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Manufacture, microstructure and mechanical properties of CrWN and CrN/WN nanolayered coatings

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Abstract

Chromium nitride and tungsten nitride coatings were fabricated in sequence to form a CrN/WN nanolayered coating by rf reactive magnetron sputtering technique with a dual-gun system. The CrWN coating was also manufactured for comparison. The bilayer period of the nanolayered CrN/WN coating were controlled at 10 and 24 nm. Periodic feature of elemental distribution of the nanolayered coatings was revealed by the Auger electron spectroscopy depth profiling analysis. The phase identification results indicated that the composite CrWN coating was composed of CrN phase with solid-solution of W, while CrN and amorphous/nanocrystalline WN and W_2N phases was observed in the nanolayered CrN/WN coatings. The CrN/WN nanolayered microstructure was evaluated by scanning and transmission electron microscopy. Nanoindentation technique was employed to evaluate the mechanical properties, including hardness and Young's modulus. The nanolayered CrN/WN coatings exhibited a high hardness around 30 GPa, which was superior to that of the CrWN coating. The nanolayered structure with confined grains of the nitrides in the nano range was beneficial to the enhancement of the mechanical performance for the multilayer coating.

Keywords: Chromium nitride; Tungsten nitride; Nanolayered; Hardness; Nanoindentation; Auger electron spectroscopy (AES); Transmission electron microscopy (TEM)

1. Introduction

Intensive investigation focused on nanostructure coating materials has recently attracted tremendous interests to explore coatings with versatile characteristics and superior performance. Among various coatings, nanocomposite or nanolayered nitride deposit systems have been the focused issue [1–3]. The transition metal nitrides have been considered as protective coating owing to their excellent properties in hardness, wear and corrosion resistance [4–6]. In the nitride systems, chromium nitride (CrN) has been postulated as a promising candidate to exhibit high hardness, excellent anti-oxidation, and good corrosion and wear resistances [7–10]. Tungsten, in the metal form, is another material frequently used due to its high melting temperature and high hardness [11]. Tungsten nitride coatings have been employed in optical and microelectronic applications, such as barrier layer and electrode [12–14]. Nevertheless, limited literatures concerning its mechanical properties could be found. Shih and Dove studied the mechanical properties of Ti/TiN, Hf/HfN, and W/WN multilayer coatings [15]. It was concluded that the coatings with nanolayer configuration by pure metal and metal nitride exhibited superior mechanical properties than the single-layer films. Significant enhancement in hardness up to 30 GPa was discovered in the W/WN coatings with an individual layer thickness down to nanoscale [15] as compared to that of the single WN film. The tungsten nitride multilayer coating was therefore proved to be a potential candidate in hard coating applications, especially in the nanolayered form.

The combination of CrN and WN coatings to form a nanostructure coating system was then proposed in this study. The composite CrWN and nanolayered CrN/WN coatings were fabricated by rf sputtering technique. Microstructure evaluation of the nanostructured coatings was

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carried out through various novel analyses, such as SEM, TEM, and AES profiling techniques. Microhardness and Young's modulus of the coatings were also investigated. In addition, the microstructure and mechanical properties of both the multilayer CrN/WN and nanocomposite CrWN coatings were then correlated and discussed for comparison.

2. Experimental details

The composite CrWN and nanolayered CrN/WN coatings were fabricated onto polished Si wafer using a dual gun sputtering apparatus with pure Cr and W metal targets. The co-sputtering of Cr and W, and sequential sputtering of Cr and W with N_2 gas inlet were performed for CrWN and CrN/WN coatings, respectively. Before deposition process, the coating chamber was pumped down to 2.0×10^{-3} Pa followed by the inlet of Ar and N_2, both at 20 SCCM, as plasma and reactive gas sources, respectively. The working pressure after gas input was controlled at 4.0×10^{-1} Pa. The input power of the Cr target was controlled at 150 W, while that for the W target was fixed at 35 W. The deposition time of individual nitride layer of the multilayer CrN/WN coating during sequential sputtering was modified from 100 to 240 s.

