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Microstructure, mechanical property and thermal stability of diamond-like carbon coatings with Al, Cr and Si multi-doping

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A B S T R A C T

In this paper, AlCrSi atoms were co-doped into DLC coatings by using a high power impulse magnetron sputtering combining with an anode-layer linear ion beam. The doped AlCrSi contents were controlled via adjusting the Ar fraction in the sputtering gas mixture of Ar and C_2H_2. The influences of the AlCrSi multi-doping on the composition, microstructure, residual stress, mechanical property and tribological behavior of the as-deposited DLC coatings were studied systemically by using EDS, XPS, TEM, stress-tester, nanoindentation and ball-on-plate tribometer as a function of the Ar fraction. The thermal stability of the coatings was also researched by a vacuum heat treatment with various temperatures. The results show that the carbide former Cr preferred to form hard carbide components which were conducive to the hardness of the coatings, while the weak carbide former Al dissolved in the DLC matrix as metallic state, which can effectively released the stress of the DLC coatings. The doped Si would bond with sp^2-C to form sp^3 C—Si, and thus maintained the sp^3-C structure stability and improved the thermal stability of the coatings. Accordingly, the DLC coatings with AlCrSi multi-doping not only exhibited relatively low residual stress and high hardness, but also showed a high thermal stability over 500 °C. It was believed that the AlCrSi multi-doping may be a good way for improving the comprehensive properties of the DLC coatings.

1. Introduction

Due to their unique combination of desirable properties including high hardness, low friction, chemical inertness and high wear resistance, diamond-like carbon (DLC) coatings have been widely used as protective coatings in many industrial applications such as magnetic storage disks, cutting tools and dies and biological implants [1–4]. Recently, many foreign elements including metallic and non-metallic atoms were incorporated into the amorphous DLC matrix to improve the residual stress, thermal stability, toughness and tribological property of the DLC coatings. The influences of the foreign element doping on the structure and property of the DLC coatings depend on the doped element type. For the strong carbide formers, like Ti [5] and W [6], the doped atoms would bond with C and form hard carbide phase embedded in the carbon matrix. The hard composite could significantly improve the hardness of the coatings. Nevertheless, the formation of Me-C bonds might increase the disorder degree of the carbon matrix and thus cause the residual stress to increase. In addition, the hard and brittle carbide would limit the plasticity and decrease the toughness of the coatings. For the weak carbide former atoms, like Cu [7] and Al [8], are incorporated into DLC without bonding with C, and favor to form ductile metal phases in the carbon matrix, which have been expected to overcome the brittleness and improve the toughness of the DLC. However, the ductile metal phases also cause the decrease of the coating hardness. The incorporation of non-metallic atoms, like Si [9] and N [10], have been found to improve of adhesion strength and thermal stability of the DLC coatings. However, the wear protection and hardness would be reduced due to the incorporation of the non-metallic atoms [9,10]. Apparently, the incorporation of one kind of foreign elements is hard to comprehensively improve the performances of the DLC coatings. Nevertheless, it is possible to acquire the DLC coatings with the combination property of low residual stress, high hardness and toughness, and thermal stability by multi-doping of foreign elements including weak carbon former metal atoms, carbide former metal atoms and non-metallic atoms [11,12].

In this article, Al, Cr and Si atoms would be co-incorporated into DLC coatings by using a high power impulse magnetron sputtering (HIPIMS) which can significantly increase the ionization rate and energy of the species for the growth coatings as compared to the DC magnetron sputtering (DCMS) [13]. The influences of the Al, Cr and Si multi-doping on the composition, microstructure, residual stress, mechanical properties and thermal stability of the as-deposited DLC coatings were studied systemically. The relationships between the effect of element doping, microstructure, residual stress, mechanical properties as well as thermal stability were discussed in detail.

