Scratch Test of TiCN Thin Films with Different Preferred Orientation

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Abstract. The purpose of this study is to examine the effect of crystallite preferred orientation on the mechanical strength of TiCN thin films in highly compressive residual stress. TiCN thin films were deposited by PVD on JIS-SKH55 (AISI M35) steel. The applied substrate bias voltages were set for –50, -80, -100, -120 and –150V. Subsequently, residual stress and crystalline preferred orientation of these specimens were investigated by X-ray diffraction methodology. The crystalline preferred orientation in thin films was evaluated by the ODF calculated from pole figures. On the other hand, dynamic hardness test (DH) and scratch test were executed to evaluate the mechanical strength of thin films.

In our study, it was observed that negative bias voltages had an effect on the preferred orientation. The orientation density at –120V was the highest of all specimens. In addition, the value of scratch section area at –120V was the largest of all specimens. As a conclusion, the relation between the scratch area and the negative bias voltages corresponded to the relation between the preferred orientation and the bias voltages.

Introduction

Ceramics thin films deposited by PVD and CVD processing on the steel substrate materials improve the ware resistance to protect the substrate surface. Existence of crystalline preferred orientation in these film materials has been reported recently. In addition, existence of highly compressive residual stress in films has been also reported [1-6]. In the material engineering, it is well known that the residual stress in the materials affects the mechanical strength of the industrial product [7]. Moreover, the crystalline preferred orientation of poly crystal materials could influence on the mechanical strength. It would be expected by an analogy based on the single crystal structure [8,9]. Therefore, it is very important to evaluate the residual stress and the preferred orientation in the film systematically.

In this study, the purpose is to examine the effect of crystallite preferred orientation on the mechanical strength of TiCN thin films in highly compressive residual stress. TiCN thin films were deposited by PVD on JIS-SKH55 steel (equivalent to AISI M35). As for the deposited condition, bias voltages were changed. Residual stress and crystalline preferred orientation of these specimens were investigated by X-ray diffraction methodology. The preferred orientation was evaluated by the pole figure and the crystalline orientation distribution function (ODF). In addition, dynamic hardness test (DH) and scratch test were executed to evaluate the mechanical strength of thin films.

Experimental

Specimen. The substrate of JIS-SKH55 (chemical composition: C0.9, Cr4.2, Mo5.0, W6.2, V2.0, Co5.0mass%) steel has dimensions of 12 x 12 x 5mm^3. The deposited surface was polished. TiCN thin films were deposited by AIP with different bias voltages. The applied substrate bias voltages were set for –50, -80, -100, -120 and –150V. The arc current was 80A. Process gases were N_2 and CH_4, and the pressure in deposition chamber was from 0.5 to 10Pa. Coating time was from 30 to 90 min. The thickness of TiCN films was about 3μm.

Pole figure measurements and ODF calculation. The pole figure was measured to calculate the ODF using Cu-Kα radiation with the Schulz method [10]. 3D-orientation distribution analysis using the ODF is more quantitative than an evaluation using pole figure. The X-ray instrument was RINT-2500 (RIGAKU Co.). Under the conditions of pole figure measurement, the X-ray tube voltage was 40kV, and the tube current was 200mA. The inclination angle normal to specimen surface α, was from 90 to 15deg in intervals of 15 deg. The rotation angle β, was from 0 to 355deg in intervals of 5deg. These angles were set on account of ODF calculation. Diffraction planes, {111}, {110} and {100} were measured. The ODF was calculated from three data sets of each diffraction pole figure. The Standard ODF software was used as an ODF calculator [11-13].

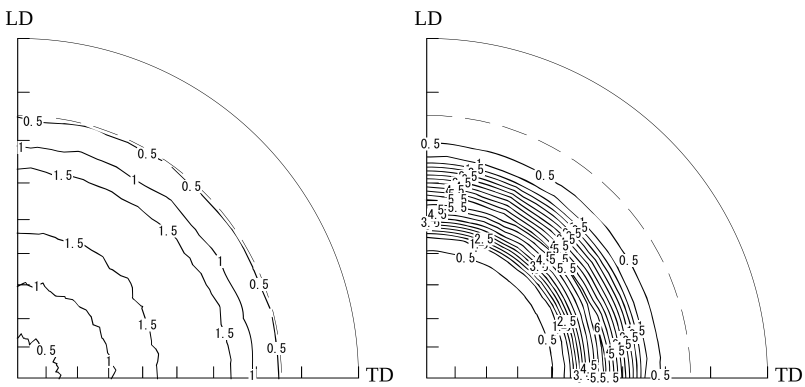
X-ray stress measurement. The residual stress of thin films was measured using Co-Kα radiation. The instrument was MSF3M (RIGAKU Co.). Under the conditions of stress measurement, the X-ray tube voltage was 30kV, and the tube current was 10mA. Measured plane was TiCN420. When the specimen has preferred orientation, the stress determination procedure should be modified because of elastic anisotropy. In our study, the procedure for the material having <111> preferred orientation close to the specimen surface normal was referred to Hanabusa et al. and others [14-15].

