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Designing superhard, self-toughening CrAlN coatings through grain boundary engineering

Zhao Li [a], Paul Munroe [b], Zhong-tao Jiang [c], Xiaoli Zhao [d], Jiang Xu [e], Zhi-feng Zhou [f], Jian-qing Jiang [a], Feng Fang [a,*], Zong-han Xie [g,*]

[a] School of Materials Science and Engineering, Southeast University, Nanjing, Jiangsu Province 211189, PR China
[b] Electron Microscope Unit, University of New South Wales, Sydney, NSW 2052, Australia
[c] School of Engineering and Energy, Murdoch University, Perth, WA 6150, Australia
[d] School of Engineering, Edith Cowan University, Joondalup, WA 6027, Australia
[e] Department of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, PR China
[f] Department of Mechanical and Biomedical Engineering, City University of Hong Kong, Kowloon, Hong Kong, China
[g] School of Mechanical Engineering, University of Adelaide, Adelaide, SA 5005, Australia

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Abstract

One of the toughest challenges that hinders the application of ceramic coatings is their poor damage tolerance. Addressing this problem requires the development of novel micro- or nanostructures that would impart to these coatings both high hardness and high toughness. In this paper, CrAlN coatings, with varying Al contents up to 30 at.%, were engineered onto steel substrates using the magnetron sputtering technique. Whilst the addition of Al does not significantly alter the columnar microstructure, it does change the preferred grain orientation and increase the compressive residual stress. Moreover, the hardness, elastic strain to failure (H/E) and plastic deformation resistance (H^3/E^2) of the resultant CrAlN coating with the highest Al content were found to increase ~47, ~29 and ~140%, respectively, as compared to CrN. Evidence collected from transmission electron microscopy and X-ray photoelectron spectroscopy experiments shows that AlN, existing in an amorphous state at the columnar CrN grain boundaries, has a crucial role in providing the unusual combination of high hardness and exceptional damage resistance. The results provide a new pathway to developing durable ceramic coatings suitable for applications involving severe loading conditions.

Keywords: Coating; Nanocrystalline microstructure; Nanoindentation; Residual stresses; Toughness

1. Introduction

The machining industry is currently under unprecedented pressure to reduce cost, increase efficiency and enhance productivity and quality. Environmental and health concerns also favour sustainable, dry machining processes. Consequently, there is considerable interest in the development of high performance coatings to expand tool life [1–3]. Transition metal nitride coatings have greatly advanced machining operations [4]. Among them CrN is commonly applied, owing to its excellent resistance to wear and corrosion [5,6]. However, the usage of this coating is limited by its relatively low hardness [7]. In order to improve its hardness, alloying CrN with Al to form a ternary CrAlN coating has attracted much attention in recent years. Extremely high hardness (i.e. 48 GPa) was obtained by controlling the concentration of Al in the CrN coating [8]. An Al-containing oxide layer also formed on the coating surface and improved its oxidation resistance [9]. Moreover, strong Al–N bonding formed and significantly increased its thermal stability [10]. All these

* Corresponding authors. Tel.: +86 25 5209 0630 (F. Fang), tel.: +61 8 8313 3980; fax: +61 8 8303 4367 (Z.-h. Xie).
E-mail addresses: fangfeng@seu.edu.cn (F. Fang), zonghan.xie@adelaide.edu.au (Z.-h. Xie).

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advantages make CrAlN coatings an attractive candidate to meet the ever-increasing demand for cutting tools used in dry, high-speed machining.

Accompanying the increase of hardness of a material is often a marked decrease in its damage resistance [11]. Consequently, a combination of high hardness and good damage resistance is rarely seen in ceramic coatings [12]. A fine columnar structure often forms in CrAlN coatings prepared by various deposition techniques, including magnetron sputtering [7,8,13–17]. Compared to a dense, equiaxed grain structure, the columnar structure has a clear advantage; that is, inter-granular shear sliding can take place under severe loading, which helps reduce stress concentrations, imparting to the coating a greater damage resistance [18,19]. According to a mechanical model that relates the columnar-grained structure to its deformation behaviour, the resistance to the shear sliding is critical to the design of extremely hard, yet damage-tolerant, coatings [18]. To regulate the shear resistance in a columnar structure, multilayer structures have been used, for example TiN/TiSiN coatings [20], which consist of hard TiSiN interlayers serving as physical barriers against the shear deformation of columnar structured TiN layers. For CrAlN coatings, an amorphous AlN phase (a-AlN) was observed at the CrAlN boundaries [13,17], which, together with high residual stress [8], increases the coating hardness [7,21]. However, there remains a lack of basic understanding of the effects of Al on the microstructural evolution and mechanical properties, in particular damage tolerance, of CrAlN coatings.

