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Effect of incorporating oxygen on microstructure and mechanical properties of AlCrSiON coatings deposited by arc ion plating

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ABSTRACT

AlCrSiON coatings with a 0–48 at.% oxygen addition were deposited by arc ion plating process in an Ar–N_2–O_2 mixture atmosphere. The influence of varying oxygen content on elemental compositions, microstructure, residual stress, and mechanical properties of the AlCrSiON coatings was investigated. The results indicate that the oxygen content increases from 0 to 48 at.% with increasing the flow ratio O_2 / (O_2 + N_2) from 0 to 18 at.%. The AlCrSiN coating reveals a nanocrystalline structure composed of fcc-CrN and c-AlN. The c-AlN dissolves into the fcc-CrN forming the solid-solution type (Cr, Al)N as the oxygen content increases to 16 at.%. Further increasing the oxygen content up to 48 at.%, both the c-(Cr, Al)N and the c-(Cr, Al)(O,N) phases were found in the coating. The AlCrSiON coating exhibits a nano-multilayer structure repeating at ~8 nm intervals due to the substrate rotation. Both the hardness and the residual stress of the AlCrSiON coatings decrease as the O content increases. The adhesion strength of the AlCrSiON coatings first increases and then decreases with the increase of oxygen content. The largest recorded value of 77 N was obtained for the coating with 8 at.% oxygen. The oxygen dissolved in the coatings reveals a minor effect on the friction coefficient at room temperature. However, the average friction coefficients of the AlCrSiON coatings decrease significantly compared to that of the O free AlCrSiN coating at 600–800 °C. The AlCrSiON coatings with a low O content (≤16 at.%) possess a superior wear resistance at elevated temperatures. However, the over added O deteriorates the wear resistance of the AlCrSiON coatings.

1. Introduction

The typical ternary AlCrN coatings have been widely used for cutting tools, molds, and mechanical parts. The addition of Al element into CrN is beneficial to improve the coating hardness, wear resistance, oxidation resistance and cutting performance during high speed, yet dry machining [1–6]. In the recent years, Si was frequently incorporated into the AlCrN coatings to prepare AlCrSiN nanocomposite coatings [7]. The quaternary AlCrSiN coatings show promoted performances such as oxidation resistance, thermal stability, and hardness compared to the ternary AlCrN coatings [8–10]. Generally, the nitride hard coatings always suffer from an undesirable incorporation of oxygen in industrial production, especially in the systems where the base pressure varies in the range of 10^{-4}–10^{-3} Pa [11]. Therefore, there is an urgent demand to investigate the influence of varying the oxygen content to the microstructure and mechanical properties of the AlCrSiN coatings. In addition, it was reported that the oxygen impurities deteriorate the mechanical properties of hard coatings significantly [12,13]. For instance, Veprek et al. [14] reported that a hardness of >50 GPa was achieved in the nc-TiN/a-Si_3N_4 system with the oxygen content below 0.2 at.%. However, the coating hardness decreases to below 35 GPa with further increasing the oxygen content up to 0.6 at.%. Researchers pointed out that incorporating the oxygen into the nitrides has made it much easier to adjust parameters like hardness, coefficient friction, and thermal stability in order to optimize the overall performances of the coatings, owing to the combined metallic-covalent-ionic bonding [15–17]. Lee et al. [18] reported that the hardness of the as-deposited CrSiON coatings increased from 28 GPa for the Cr–Si–N film to a maximum value of approximately 47 GPa with 16 at.% oxygen addition. Both the mechanical and the tribological properties of the CrSiON films with an appropriate addition amount of the oxygen are better than those of the ternary CrSiN film. To date, oxynitride coatings such as Cr–O–N [19,20], Al–O–N [21], Cr–Al–O–N [22,23], Cr–Si–O–N [12,24], Ti–Si–O–N [16,25], etc. have been synthesized. Although scant information about the deposition of the AlCrSiON coatings has been recorded [15], the influence of varying the oxygen content to the microstructure and mechanical properties of the AlCrSiON coatings is still relatively unclear.