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2. Experimental details

Series of Al, Cr and Si multi-doping DLC (AlCrSi-DLC) coatings were deposited using a hybrid beams system which consists of an anode-layer linear ion beam source (LIS) and the HIPIMS equipped with a 70 mm (diameter) × and 594 mm (length) AlCrSi (Al/Cr/Si = 50/30/20 at.%) revolving target (purity 99.99%). The LIS with a cross-sectional area of 102 mm (wide) × and 530 mm (length) faces to the substrate at an angle of 23°. The HIPIMS also faces to the substrate at an angle of 23°. The distances between the targets and the substrates are approximately 15 cm. The Si substrates were cleaned ultrasonically in acetone, ethanol, and dried in air before being put into the vacuum chamber. In order to facilitate the characterization of the as-deposited coatings, silicon (100) wafers were used as the substrates. Prior to deposition, all the substrates were sputter-cleaned for 10 min using Ar ion beam by the LIS at a bias voltage of −300 V. The base pressure was evacuated to the vacuum of 3×10^{-3} Pa. During depositing process, the pressure was kept at about 0.5 Pa, and the substrate holder rotation speed was set at 6 rpm. A gas mixture of C_2H_2 and Ar was introduced into the chamber as the gas precursor. The doping contents of Al, Cr and Si in the coatings were controlled by varying the Ar fraction in the precursor gases and the total gas flux (Ar and C_2H_2) was kept at 100 sccm. Typical value of the LIS power was 1 kW (400 V and 2.5 A). For the HIPIMS unit, an average target power of 2 kW was maintained for all experiments. The target peak voltage was kept around 655 V. The pulse repetition frequency was 300 Hz and the pulse width was approximately 100 μs (3% duty cycle). A bias voltage of −100 V was applied to the substrate. The whole deposition process time was 2 h.

The thicknesses of the deposited coatings ranging from 2.3 μm to 3.3 μm were measured by a cross-section SEM (Nova nanoSEM 430, FEI) measuring scale. The chemical composition of the coatings was analyzed using energy-dispersive X-ray spectroscopy (EDS). For simplicity, the hydrogen content in the coatings was neglected due to the lack of signal intensity in the current EDS detection measurement. The chemical bonds of the coatings were analyzed by X-ray photoelectron spectroscopy (XPS, Axis ultraDLD) with the Al (mono) Kα irradiation at a pass energy of 160 eV. Before commencing the measurement, an Ar^+ ion beam with an energy of 2 keV was used to etch the sample surface for 5 min to remove any contaminants. High-resolution transmission electron microscopy of the coatings was performed using a FEI Tecnai G2 F20S-Twin microscope with a 200 kV acceleration voltage. The TEM specimens were prepared using mechanical polishing and precision ion polishing system (Gatan PIPS691).

The residual stress of the coatings was calculated via the Stoney equation [14], where the curvature of the coating/substrate composite was determined by a laser tester. The mechanical properties of the coatings were measured using the nano-indentation technique (MTS-G200) in a continuous stiffness measurement (CSM) mode with a maximum indentation depth of 500 nm. The characteristic hardness was chosen in the depth where the measured value was not affected by the soft Si substrate. A rotary ball-on-disk tribometer was employed to characterize the tribological behavior of the coatings at room temperature with a relative humidity of about 50%. A steel ball (SUJ-2, HRC60) with a diameter at 7 mm was used as the friction counter ball. All the tests were performed at 0.2 m/s sliding velocity for a distance of 360 m and the applied load was 3 N (the initial Hertzian contact pressure was about 0.6 GPa).

Heat treatments were performed to investigate the thermal stability of the synthesized coatings. The DLC coatings were annealed in a vacuum furnace with different temperatures from 300 to 700 °C for 1 h. After treatment, the specimens were characterized using the Raman with an incident Ar^+ beam at a wavelength of 514.5 nm.