Dynamic hardness test. Dynamic hardness test was used to evaluate the effect of preferred orientation and residual stress on hardness of thin films. Hardness was measured by DUH-W201 (Shimadzu Co.). The mechanism of dynamic hardness measurement is as same as universal hardness, which is prescribed in DIN. Under the condition of DH measurement, Berkovich indenter made of triangular diamond pyramid has a width tip angle of 115 degrees was used. Test force was 98mN at a constant, and loading speed was 2.64mN/sec, and hold time was 10sec.

Scratch test. Scratch test was performed to evaluate the effect of preferred orientation and residual stress on abrasive wear of the thin films. This test not only can observe orientation influences in the normal direction, but also can show the influences in the direction parallel to the specimen surface. Scratch tester was TUS-10 (Toshiba Tungaloy Co.). Tip of indenter made of diamond has a dimension of 0.2mm in radius direction. After the stylus stuck in thin films with constant load, the specimen was displaced at constant speed. Scratch speed was 10mm/min. As the specimen was displaced, the resulting stresses at the interface caused flaking or chipping of the coating. The smallest load at which a specific failure event was recorded is called the critical load (L_C). L_C, and the roughness of scratch surface were evaluated by laser microscope 1LM21W (Lasertec Co.) observations.

Results and Discussion

Orientation evaluation. Figure 1 shows a difference of {100} pole figures for the bias voltage –50V and –150V. The pole densities of these pole figures were normalized by the calculation. The pole density at –150V was higher than that at –50V. In the case of other measured diffraction planes, the pole densities at –150V were also higher than those at –50V such as the {100} pole figure. Here, it is difficult to evaluate three pole figures quantitatively at the same time. Best technique to analyze the crystallite preferred orientation would be in combination with all pole figure information. Therefore, the ODF was introduced into crystalline orientation analysis. Figure 3(a) is the position of ideal orientation for ODF on $\phi_2 = 45$deg, defined by Euler angles shown in Fig. 2. LD, TD and ND are abbreviations for longitudinal direction, transverse direction, and normal direction, respectively. Figure 3(b) shows an example of the section $\phi_2 = 45$deg calculated from experimental data sets. All specimens had the <111>orientation texture, because the orientation density of the experimental data was conglomerated near $\Phi = 55$deg. Accordingly, changes of orientation densities due to applied bias voltage were evaluated by the comparison of ϕ_1 sections. The $\phi_1 = 45$deg sections of ODF for all specimens are shown in Fig. 4. Moreover, peak top enumeration from the pattern drawn in Fig. 4 is shown in Fig. 5. As a result, orientation densities near $\Phi = 55$deg increased as the negative applied bias voltage increased except –150V. The orientation density at –150V was smaller than the density at –120V. As for vapor phase epitaxy (VPE) just like CVD, VPE process brings about crystal growth [16]. About plasma PVD used in this study, the temperature of substrate is lower than usual CVD process. However, thermal energy generated by collision between vaporized particles and substrate should be high as the bias voltage increases. Generated heat could cause the crystal growth.



(a) Bias voltage –50V (b) Bias voltage –150V

Fig. 1 Difference of pole density due to bias voltage

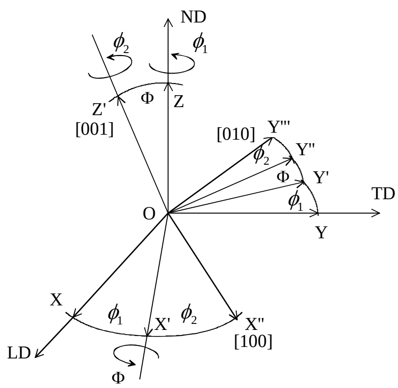
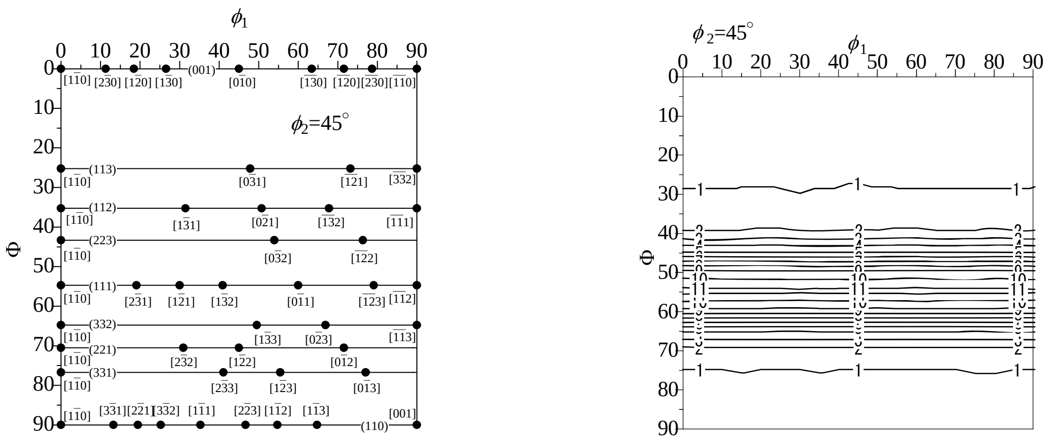
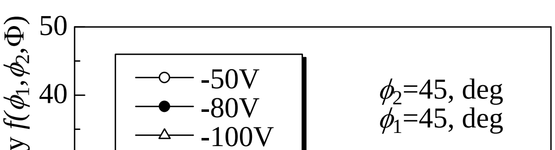


