{0.63}Ti_{0.37}N$ and CrN layers in the multilayered $Al_{0.63}Ti_{0.37}N/CrN$. Hardness enhancement is a consequence of dislocation blocking. The multilayered $Al_{0.63}Ti_{0.37}N/CrN$ coatings possessed higher hardness (35–36 GPa) and better fracture toughness (K_{IC} = 1.65–2.05 MPa $m^{1/2}$) than those of the graded $Al_{0.63}Ti_{0.37}N/CrN$.

1. Introduction

Transition metal nitride coatings, such as TiN, CrN, $Ti_xCr_{1-x}N$, and $Al_xTi_{1-x}N$, were applied for use as hard coatings because of their high hardness, wear resistance, and chemical stability [1–6]. Among these coatings, $Al_xTi_{1-x}N$ and CrN coatings in a form of multilayer and graded-layer exhibited superior mechanical properties than in the form of a single layer. Industrial applications of these coatings synthesized by physical vapor deposition (PVD) are rapidly increasing because they have higher hardness and toughness value, better tribological resistance and higher temperature oxidation stability than constituent coatings deposited in a single layer [5–7]. The $Al_xTi_{1-x}N$ coating structure is based on the fcc TiN structure, where the addition of Al in the form of solid solution has been shown to increase the hardness and high temperature oxidation resistance (700–800 °C) [8]. CrN has lower hardness value (~18 GPa) but it is tougher. By incorporation of another element, chromium based ternary compounds, such as $Cr_xAl_{1-x}N$ coatings, possess high hardness and thermal stability [9–13].

Previous studies revealed the oxidation resistance of the $Al_xTi_{1-x}N$ coating can be improved by the incorporation of chromium to form Cr based nitrides which are known for their excellent corrosion and tooling performance [14,15]. This improved high temperature oxidation resistance results in outperformance of the AlTiCrN over the $Al_xTi_{1-x}N$ [16]. The periodic thickness and alloy content may influence the microstructure and mechanical properties of multicomponent coatings in a form of multilayer and graded-layer [17–27]. Such coatings can be produced by different PVD techniques, such as magnetron sputtering and cathodic-arc evaporation (CAE) with several target sources. The cathodic-arc ion plating process for the deposition of hard coatings is well known of high ionization in the plasma and allows the deposition of dense coatings. Rotation of samples and evaporation rate of target sources are usually used to control the periodic thickness and stoichiometry of these coatings. However, in an industrialized deposition system, samples usually rotate around two or three axes at a fixed speed. In the present study, a cathodic-arc ion plating process with chromium, and $Al_{0.67}Ti_{0.33}$ alloy cathodes was used for the deposition of graded $Al_xTi_{1-x}N$ and multilayered $Al_xTi_{1-x}N/CrN$ coatings. Regulating the cathode power or cathode current controlled the evaporation rate of each target source, and then multilayered structures with different periodic thickness and layer thickness were synthesized. The effect of alloy content (Al, Ti, and Cr) on the microstructure and mechanical properties (hardness, elastic modulus, and fracture toughness) of graded $Al_xTi_{1-x}N$ and multilayered $Al_xTi_{1-x}N/CrN$ coatings were studied.

2. Experimental details

Graded $Al_xTi_{1-x}N$, and multilayered $Al_xTi_{1-x}N/CrN$ coatings were deposited on polished silicon using a CAE system. Chromium and

