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Deposition of CrSiN/AlTiSiN nano-multilayer coatings by multi-arc ion plating using gas source silicon

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ABSTRACT

Quinary CrAlTiSiN coatings have been prepared on cemented carbide and Si substrates using Cr and AlTi (67:33 at.%) alloy targets in the mixture flow of N_2 and SiH_4 gas by multi-arc ion plating method. X-ray diffraction and transmission electron microscopy revealed that the multi-element coatings had a nc-CrSiN/nc-AlTiSiN multilayered structure with a thickness period of 10 nm. The microhardness and wear of the coatings were found to be strongly influenced by SiH_4 flow rate. The hardness increased monotonically with the increase of SiH_4 flow rate and reached 37 GPa at 23 sccm. The coatings exhibit friction coefficients varying between 0.58 and 0.76 against Si_3N_4 ball.

1. Introduction

Transition metal nitrides are attractive materials for machining industries due to their remarkable physical and mechanical properties including high hardness, high wear resistance and chemical inertness [1,2]. The first generation hard coatings prepared by physical vapor deposition are binary compounds such as TiN and CrN coatings [3,4]. Though they enhance the performance of tools, there are a lot of drawbacks such as poor thermal stability at high temperatures, limited enhancement in hardness and defects in the structure of columnar crystals [5]. To overcome these shortcomings, light elements including Al and B were incorporated to form TiAlN, CrAlN and TiBN and improved properties were achieved [6–8]. Further researches aiming to enhancement of the oxidation resistance and mechanical properties led to the development of TiSiN and CrSiN coatings [9–12]. More recent examples are quaternary CrAlTiN, CrAlSiN and TiAlSiN coatings [12,13] which have produced even better performance and provide a better alternate to TiN and TiAlN for the foreseeable future.

In order to further meet the demands of machining tools, multiple-element and multilayered coatings have become considerably attractive, such as multilayered TiCrAlSiN obtained an ultrahigh hardness of 43 GPa [14–16]. The elements of such coatings are mostly produced from pure metal or alloy sources. For example, Kim et al. prepared multilayered nc-TiCrN/nc-AlSiN coatings from TiCr and AlSi sources by cathodic arc deposition. At present, it is difficult to obtain multiple-element coatings with homogeneous Si element from pure Si target, because of the intrinsic properties of Si, such as poor conduction and thermal shock resistance of the Si target. This paper reports the successful synthesis of nano-multilayered CrAlTiSiN coatings with homogeneous Si content by cathodic arc deposition using silane gas as Si source. It is convenient to control the concentration of Si by tuning the flow rate of SiH_4, making it possible to investigate the influences of SiH_4 flow rate on the microstructure and mechanical properties of CrSiN/AlTiSiN coatings.

2. Experiment details

The CrAlTiSiN coatings were deposited on cemented carbide and Si substrates using a home-made eight target cathodic arc evaporation system. The deposition chamber is $\phi 800 \times 1000$ mm in dimension and equipped vertically with four AlTi (67:33 at.%) alloy targets and four Cr targets mounted at alternative positions on the opposite sides of the chamber wall, so that the substrates alternatively faced each cathode. The substrates, after ultrasonically cleaned in acetone and methanol solutions, were mounted onto the substrate holder, and then subjected to etching and preheating in argon glow discharge plasma for 20 min. Before deposition, 10 min bombardment with Cr ions in argon ambient at 1.2×10^{-2} Pa was carried out to further remove the contamination on substrate surface and enhance the adhesion strength. The substrates were biased by a pulsed dc power supply with a fixed voltage of −200 V and a duty cycle of

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80%. Then, the argon gas was exhausted and Ar + SiH_4 mixture gas (with an Ar/SiH_4 ratio of 9:1) was fed into the chamber at working pressure of 3.3 Pa balanced by tuning the N_2 flow rate. All the target sources were powered at a constant arc current of 70 A and the duration of deposition of CrAlTiSiN coatings was 30 min with the substrate holder rotating at a speed of 4 rpm.

The crystal structure was characterized by X-ray diffraction (XRD, Bruker-axs D8 advanced) with a Cu kα radiation (0.15418 nm) and JEOL JEM 2010 transmission electron microscopy (TEM). A Renishaw RM-1000 confocal micro-Raman spectrometer excited by an Ar-ion laser at 514.5 nm was employed to conduct point analysis of phonon scattering of the films. The composition of the CrAlTiSiN coatings was determined by using an EDAX genesis 7000 energy dispersive spectrometer (EDS) operated at 12 kV. The chemical bonding of the coatings was measured by using a Kratos XSAM800 XPS system using Mg Kα (1253.6 eV) X-ray radiation.

The hardness was measured on HX-1000 microhardness tester with a load of 0.1 N and the average of 10 values was taken. Dry-sliding tribological tests were performed against Si_3N_4 ball using a MS-T3000 ball-on-disk tester, and the tests were conducted with a sliding speed of 0.02 m/s under a load of 5 N at room temperature (around 30 °C) and 70–75% relative humidity. The sliding proceeded at 0.02 m/s for a preset sliding time of 60 min and the friction coefficients were recorded during the test. The groove dimensions, determined by a FTSS2-S4L-3D step profiler, were used to calculate the volume of the wearing part of the coatings.

