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Synthesis of WC - CrN superlattice film by cathodic arc ion plating system

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Abstract

New WC - CrN superlattice film was deposited on Si substrate (500㎛) using cathodic arc ion plating system. The microstructure and mechanical properties of the film depend on the superlattice period (λ). In the X-ray diffraction analysis (XRD), preferred orientation of microstructure was changed according to various superlattice periods (λ). During the Transmission Electron Microscope analysis (TEM), microstructure and superlattice period (λ) of the WC - CrN superlattice film was confirmed. Hardness and adhesion of the deposited film was evaluated by nanoindentation test and scratch test, respectively. As a result of nanoindentation test, the hardness of WC - CrN superlattice film was gained about 40GPa at superlattice period (λ) with 7nm. Also residual stress with various superlattice period (λ) was measured on Si wafer (100㎛) by conventional beam - bending technique. The residual stress of the film was reduced to a value of 0.2 GPa by introducing Ti - WC buffer layers periodically with a thickness ratio ($t_{buffer} / t_{buffer+superlattice}$). To the end, for the evaluation of oxidation resistance at the elevated temperature, CrN single layer and WC - CrN superlattice films with various superlattice periods on SKD61 substrate was measured and compared with the oxidation resistance.

1. Introduction

Hard coating played an important role in industry for improving tool lifetime and performance. Transition metal nitrides such as TiN and HfN have received considerable attention as wear-resistant coatings due to their high mechanical hardness & wear resistance and chemical inertness. Recently, a great deal of attention has been paid to compositionally modulated multilayer films, specific metals and nitrides with each layer on the nanometer scale because of their possibility to achieve superhardness[1-3]. Films with these characteristics are typically known as superlattice. For example, most of the accomplished works to the moment describe superlattice with metal/metal structure such as Cu/Fe[4], Al/Cu[4], Al/Ag[4], Cu/Ni[5] and some ceramics such as Ti/TiN[6], TiN/NbN[4], TiC/TiB_2[4], TiC/Mo[4,7] with a large range of hardness values varying approximately between 10 and 70GPa. The mechanical properties of multilayered films were found to be affected greatly by the modulation period, and a conventional Hall-Petch type relationship[8, 9] or Koehler's model[10] was applied to explain the mechanism of hardness enhancement.

As the hardness, the coatings are usually divided into two groups: (1) hard coatings having a hardness < 40GPa, and (2) superhard coatings having a hardness > 40GPa. Compared to a large number of hard materials, there are only a few superhard materials, i.e. cubic boron nitride (c-BN), amorphous diamond like carbon (DLC), amorphous carbon nitride (a-CN_x) and polycrystalline diamond. Moreover, these superhard materials are thermodynamically unstable. This is a serious disadvantage that strongly limits their utilization in some applications. For instance, the high chemical affinity of carbon to iron limits the applicability of diamond coated cutting tools to machining of aluminum, their alloys and wood only. Similar problems can be expected when the c-BN coating is used in cutting of steels due to the chemical dissolution of boron in iron[11].

To our survey, these prominent mechanical properties of superhard coatings forced us to consider WC-CrN superlattice film to develop new superhard coatings by cathodic arc ion plating. We have characterized WC-CrN superlattice film with various superlattice period (λ) using X-ray diffraction (XRD), Glow discharge optical emission spectroscopy (GDOES), cross-sectional TEM and electron diffraction pattern. Mechanical properties WC-CrN superlattice films were evaluated by microhardness, residual stress. Also, for the evaluation of oxidation resistance at the elevated temperature, CrN single layer and WC-CrN superlattice films with various superlattice periods was measured and compared with the oxidation resistance.

2. Experimental procedures

2. 1 Film deposition

WC-CrN films were synthesized on Si wafer (500㎛), S45C and SKD61 substrate by cathodic arc ion plating. Three circular Ti cathodes were installed on one side of chamber wall and three circular WC-Co ones were attached on the other side. A rotating substrate holder operated from 1 to 12 rpm was used to obtain layered structure with various superlattice period (λ). And then, for the reduction of film stress, interlayer of Ti-WC is deposited by selective arc discharge and modulation of N_2 flow rate during the deposition of WC-CrN films. Also the t_b to t_{b+s} ratio was changed from 0.1 to 0.5 for the evaluation of adhesion and residual stress. The detailed deposition conditions are listed in Table 1.