In this work, the AlCrSiON coatings were deposited by an arc ion plating system. The effect of varying the oxygen content to the microstructure, hardness, adhesion strength and tribological behavior of the coatings was investigated. The mechanisms behind evolution of the microstructure and the mechanical properties have been discussed as well.

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2. Experimental details

2.1. Coating deposition

The AlCrSiON coatings were deposited on polished WC–6Co (nominally 6 at.% Co) substrates by an arc ion plating system. All the substrates were ultrasonically cleaned for 10 min, each successively in baths of acetone and alcohol, and blown dried. A Cr target (Ø 100 mm, thickness 20 mm, purity 99.99%) and an $Al_{55}Cr_{25}Si_{20}$ alloy target (Ø 100 mm, thickness 20 mm, purity 99.5%) were used for the arc ion plating. A schematic diagram of the apparatus is depicted in Fig. 1. Prior to deposition, both targets were pre-sputtered for 5 min to remove the surface contaminants after reaching the base pressure of 5×10^{-3} Pa. During the deposition, a Cr sublayer was deposited initially to release the mismatch of the thermal expansion coefficients between the substrates and the AlCrSiON coatings. The deposition was performed in a pure Ar atmosphere (purity 99.999%) with a pressure of 0.7 Pa. The substrate bias and the cathode current of the Cr target were fixed at −800 V and 80 A, respectively. Subsequently, the substrate bias was reduced to −100 V and a CrN transition layer was deposited at a N_2 pressure of 1.2 Pa with the N_2 gas (purity 99.999%) flow of 300 sccm. The cathode current of the Cr target was maintained at 80 A as well. Finally, the AlCrSiON layer was deposited using the AlCrSi alloy target with a cathode current of 80 A. The substrate bias and the working pressure were kept at −100 V and 1.2 Pa, respectively. The deposition temperature was 400 °C and the thickness of the coating was controlled at ~4 μm. In addition to the N_2 gas, O_2 gas (purity 99.99%) was introduced and the flow rate ratio O_2 / (O_2 + N_2) was set at 0%, 2%, 4%, 8%, 12% and 18%, respectively.

2.2. Characterization

The morphologies and elemental compositions of the AlCrSiON coatings were investigated using scanning electron microscope (SEM, FEI, Nano430) equipped with an energy-dispersive X-ray spectrometer (EDS)·The phase structure of the as-deposited coatings was characterized by X-ray diffraction (D8 Advance Backer, Cu K_α). X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) combined with Ar^+ sputtering etching (~50 nm depth) were employed to investigate the chemical bonding states of the coatings. Transmission electron microscopy (TEM, Tecnai G2 F20, U.S.) were used to observe the microstructure of the coatings. The coating hardness was measured using a nanoindentation tester (CSM, TTX-NHT). The penetration depth was controlled about 10% of the coating thickness in order to minimize the influence of the substrate. The residual stresses of the AlCrSiON coatings were calculated via the Stoney equation [26], where the curvature of the coating/substrate composite was determined by a laser tester. Scratching test was carried out to measure the adhesion strength of the coating to the substrate using a scratch tester (CSM, Revetest scratch tester). The parameters of scratch test were as follows: scratch length 3 mm, scratch speed 6 mm/min and load 1– 120 N. The tribological properties of the coatings were investigated using a ball-on-disc tribometer (CSM HT-1000) in air at RT–800 °C. Al_2O_3 balls with a diameter 6 mm were used as the friction pairs and a 5 N load was applied. The wear rate W of the AlCrSiON coatings was determined using the equation [27]: $W = V/(L \times s)$ (V is the loss of volume by wear, L is the loading and s is the sliding distance).

3. Results and discussion

Fig. 2 shows the elemental compositions of the AlCrSiON coatings as a function of the oxygen flow rate. The Cr, Al, and Si contents are ~14 at.%, 23 at.% and 8 at.%, respectively, independent of the O_2 flow rate. However, the oxygen content in the AlCrSiON coatings increases from 0 to 48 at.% with increasing the O_2 flow rate from 0 to 54 sccm. Correspondingly, the N content decreases from 53 to 10 at.%. The sum of the O and N contents remains unchanged, i.e. ~55 at.%.