When incorporating Al into CrN coatings, there is a tendency to form an AlN (B4-wurtize type) phase, since the coordination number of Al and N is lower than that of Cr and N [22]. When it occurs, the hardness of the coatings decreases [23]. The theoretical solubility of Al in CrN is determined to be ~77 at.%. Experiments also found that the phase transition from CrN to AlN occurred in Al concentrations from 67 to 75 at.% [24]. To avoid such a transformation and maintain high hardness, CrAlN coatings with Al contents less than the above transition concentration were prepared in this study. Multiple surface and subsurface characterization techniques, assisted by finite element analysis, were used to investigate the roles of Al in shaping the microstructure and mechanical properties of these coatings.

2. Experimental procedure

2.1. Sample preparation

CrAlN coatings, with differing Al contents, were deposited onto AISI M2 steel substrates using a closed field unbalanced magnetron sputtering system (UDP650, Teer Coating Ltd., UK). The substrates were polished, ultrasonically cleaned and then dried. The average surface roughness of the substrates was ~30 nm. Before deposition, the background pressure was evacuated to 2.0×10^{-6} torr, and sputter etching was carried out in an Ar gas environment at a bias voltage of −500 V for 30 min to remove surface oxides and other contaminants. The deposition of CrAlN was conducted in mixed N_2 and Ar gases by reactive sputtering from Cr and Al targets. Two Cr targets, one Al target and one "dummy" Si target, were used. During deposition, the substrates were heated at 550 °C and rotated at a speed of 10 rpm. The bias voltage was set to −80 V. The working pressure of Ar/N_2 was kept at ~1.3 mtorr with the flow rate of Ar and N_2 at 50 and 60 sccm, respectively. A chromium wetting layer was first deposited. CrAlN coatings with varying Al contents were then grown by changing the currents of the Cr and Al targets (Table 1). The four coatings are named C1, C2, C3 and C4, where C1 is the binary and C4 has the highest Al content.

Table 1
Processing parameters used in the synthesis of the CrAlN coatings.

Sample no.	C1	C2	C3	C4
Cr current (A)	5.0	5.0	4.0	3.0
Al current (A)	0.0	5.0	10.0	10.0
Bias current density (mA cm^{-2})	1.2	1.5	2.5	1.6
Deposition duration (min)	60	60	50	55

2.2. Composition and microstructure analysis

The composition and surface chemical bonding states of the coatings were investigated using X-ray photoelectron spectroscopy (XPS) with a Kratos-Axis Ultra XPS Spectrometer (Manchester, UK). Mg K_α radiation was used as the X-ray source with a photon energy, hv, of 1253.6 eV. The accelerating voltage and the emission current X-ray source were kept at 12 kV and 12 mA, respectively. The pressure of the sample analysis chamber was maintained at ~10^{-9} torr. The pass energy of the semi-spherical photoelectron energy analyser was set to be 80 eV for survey scans and 10 eV for the acquisition of high resolution spectra. The electrostatic lens mode and analyser entrance were selected in the Hybrid and Slot modes. The binding energies of Cu2$p_{3/2}$ (932.67 eV), C1s (284.6 eV), Ag3$d_{5/2}$ (368.27 eV) and Au4$f_{7/2}$ (83.98 eV) were used to calibrate the spectra energy scale. The chemical composition of the coatings was quantified using the Vision Processing Kratos software, following a Shirley background subtraction. The crystal structure of CrAlN coatings was characterized by grazing incidence X-ray diffraction (GI-XRD) with Cu K_α radiation (wavelength = 0.1542 nm) at an incident angle of 0.5° to circumvent the influence of the substrate. The scanning runs from 20 to 90° with a step size of 0.02°.

The coating microstructure was observed using a focused ion beam (FIB) microscope (xP200, FEI, USA). The detailed procedure has been given elsewhere [25]. A brief description is given here. A Ga^+ beam was used at a high current (2700 pA) to create a cross-section, followed by polishing at a medium beam current (350 pA) to remove