Table 1. Deposition conditions for WC-CrN coating process

Deposition parameters	Conditions
Base pressure	3×10^{-6} torr
Ar pressure	2×10^{-3} torr
Working pressure	$1\times1.5\times10^{-2}$ torr
Target power density	WC : 80W/㎠
	Ti: 50W/㎠
Jig rotation speed	1 ~ 12
Distance between substrate and target	200mm
Substrate bias voltage	-200V
Substrate temp	300℃ /
Interface	Cr and CrN
Buffer layer control	$t_b/t_{b+s} = 0.1 \sim 0.5$

2. 2 Evaluation of films

Compositional variations of WC-CrN films were analyzed by GDOES. For the evaluation of crystal structure and compounds formation behavior, XRD and XTEM analysis were performed. Micro-hardness of WC-CrN films was measured at a normal load of 30mN by commercially available nano-indentation instrument×nano-indenter II) developed by MTS instrument Co. The residual stress was calculated from the curvature measured using the stylus method[12]. And then, the scratch test was measured to assess a quantitative value of adhesion of WC-CrN film deposited on S45C substrate through acoustic emission and friction force. Also, for the evaluation of oxidation resistance at the elevated temperature, CrN single layer and WC-CrN superlattice films with various superlattice periods was measured during TGA.

3. Results & Discussions

3. 1 chemical composition and crystal orientation of WC-CrN film

For the evaluation of chemical composition of WC-CrN films with various superlattice period×λ), the compositional depth profile of the coatings were analyzed by GDOES×Glow Discharge Optical Emission Spectroscopy). The average composition of each element was listed in Table 2.

It was confirmed that chemical composition of N_2 repeated increasing and decreasing in all depth profiles due to alternatively deposited buffer layer

Table 2. Chemical composition of WC-CrN superlattice film

Materials	W	C	Co	Cr	N
At%	19	10	5	28	30

(WC-Cr). Also remarkableness about this state was that repeated increasing and decreasing of chemical composition of N_2 effected carbide & cobalt chemical composition in WC-Co alloy material. This reason was decided that relative light element than W in WC-Co alloy target was preferential sputtered because atom having high energy reached on WC-Co target. Also, extent of perturbation of N_2 chemical composition was decreased from film surface to substrate owing to the existence of diffusion layer near substrate.

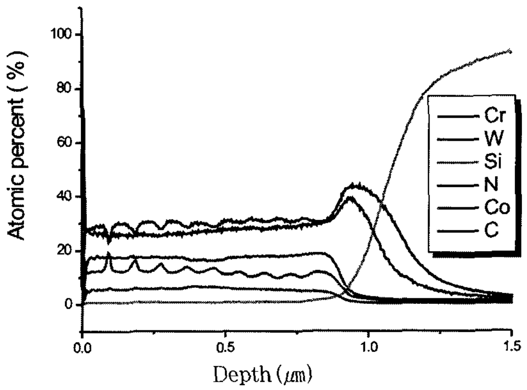


Fig. 1 GDOES depth profile of WC-CrN film

Figure. 1 appears depth profile of WC-CrN film.

Figure. 2 shows XRD patterns of WC-CrN films coated on Si wafer with various jig rotation speeds. It is possible to observe that the crystal orientations of the WC-CrN films depend on superlattice period(λ). For all samples NaCl type CrN and β-WC1-x peaks were identified. These result suggest that α-W_2C in the WC-CrN films transforms into a cubic structure by a template effect of CrN superlattice[13]. The crystal preferred orientations of WC-CrN films with various jig rotation speeds were changed from(111), (311) to (200), (220). In the film at superlattice period

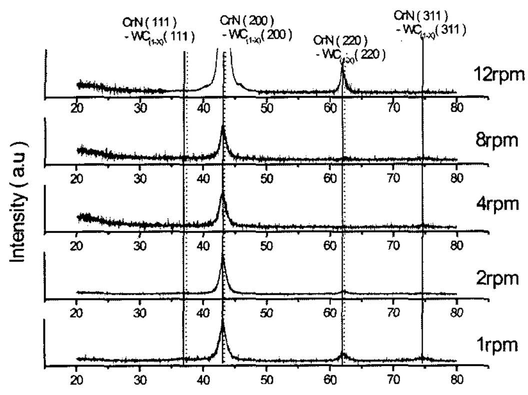


Fig. 2 The XRD patterns for WC-CrN films with various jig rotation speeds

with 11nm, however, WC-CrN superlattice has α-W_2C (101) XRD peaks as a result of precipitation of low temperature phase from NaCl type β-WC_{1-x} phase.