3. Results and discussion

Fig. 1 shows XRD spectra of the CrSiN/AlTiSiN coatings deposited at various SiH_4 flow rates and spectra of monolithic CrN and AlTiN coatings deposited on Si substrates. The spectra show that the CrSiN/AlTiSiN coatings exhibit a single face-center-cubic structure. The dashed lines show the Bragg angles of corresponding planes from the standard reference samples (JCPDS 38-1420 and 11-0065). For nanomultilayers, the plane orientations of (111), (200) and (220) are observed at the positions between CrN and AlTiN phases. Tensile and compressive stress are present in the CrN and AlTiN layers, respectively. The diffraction intensity of (111) plane decreases, while the intensity of (200) peak increases, and that of the (220) plane remains almost unchanged with the increase of SiH_4 flow rate from 0 to 23 sccm. This variation is attributed to the increase of SiH_4 and decrease of N_2, since the total pressure was identical for all the samples. The variation in the orientations affects the microhardness of nanomultilayer coatings. There is no obvious shift of the diffraction peaks of the coatings when the SiH_4 flow rate changes, which suggests that the Si atoms are not dissolved into the coatings lattice [17,18]. Moreover, the grain size of the coatings is about 13 nm calculated by Debye–Scherrer equation and does not change much with variation of the SiH_4 flow rate.

The bright-field cross-sectional TEM image and the corresponding selected-area electron diffraction (SAED) pattern of the CrAlTiSiN coatings are shown in Fig. 2. One sees a typical nano-multilayer structure, in which the bright AlTiSiN layers alternate with the dark CrSiN layers, as a result of substrate rotation at a specific speed around the alternatively mounted Cr and AlTi targets on the chamber wall. The bilayer thickness period of the coatings is approximately 10 nm. The insert HRTEM image shows that the size of crystal is 12 nm, which agrees with the value calculated from XRD spectra by Debye–Scherrer equation. Moreover, the thermal expansion coefficient of Si substrate is smaller that of metal nitride coatings, thus, a curved interface which is observed between substrate and multilayers indicates that thermal contraction tensile stresses are induced in CrAlTiSiN coatings upon cooling from deposition temperature. The diffraction rings correspond to crystal planes of (111), (200) and (220), which accords with the XRD results shown in Fig. 1. Table 1 shows the elemental content in the films for different SiH_4 flow rates. With the increase of SiH_4 flow rate, the Si content in the film increases linearly, while the contents of N, Cr, Al, and Ti remain the same in the ranges of 45.0–47.2 at.%, 29.9–33.4 at.%, 14.3–17.3 at.%, and 6.7–7.8 at.%, respectively. Since the nitrogen content in the films is blow 50 at.%, the deposited coatings are slightly under-stoichiometric.

Fig. 3 shows Raman spectra of the multilayer coatings deposited at different SiH_4 flow rates. Since the nitride coatings crystallize in fcc structure, they have O_h site symmetry. However, it is expected that the lattices carry stoichiometric and crystalline defects, which produce defect-induced first-order phonon scattering [19]. It has been found that both optic and acoustic branches give rise to Raman bands according to $\Gamma = A_{1g} + E_g + T_{2g}$ in the O_h impurity-site symmetry [20,21]. In the case of nano-multilayer films, Raman scattering with contributions from different sublayers are cumulative [22]. In Fig. 4 the Raman spectra of CrAlTiN coatings show three broad bands centered at 256, 671 and 1264 cm^{-1}, related to the first-order acoustic (LA and TA), optical (LO and TO), and second-order optical (2O) modes, respectively. The scattering in acoustic branch is primarily determined by vibrations of the heavier metal ions, and the process in optical branch is determined

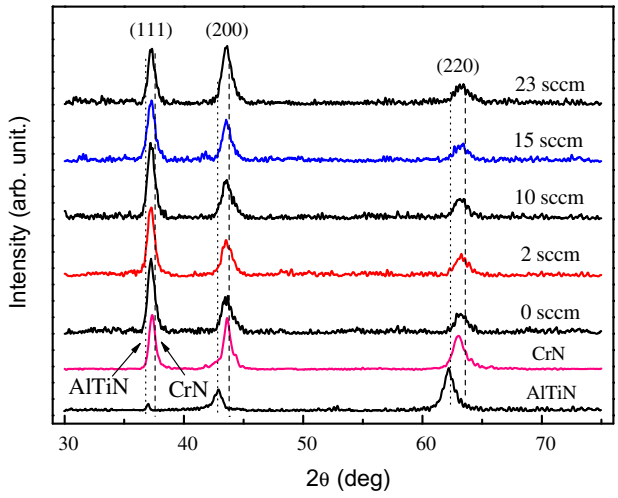

Fig. 1. XRD patterns of the CrAlTiSiN coatings synthesized with different SiH_4 flow rates as well as monolithic CrN and AlTiN films.

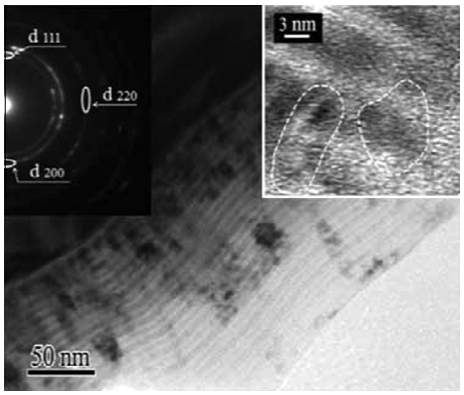

Fig. 2. Bright-field cross-sectional TEM micrograph and corresponding SAED pattern of the coatings synthesize at 23 sccm SiH_4 flow rate. The insert is an HRTEM image.