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$Al_{67}Ti_{33}$ (67/33 at.%) alloy targets were arranged on opposite sides of the chamber to deposit the coatings. The samples were mounted on a rotational substrate holder for the deposition of the graded $Al_xTi_{1-x}N$ and multilayered $Al_xTi_{1-x}N$/CrN coatings. Ar and reactive gas (N_2) were introduced through a conducting duct around the target to enhance the reaction of the plasma and reduce the droplet on the deposited coatings. The total thickness of the coatings was 1.3–1.8 μm, which was controlled by a deposition time of 50 min. Table 1 shows the deposition parameters of the multilayered $Al_xTi_{1-x}N$/CrN coatings. The total cathode current of both cathodes was 140 A ($I_{[AlTi]}+I_{[Cr]}=140$ A) and the ratios of $Al_{67}Ti_{33}$/Cr cathode current ($I_{[AlTi]}/I_{[Cr]}$) were 0.75 (AlTiN/CrN-0.75), 1.0 (AlTiN/CrN-1.0), and 1.33 (AlTiN/CrN-1.33). For the deposition of graded $Al_xTi_{1-x}N$/CrN coatings, a top $Al_xTi_{1-x}N$ layer (thickness = 0.6 μm) was deposited on a 0.8 μm thick multilayered $Al_xTi_{1-x}N$/CrN at an $I_{[AlTi]}/I_{[Cr]}$ cathode current ratio of 0.75.

The deposited coatings were examined in a Joel JSM-7000F high resolution field emission scanning electron microscope (FESEM) equipped with secondary electron imaging (SEI) and backscattered electron imaging (BEI) detectors. Chemical composition of the deposited coatings was identified by using a high resolution electron probe microanalyzer (FE-EPMA, JEOL JXA-8500F) equipped with a wavelength dispersive X-ray spectrometer (WDS). The microstructure and periodic thickness of the multilayered $Al_xTi_{1-x}N$/CrN coatings were examined by a FEI Tecnai G^2 20 S-Twin field emission high resolution transmission electron microscope operated at 200 keV for high resolution imaging. The point resolution and the line resolution are 0.248 nm and 0.144 nm, respectively. Glancing angle X-ray diffractometer (PANalytical X'pert Pro) with a high resolution ψ goniometer and Cu radiation was employed for phase identification and residual stress analysis. The diffractometer was operated at 40 kV and 30 mA with a glancing angle of 1°–2°. The residual stresses of the deposited coatings were calculated from the $\sin^2\psi$ method [28]. Hardness and Young's modulus of the films were obtained using XP-MTS nanoindentation with a Berkovich indenter, under load-unloading condition, and measured as a function of indenter displacement using continuous stiffness measurement method. Fracture toughness was determined by a Vickers diamond pyramid indentation method at a load of 9.8 N. By measuring the length of radial cracks (c) using SEM, the fracture toughness (K_{IC}) was calculated by the equation: $K_{IC}=\delta(E/H)^{1/2}(P/c^{3/2})$, where P is the applied indentation load, E and H are the elastic modulus and hardness of the film, respectively. δ is an empirical constant which depends on the geometry of the indenter. For standard Vickers diamond pyramid indenter, value of δ is taken as 0.016 [29,30].

3. Results and discussion

3.1. Microstructure analysis

From the WDS analyses, the graded $Al_xTi_{1-x}N$/CrN coating deposited from the $Al_{67}Ti_{33}$ alloy target was identified as $Al_{0.63}Ti_{0.37}N$/CrN. An atomic ratio of Al/(Ti+Al) in the $Al_{0.63}Ti_{0.37}N$ film was reduced to 0.63 compared with the $Al_{67}Ti_{33}$ cathode material. It can be related to the lower atomic mass of Al that suffers higher scattering in the collisions with nitrogen, and leads to a lower volume density in the vapor [19,31]. With different ratios of AlTi/Cr cathode current ($I_{[AlTi]}/I_{[Cr]}=0.75$, 1.0, and 1.33), the multilayered $Al_xTi_{1-x}N$/CrN coatings were identified as $(Al_{0.39}Ti_{0.22}Cr_{0.39})N$, $(Al_{0.46}Ti_{0.30}Cr_{0.24})N$, and $(Al_{0.51}Ti_{0.33}Cr_{0.16})N$, respectively. Obviously, higher Al and Ti contents were obtained by increasing the AlTi/Cr cathode current ratio.

Table 1
Deposition parameters of the multilayered Al_xTi_{1-x}/CrN coatings.