3. 2 Microstructure of WC-CrN film

A cross sectional TEM micrograph of a WC-CrN is illustrated in Fig. 3(a), (b) with various jig rotation speeds. The film structure is varied to dense columnar structure according to approach larger the superlattice period (λ). The CrN layers appear lighter than the WC layers. The layers are well-defined and only slightly non-planar. The superlattice consists of columnar grains that are 25-30nm wide in the lateral direction. It was confirmed that superlattice structure of WC-CrN was found as the superlattice period (λ) was changed from 3 nm to 10 nm as the jig rotation speed decreased from 12 to 1rpm. A HR-TEM micrograph of a WC-CrN is shown in Fig. 4. HR-TEM analysis also revealed that the lattice fringes having a spacing (d_{111}) of 2.18Å are continuous through the CrN and WC layers. This suggests that the crystal structure of WC in the WC-CrN superlattice in NaCl type which is the same as CrN and interface between WC and CrN matches coherently.

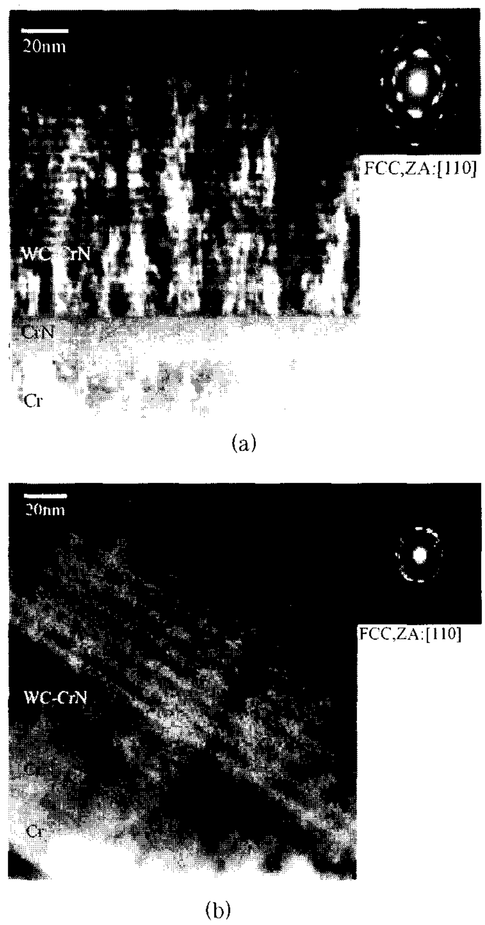


Fig. 3 Cross-sectional XTEM micrograph and electron diffraction patterns of WC-CrN film on Si wafer with various jig rotation speeds
(a) 12rpm (b) 1rpm

3. 3 mechanical properties of WC-CrN film

Figure. 5 (a), (b) illustrate graph after scratch test with various jig rotation speed and various buffer layer thickness. All the sample which has same film thickness of 1㎛ was deposited on S45C substrate. All the condition, critical load value was estimated about upper 50N. As the jig rotation speed was 4rpm which superlattice period was

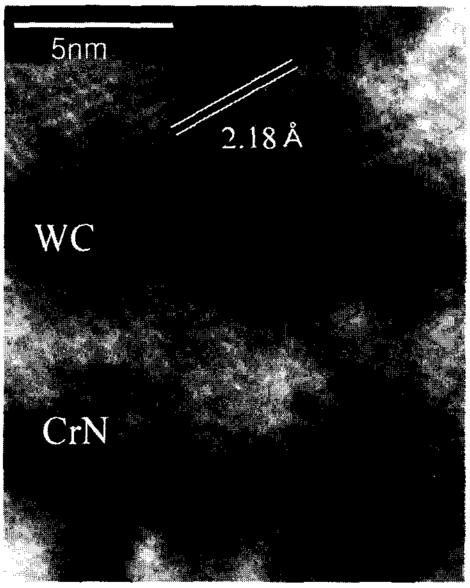


Fig. 4 HR-TEM micrographs of WC-CrN film

7nm, critical load came up about 70N. This implied that withstand of superlattice film which has superlattice period (7nm) is very strongly applied force. Also, during the buffer layer thickness is increased, adhesion strength of WC-CrN film was reduced for the hardness drop due to increase of ductile layer thickness.

