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Investigation of the properties of $Ti_xCr_{1-x}N$ coatings prepared by cathodic arc deposition

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Abstract

The structure, composition and mechanical properties of $Ti_xCr_{1-x}N$ coatings have been investigated. Processing by cathodic arc evaporation using cathodes with different arc currents was performed to obtain coatings with compositions $x=0.52$, $x=0.59$, $x=0.68$, $x=0.72$ and $x=0.81$. The $Ti_xCr_{1-x}N$ hard coatings were characterized by nanoindentation, scanning electron microscopy and X-ray diffraction. The results showed the coatings consisted of B1-NaCl type cubic structure, the Cr content promoted a (200) preferred crystallographic orientation and has a dramatic influence on the hardness of $Ti_xCr_{1-x}N$ coatings, which indicated the alloy-strengthening of the Cr element on TiN-based coatings.

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1. Introduction

TiCrN coatings deposited on cemented carbide cutting tools considerably improve tools life-time because of their superior resistance to chemical wear and oxidation at high temperature. Most of the transition metal nitride such as TiAlN, TiCrN, and AlCrN are multi-phase material by different PVD techniques. The Cathodic arc evaporation for hard coatings is a useful process due to its high ionization in the plasma, outstanding deposited efficiency and dense coating.

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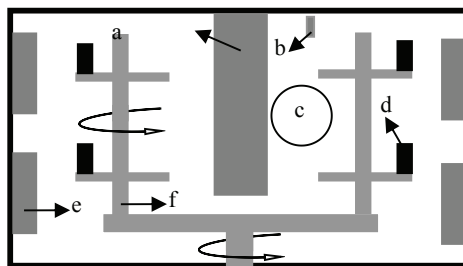


Fig. 1. Schematic illustration of XH-800 cathodic arc evaporation system

a) heating tubes(tube×12) b) gas inlet(Ar and N₂) c) vacuum pump d) substrate e) arc sources f) sample steady

Comparing with binary hard coatings such as TiN and CrN, multi-phase coatings are very versatile due to their performances may be tailored for various applications^[1-2]. In addition, the nanocrystalline structure more readily is formed in ternary multi-coatings than binary coatings, because of addition atoms interrupt the base-phase growing in deposition. TiN is fcc B1(NaCl) structure, and then the addition of chromium in the cubic leads to improve the coatings thermal stability. Chen previous proposed that chromium atoms are located in crystalline lattice sites of base-phase(TiN) substituting Ti atom to form a solid solution, and the CrN or element Cr can't be exist as a individual phase^[3]. However the development investigation of TiCrN by addition Cr to TiN, the Cr solution in TiN cubic is limited, the rich Cr react with nitrogen to CrN or Cr₂N^[4-5]. The microstructure, hardness and oxidation resistance of multi-phase TiCrN coatings may be influenced by Cr content. This paper aims at discussing the properties of Ti_xCr_{1-x}N coating prepared by XH-800 cathodic arc evaporation system, base upon nanoindentation, scanning electron microscopy and X-ray diffraction.

2. Experimental details

XH-800 cathodic arc evaporation system with 9 individual target and bias direct pulse power supply is researched and developed by Xihua University. The Ti_xCr_{1-x}N coatings were deposited on cement carbide samples by using the XH-800 cathodic arc evaporation system. A schematic figure of deposition system is illustrated in Fig. 1. Before deposition, the substrates were etched by high energetic Cr metal ions with an exposure time of 5mins through -800V pulse bias voltage, frequency and duty ratio of pulse bias voltage were 50 KHz and 25%. Each 4 circular pure Titanium and Chromium targets (102 mm in diameter) were arranged on the eight different positions of around the chamber wall to deposit the Ti_xCr_{1-x}N. Five kinds of Ti_xCr_{1-x}N coatings samples were deposited by changing the ratio of Ti and Cr targets current. Ti target current is from 70A to 100A and Cr target current was from 110A to 80A by welding power dc supply. Ar and N₂(99.99% purity) were introduced through a conducting duct on the top of chamber, and N₂ press is 0.5E-1 in process. The deposition temperature during the process is measured by a digital thermocouple located on the top of chamber and controlled at 300°C by 12 resistance heating tubes. All of the samples used the same deposition parameter of bias voltage, the direct bias voltage was -200v, pulse bias voltage are -150V for enhancing the ions energy and reducing the quantity of macro droplets, the frequency and duty ratio of pulse bias voltage are 50 KHz and 50%.