The crystal structure of the AlCrSiON coatings was investigated by XRD. As shown in Fig. 3(a), the diffraction patterns indicate that both the as-deposited AlCrSiN and AlCrSiON coatings reveal a polycrystalline structure. For the AlCrSiN coatings (in Fig. 3(a) and (b)), the diffraction peaks were identified to be the (111) and (200) characteristic peaks of the cubic CrN. Additionally, cubic AlN(200) was observed in the AlCrSiN coating. As shown in Fig. 3(b) and (d), it can be found that the phase composition of the AlCrSiON coatings with a low amount of oxygen (≤16 at.%) gradually changes from the mixture of fcc-CrN and AlN to the metastable solid-solution fcc-(Cr, Al)N. However, another crystalline phase fcc-(Cr,Al)(O,N) could be found as the oxygen content

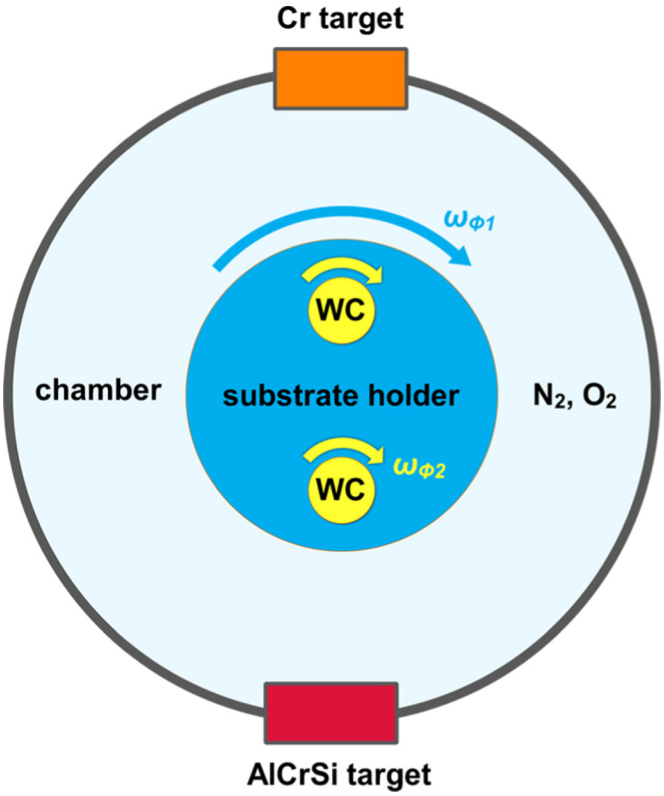

Fig. 1. Schematic of the arc ion plating system used in this work.

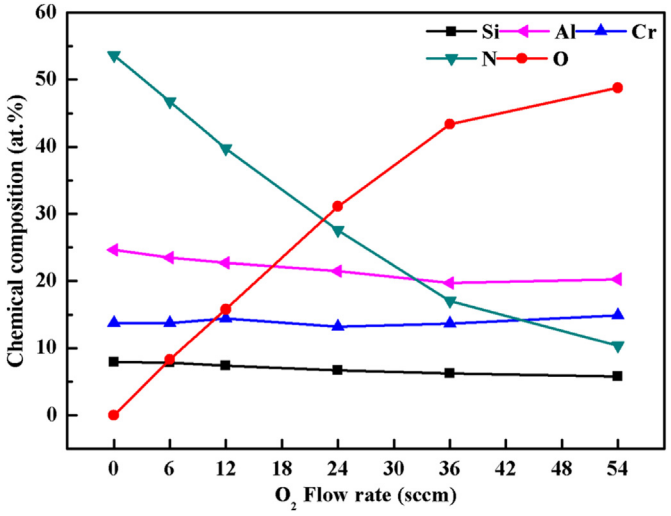

Fig. 2. Elemental compositions of the AlCrSiON coatings as a function of oxygen flow rate.