3. Results and discussion

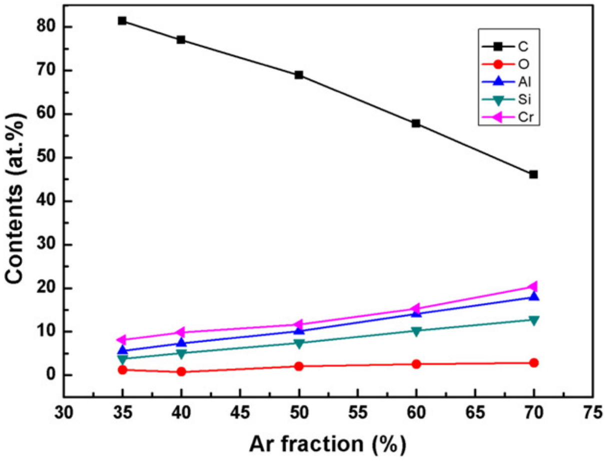

Fig. 1. Al, Cr, Si and C contents of AlCrSi-DLC coatings as a function of the Ar fraction in the gas mixture.

Fig. 1 shows the evolution of the Al, Cr, Si, C and O contents in the AlCrSi-DLC coatings. As the Ar fraction in the Ar/C_2H_2 gas mixture increased from 35% to 70%, the Al, Cr and Si contents increased straightly from 5.63 at.% to 17.94 at.%, 8.08 at.% to 20.4 at.% and 3.76 at.% to 12.82 at.%, respectively. This means that the doped Al, Cr and Si contents in the DLC coatings could be controlled by adjusting the Ar fraction. The ratio of Ar/Cr/Si in the coatings was kept at around 35/40/25, different from that in the target (Al/Cr/Si = 50/30/20 at.%) used in this experiment. The difference of the composition is mainly attributed to the different sputtering yields of Al, Cr and Si elements. In addition, a small amount of oxygen (<3 at.%) was found in the coatings, and the content increased slowly with the Ar fraction. The presence of oxygen might be due to the residual oxygen in the chamber and the oxide in the target.

To characterize the chemical states of the doped elements and carbon, XPS test was processed for the as-deposited coatings. Fig. 2 (a-d) show the high resolution XPS spectra for the Al2p, Cr2p, Si2p and C1s regions of the coatings deposited with different Ar fractions. It can be seen that the intensities of the Al2p, Cr2p and Si2p peaks increased with increasing Ar fraction, indicating that the doped Al, Cr and Si contents of the coatings increased. The Al2p spectra could be deconvoluted into two peaks: a major peak around 74 eV and a weak peak around 75.8 eV, corresponding to Al in the metallic state and Al in oxide state, respectively, implying that aluminum did not bond with carbon. As shown in Cr2p XPS spectra, there is a symmetrical sharp peak centered at ~574 eV, as expected for the Cr2p3/2. A small peak at ~575 eV deconvoluted from the major peak could be assigned to Cr—O bonds. It can be seen that there was no significant difference between the Cr2p peaks in the coatings deposited with various Ar fractions, since that the Cr2p peak could not be used effectively to differentiate the chemical bonds between metallic Cr and Cr carbide [15]. Regarding XPS Si2p spectra, the main peak Si2p is placed at around 100.5 eV, which indicates the existence of Si—C bond, and a small peak presents around 101.8 eV, owing to the Si—O bond. The C1s spectra of the coatings could be deconvoluted into four peaks at binding energies of 283 eV, 284.5 eV, 285.5 eV and 286.5 eV. The peak at the relatively lower binding energy of about 283 eV could be assigned to C in carbide bonds (Si—C or/and Cr—C). The peaks around 284.5 eV and 285.5 eV were expected to originate from the sp^2-C bond and sp^3-C bond, respectively. A weak peak appears at the binding energy of about 286 eV corresponding to C—O bonds. It is worth noting that a shift of the major peak of the C1s spectra from the higher C—C or C—H bonding energy to the lower carbide binding energy was observed as the Ar fraction increased from 50% to 60%, implying that the structure of the coatings transformed from a amorphous DLC structure to a carbide structure.

The bond fractions of the carbide bonds (Si—C and Cr—C), carbon bonds (sp^2-C and sp^3-C bonds) and C—O bonds in coatings were determined by the relative peak areas of the fitted peaks of the C1s spectra and are shown in Fig. 3. It can be seen that as the Ar fraction increased