Table 1. Chemical composition of as-deposited coatings

| Sample No. | Titanium (at.%) | Chromium (at.%) | Nitrogen (at.%) |
|---|-----------------|-----------------|-----------------|
| Ti _{0.52} Cr _{0.48} N | 27.3 | 25.2 | 47.5 |
| Ti _{0.59} Cr _{0.41} N | 30.5 | 21.2 | 48.3 |
| Ti _{0.68} Cr _{0.32} N | 35.8 | 16.9 | 47.3 |
| Ti _{0.72} Cr _{0.28} N | 39.5 | 15.3 | 45.2 |
| Ti _{0.81} Cr _{0.19} N | 43.1 | 10.1 | 46.8 |

The hardness of coatings was tested at room temperature by means of a Nanoindentation Test system. Indentation was performed in the load controlling mode to a maximum depth of 200 nm. And then the loading–unloading process was as follows: loading to maximum load with 1 mN/s, plateau at maximum load for 5s, unloading in 60s. Because of avoiding the effect of substrate contribution to coatings elastic modulus, an appropriate indentation depth can minimize error and provide a reasonable estimate of the elastic modulus. For each sample load tests were repeated five times and calculated the average values. The surface and cross-section of $\text{Ti}_x\text{Cr}_{1-x}\text{N}$ coatings sample were used for characterization and analysis conducted with scanning electron microscopy (JEOL JSM—5900LV). It was operated at an accelerating voltage of 20Kv, and a working distance of 11.1mm. Chemical compositions were determined by energy-dispersive X-ray (EDX) analysis, and the chemical composition of as-deposition coatings is showed in table 1. The X-ray diffraction investigations were carried by DX-1000 X-ray diffractometer system with a Cu Ka radiation over the 2θ range 20° - 80° , screen ratio 0.05/s.

3. Result and discussion

3.1. Microstructure

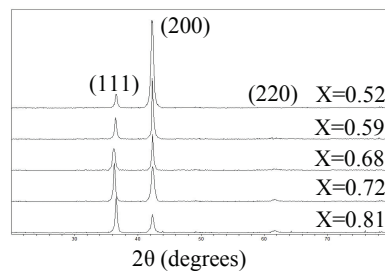


Fig. 2. X-ray diffraction spectra of as-deposited

Fig.2 showed X-ray diffraction patterns from as-deposited $\text{Ti}_x\text{Cr}_{1-x}\text{N}$ coatings with $x=0.52, 0.59, 0.68, 0.71, 0.81$, respectively. The major peaks corresponding to the (111), (200) and (220) plans for the NaCl type of cubic structure were observed. For coating with $x=0.81$, the preferred crystallographic orientation was (111) plane. As the chromium content of coating increased, the peaks corresponding to (111) and (220) plane decreased and the peak corresponding to (200) plane increased. And then, Strong preferred orientations along $\text{TiCrN}(200)$ are noticed in $\text{Ti}_{0.52}\text{Cr}_{0.48}\text{N}$. The crystalline structure of TiN and CrN was extremely similar with same space group ($\text{Fm}\bar{3}\text{m}$), and lattice constant of TiN and CrN was closed, so the major peaks of TiN or CrN were not detected as an individual phase. According to calculating by jade5.0 program, the lattice constant of the as-deposited $\text{Ti}_x\text{Cr}_{1-x}\text{N}$ coatings is intermediate between $\text{TiN}(4.24 \text{ \AA})$ and $\text{CrN}(4.14 \text{ \AA})$, and was indicate of solid solution^[6-8]. It has been reported that the change in lattice parameter was attributed to Cr atoms locating in crystalline lattice sites of base-phase (TiN) to substitute Ti atom. The increasing FWHM indicated decreasing grain size. Because of the ionization proportion of Cr target was more than Ti target with the same current parameter and deposition environment, accompany with more Cr atom substituting Ti atom, the nucleation rate was improved by substituted Ti atoms and ionization Ti atoms from target^[9].