For the control of residual stress in superlattice film, WC-Cr buffer layer is deposited between WC-CrN superlattice film, alternatively. Figure. 6 (a), (b) show diagrams after the residual stress test with the same parameter of scratch test condition. This high stress of films is reduced to a value of 0.2GPa by the decreasing superlattice period and the increasing buffer layer thickness.

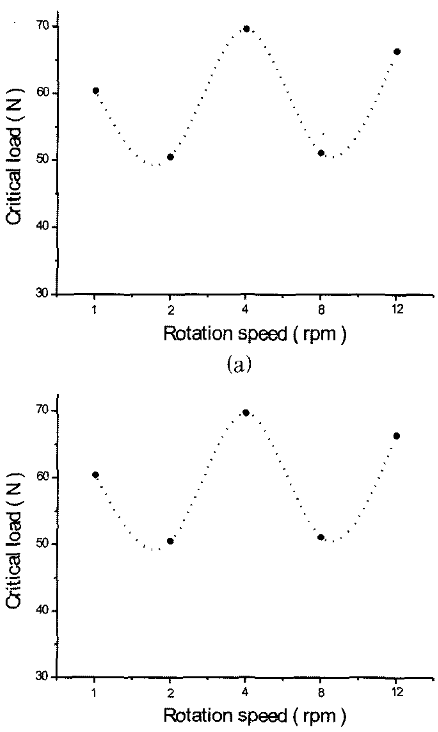


Fig. 5 Critical load×LC) of WC-CrN film
(a) various jig rotation speeds
(b) various buffer layer thickness

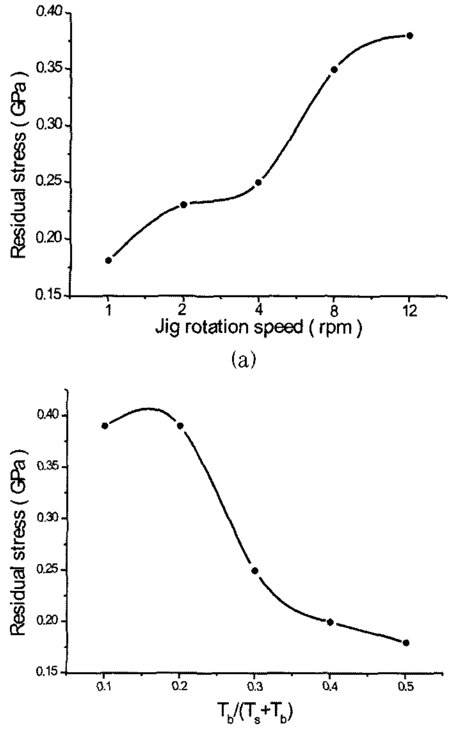


Fig. 6 Residual stress of WC-CrN film
(a) various jig rotation speeds
(b) various buffer layer thickness

Also, hardness with various superlattice periods was measured by nanoindentation. The microhardness of WC-CrN film was estimated to be in the range of 30 ~ 40GPa. The highest value of film hardness was obtained from WC-CrN film as jig rotation speed is 4rpm which is confirmed that superlattice period (λ) are about 7nm.

The mechanical properties of WC-CrN films with various superlattice period and buffer layer thickness are listed in Table 3.1, 3.2

3. 4 oxidation test of WC-CrN film

Fig. 7 illustrates oxidation test at elevated temperature by TGA. CrN single layer and WC -CrN superlattice film that is deposited on SKD61 substrate with various superlattice periods was measured and compared each other. All the condition of WC -CrN superlattic was better oxidation resistance than CrN single layer. Among the WC-CrN superlattice film with various superlattice periods, film at superlattice period with 7nm is obtained excellent oxidation resistance. After oxidation test, surface morphology was observed by SEM. In the case of CrN single layer in Fig. 8(a), broken film at the elevated temperature was viewed all film surface, but WC -CrN superlattice at superlattice period with 7nm is not investigated an oxide or broken film in Fig. 8(b).