Parameters	Values
CAE target	Cr and Al_{67} Ti_{33} (100 mm in diameter)
Cathode current ratio ($Al_{67}Ti_{33}$/Cr)	0.75, 1.0, 1.33
Distance between cathode and substrate (mm)	250
Base pressure (Pa)	1.0×10^{-3}
Reactive gas pressure (Pa)	2.7 (N_2)
Deposition time (min)	50
Bias voltage during deposition (V)	−80
Substrate temperature (°C)	250–300
Rotational speed of the substrate (rpm)	1.5 rpm

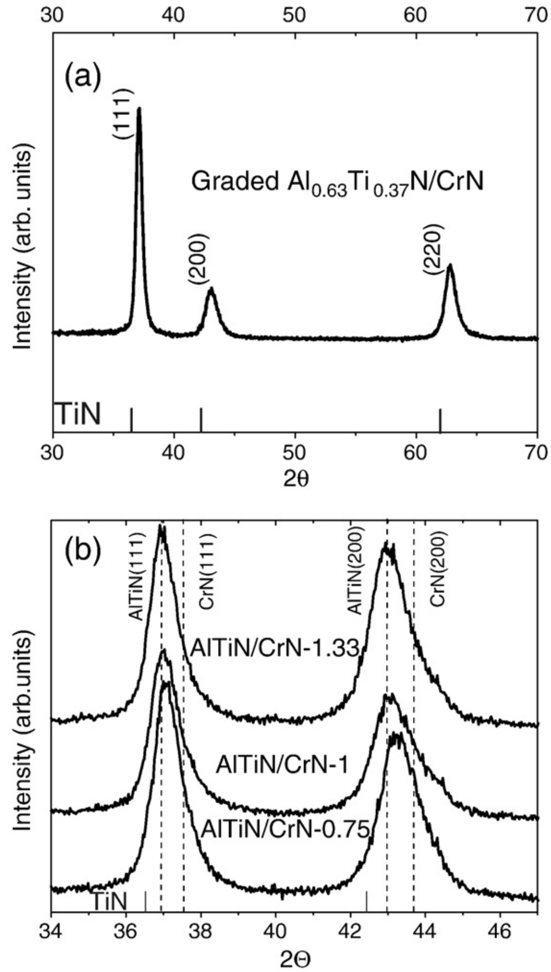

Fig. 1. (a) Glancing angle X-ray diffraction spectra of the graded $Al_{0.63}Ti_{0.37}N$/CrN. (b) The (111) and (200) diffraction peaks of multilayered $Al_xTi_{1-x}N$/CrN (AlTiN/CrN-0.75, AlTiN/CrN-1.0, and AlTiN/CrN-1.33) coatings. Standard peak positions of bulk TiN are also revealed for comparison (JCPDF file No.: #870629).

Typical glancing angle X-ray diffraction spectra from the graded $Al_{0.63}Ti_{0.37}N$/CrN and multilayered $Al_{0.63}Ti_{0.37}N$/CrN (AlTiN/CrN-0.75, AlTiN/CrN-1.0, and AlTiN/CrN-1.33) coatings are shown in Fig. 1. Standard peak positions of bulk TiN are also revealed for comparison (JCPDF file No.: #870629). The result revealed that all the graded $Al_{0.63}Ti_{0.37}N$/CrN and multilayered $Al_xTi_{1-x}N$/CrN exhibited the NaCl crystal structure, and no softer hcp-AlTiN phase was found [18,19]. The XRD pattern of the graded $Al_{0.63}Ti_{0.37}N$/CrN revealed the crystalline structure of the top $Al_{0.63}Ti_{0.37}N$ layer by using a glancing angle of 1°. The lattice parameter of the graded $Al_{0.63}Ti_{0.37}N$/CrN was 0.419 nm, which was smaller than that of TiN (0.424 nm). As compared with TiN, the observation that the (200) peak position shifted toward higher Bragg angles as the Al content increases. It revealed lattice contraction because of the smaller atomic radius of Al (0.143 nm) than that of Ti (0.146 nm). For the multilayered $Al_{0.63}Ti_{0.37}N$/CrN, the peak positions represented the weighted mean of the individual reflections