3.2. Cross-section and surface

Fig.3 fracture cross-section of $\text{Ti}_{0.52}\text{Cr}_{0.48}\text{N}$ and $\text{Ti}_{0.81}\text{Cr}_{0.19}\text{N}$ are showed. Coatings were very dense and ostensibly not columnar, thickness was $4\mu\text{m}$, due to the intensive ion bombardment through the high ionization rate of cathodic arc processes and pulse bias accelerating. The fracture cross-section surface morphology of the coatings phases showed a fine equiaxial crystalline growth, a typical T zone according to the zone classification proposed by

Thornton^[10]. The growth of base-phase TiN was interrupted by Cr atoms instituting which decreasing crystalline size. An obvious evolution of microstructure in the coatings was showed with increasing Cr content.

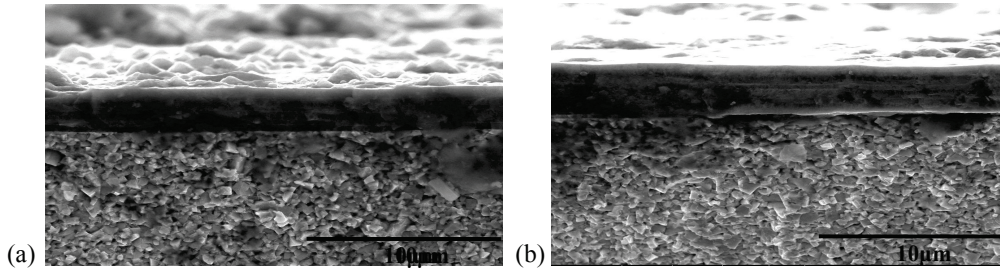


Fig. 3. Fracture cross-section of $Ti_xCr_{1-x}N$ coatings. a) $Ti_{0.81}Cr_{0.19}N$ b) $Ti_{0.52}Cr_{0.48}N$

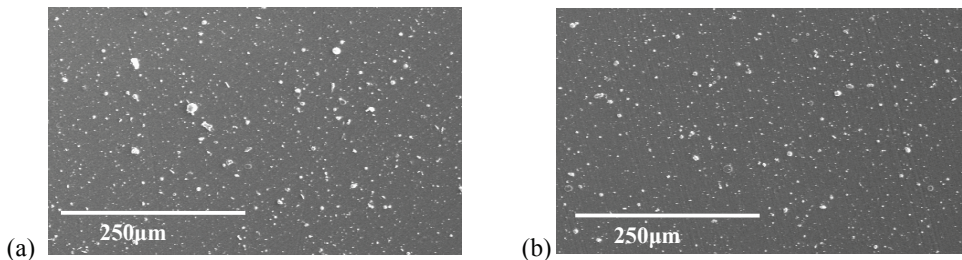


Fig. 4. surface morphology of $Ti_xCr_{1-x}N$ coatings. a) $Ti_{0.81}Cr_{0.19}N$ b) $Ti_{0.52}Cr_{0.48}N$

Fig.4 demonstrated the surface morphology of $Ti_{0.52}Cr_{0.48}N$ and $Ti_{0.81}Cr_{0.19}N$. Some macro droplets with size blow $1\mu m$ were found on the surface of coatings. The presence of the macro droplets was generated from the cathodic arc plasma which produce small liquid droplets, and than the difference value between melting point temperature and evaporating point temperature was great, the macro droplets was obvious^[11-12]. Increasing Cr target current and decreasing Ti target current could reduce effectively size and quantity of macro droplets, due to Cr was a kind of sublimation element which could avoid to melt micro-liquid-zone on surface of target. These macro droplets below $0.5\mu m$ could be tolerated in some industrial coatings, but they were impossible qualified for the application of optics and electronic coatings which used magnetron sputter widely^[13].