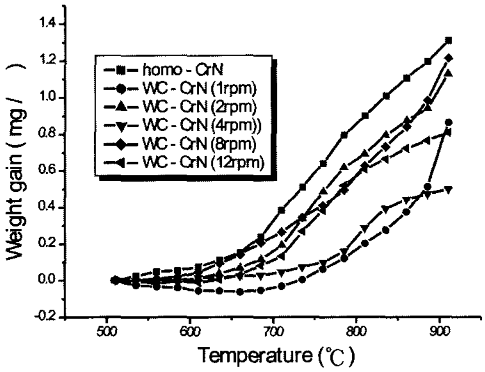


Fig. 7 Oxidation test of WC-CrN film by TGA

4. Conclusions

1) Microstructures of WC-CrN films depend on superlattice period (λ). The crystal orientations of WC-CrN films are (200), (220), (111) and (311) orientations which are from NaCl structure. For the WC-CrN films with decreasing superlattice period (λ), however crystal grows in preferred orientation of (200), (220).

2) Superlattice period was evaluated by TEM.

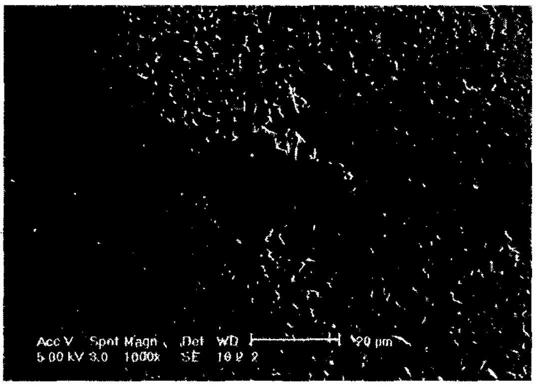
Table 3. 1. Mechanical properties of WC-CrN superlattice film with various superlattice period

Superlattice period (nm)	3	5	7	9	10
Hardness (GPa)	30 ± 5	35 ± 5	40 ± 5	34 ± 5	28 ± 5
Critical load (N)	60	51	70	52	65
Residual stress (GPa)	0.175	0.225	0.25	0.35	0.38

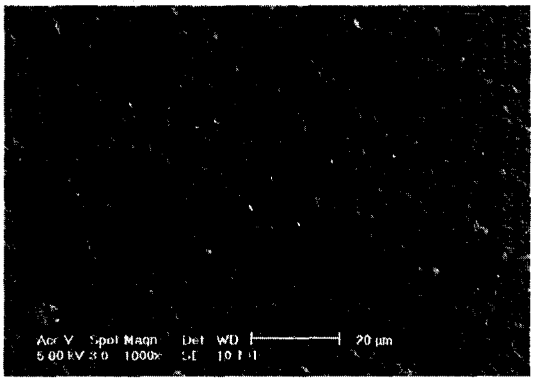
Table 3. 2. Mechanical properties of WC-CrN superlattice film with various ratio of t_b/t_{b+s}

t_b/t_{b+s}	0.1	0.2	0.3	0.4	0.5
Critical load (N)	70	53	47	60	46
Residual stress (GPa)	0.38	0.37	0.25	0.20	0.18

* t_b : buffer layer thickness, t_s : superlattice layer thickness



(a)



(b)

Fig. 8 Surface morphology after oxidation test by SEM (a) CrN single layer (b) WC-CrN superlattice with superlattice period at 7nm

According to the various jig rotation speeds, superlattice periods were controlled from 3 nm to 10nm. Also, This is suggested that the crystal structure of WC in the WC-CrN superlattice in NaCl type which is the same as CrN and interface between WC and CrN matches coherently.

3) The microhardness of WC-CrN films were measured to be in the range of 30~40GPa. The highest value of film hardness was obtained from WC-CrN film as jig rotation speed is 4 rpm which is estimated that superlattice period (λ) are about 7nm. Critical load was estimated 50~70N after scratch test. Residual stress is also obtained in a range of 0.2~0.4 GPa.

4) Oxidation resistance was compared with WC-CrN and CrN. As a result of that, WC-CrN film which has superlattice period (λ) of about 7nm was proved better oxidation resistance than any other condition.

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