To investigate the detailed microstructure of the nanostructured coatings, the high-resolution transmission electron microscope (HRTEM, JEM-2010, JEOL, Japan) was employed. The coating uniformity, thickness and cross-sectional morphology of the coatings were observed with a scanning electron microscope (FESEM, JSM-6700, JEOL, Japan). The Auger depth profile technique was applied to evaluate the elemental distribution and periodic characteristic of the multilayer coating with an Auger electron spectrometer (AES, Auger NanoProbe, 670 PHI Xi, Perkin Elmer, USA). Phase identification was carried out with an X-ray diffractometer (Rigaku Dmmax-B, Tokyo, Japan) using grazing angle diffraction technique with X-ray incident angle at 1°. Mechanical properties, including hardness and reduced modulus of the coatings were investigated with a nanoindentation apparatus (TriboScope, Hysitron, Minneapolis, MN) using Oliver–Pharr method [16]. The maximum load adopted for all the coating was fixed at an adequate value of 3000 μN.

3. Results and discussions

3.1. Microstructure of the CrWN coating

Using co-sputtering of Cr and W with N_2 reactive gas inlet, the composite CrWN coating was fabricated. Fig. 1 shows the TEM image and diffraction pattern of the composite CrWN coating. Nanocrystalline structure of grain size down to 5–10 nm was observed in the TEM image. The ring electron diffraction pattern also indicated a

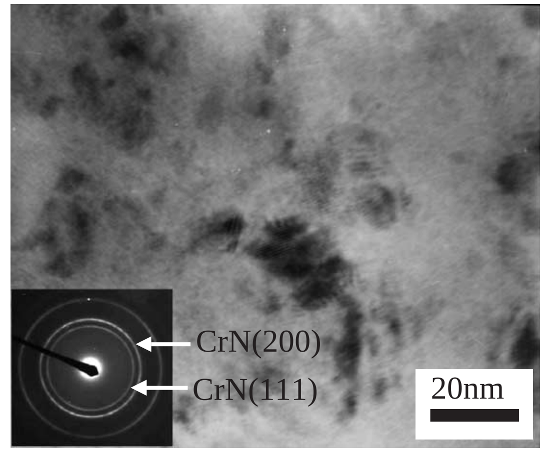

Fig. 1. TEM image and diffraction pattern of the composite CrWN coating.

nanocrystalline microstructure with randomly distributed grain in the CrWN coating. In recent report by Hones and coworkers [6] concerning the microstructure of CrWN systems, the tendency to form dense and fine grain microstructure was revealed with the doping of W into the CrN coating. However, the grain size of CrWN coating evaluated by Hones was from 10 to 20 nm, which was slightly higher than that in the present study. It was believed that the lower deposition temperature of 350 °C used in this work, as compared to 500 °C for Hones' experiment, resulted in slower grain growth rate during CrWN deposition.

In addition, the CrN phase with (111) and (200) orientations was identified from the electron diffraction pattern, whereas no significant WN phases was observed. It was argued that the co-deposition of W and Cr with reactive N_2 gas tended to form a CrN crystalline structure with W incorporated as solid solution agent. Consequently, a nanocrystalline CrWN composite coating with crystallite size of 5–10 nm CrWN was revealed by rf magnetron co-sputtering technique.

3.2. Nanolayered structure of the CrN/WN films

Sequential deposition of CrN and WN layers with controlled modulation periods was applied to visualize the multilayered CrN/WN coatings. Fig. 2 indicates the cross-sectional SEM images of the multilayer CrN/WN coatings with a total film thickness of approximately 650 nm. Dense and smooth microstructure for the multilayer coatings was developed with rf magnetron sputtering. It was apparent that the 51-layer CrN/WN coatings exhibited a layered configuration, comprised of the darker and the lighter nanolayer stacking sequentially. The thickness of bilayer periods in the 51-layer CrN/WN coatings were calculated to be 24 nm, as indicated in Table 1. The control of the bilayer thickness in the nanolayered coatings was achieved by adjusting the deposition time. The cross section SEM image of the 121-layer CrN/WN coating is shown in Fig. 2b. Similar smooth