3.3. Cross-section and surface

Fig.5 showed the hardness and residual stress of the $Ti_xCr_{1-x}N$ coatings with different Chromium content as a function. The maximum hardness was $Ti_{0.72}Cr_{0.28}N$ (28GPa) which Chromium content was 0.28 and the minimum hardness was $Ti_{0.52}Cr_{0.48}N$ (25GPa) which Chromium content was 0.48, all of the coating hardness were above average hardness of TiN(22-24GPa). And than the maximum residual stress also was $Ti_{0.72}Cr_{0.28}N$ (5GPa). The hardness of $Ti_xCr_{1-x}N$ coatings rose with increasing Chromium content concentration range between 0.19 and 0.28 and reduced with decreasing gradually Chromium content concentration range between 0.32 and 0.48. The effects in coatings hardness can be explained by the institution of Chromium atoms in the TiN lattice. The Titanium atomic radius(1.46\AA) was greater than Chromium atomic radius(1.25\AA). It was reported that Negron atoms prefer to form TiN with Ti due to electron configuration, electron negativity, atomic radius and thermodynamics theory. Because of the institution of Chromium atoms inducing intensively lattice distortion base-phase TiN, the hardness was enhanced by improving strain in the lattice. In addition, the dissolution of Chromium atom could hinder the dislocations movement with the effect of improving hardness of coatings. With increasing Chromium content, the base-phase was changed gradually to multi-phase due to the rich Cr forming CrN. Comparing with $Ti_{0.81}Cr_{0.19}N$,

preferred crystallographic orientation of $\text{Ti}_{0.52}\text{Cr}_{0.48}\text{N}$ was change to (200) plane, indicating the rich Cr inducing the microstructure transforming.

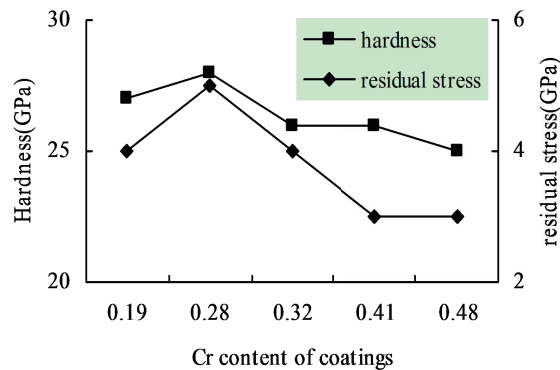


Fig. 5. Hardness and residual stress of $\text{Ti}_x\text{Cr}_{1-x}\text{N}$ coatings

4. Result and discussion

In this study, $\text{Ti}_x\text{Cr}_{1-x}\text{N}$ coatings were prepared by XH-800 cathodic arc evaporation system using pure Cr and Ti target with different current. The effect of different Ti and Cr content on microstructure, cross-section, surface and hardness of the as-deposited coatings were investigated by XRD, SEM, EDS, nanoindentation.

The investigation revealed that the $\text{Ti}_x\text{Cr}_{1-x}\text{N}$ was fcc NaCl structure, which the lattice parameter was between TiN and CrN. For coatings with Cr content < 0.28, the dominated phase was TiN, which part of Ti atoms in crystalline were substituted by Cr atoms. With increasing Cr content, the preferred crystallographic orientation was changed from (111) plane to (200) plane. Due to Cr content > 0.28, the CrN phase dominated gradually phase in $\text{Ti}_x\text{Cr}_{1-x}\text{N}$. Comparing with single composition coating, the hardness of multi-composition coatings could be enhanced by lattice distortion and solid solution. Both of the maximum hardness and residual stress were $\text{Ti}_{0.72}\text{Cr}_{0.28}\text{N}$ (28 GPa), indicating the improvement of coating hardness by lattice distortion. With the increasing Cr content, the hardness reduced gradually with microstructure transformation.

Acknowledgements

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