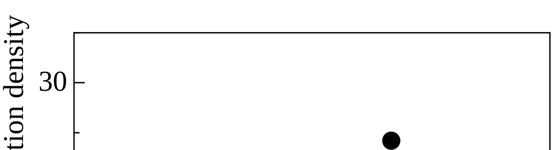
Fig. 2 Definition of Euler angles.



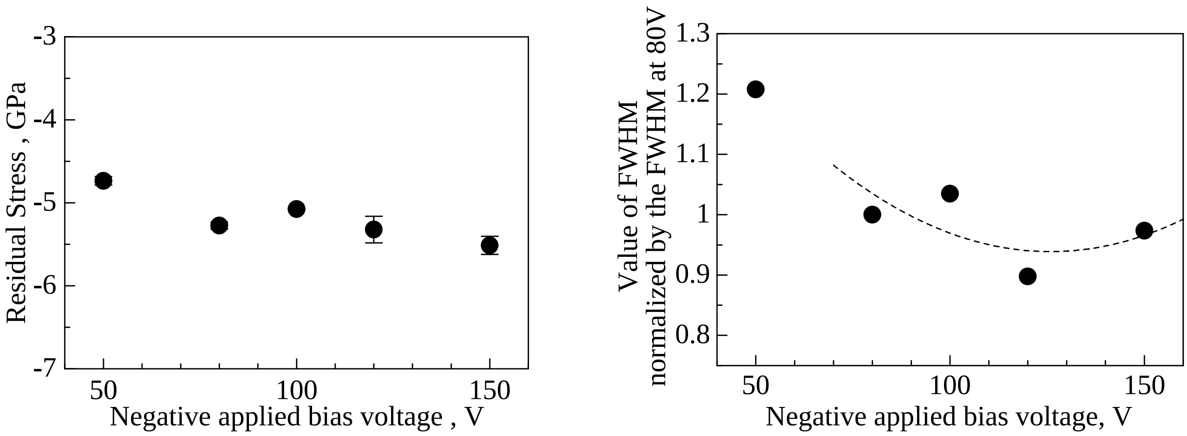
(a) Position of ideal orientation (b) Experimental data of bias voltage –80V

Fig. 3 Results of ODF calculation at $\phi_2 = 45$deg





Residual stress. Figure 6(a) shows the relation between the residual stress in thin films and negative applied bias voltages. As bias voltage increased, the value of residual stress gets high compressive gradually. However, its tendency is not rapid. The relation between the full-width at half maximum (FWHM) of X-ray profile and bias voltages is shown in Fig. 6(b). The value of FWHM also becomes small gradually throughout a figure except –150V. The value of FWHM at –150V is the same tendency as that the value of orientation density decreased. At present, a reason of high compressive residual stress state in thin films has not been clearly. The speed of vaporized particles in PVD processing should be fast as the bias voltage increases. Therefore, the shot-peening effect of ionized particles could cause compressive residual stress in the material.



(a) Residual stress (b) FWHM

Fig. 6 Relation between X-ray stress measurement parameter and negative bias voltage

Mechanical strength. As for the single crystal, it has the anisotropic mechanical properties [8,9]. The poly crystal materials having crystalline preferred orientation also could influence on the mechanical strength. Figure 7 shows the relation between the dynamic hardness of thin films and negative applied bias voltages. As a result, the hardness changed a little through all voltages in this study. One of the reasons is thought that the penetration depth of indenter is so deep. The depth was 1/3 of film thickness because of the reduction of measurement error due to surface roughness.

Subsequently, the scratch test was executed. The mechanical strength should be different with the direction of action load on the single crystal structure. The strength of preferred orientation structure also should be affected by the damaged direction. Figure 8 shows an observation of scratch surface using the laser microscope. The flaking was not observed at normal load L=25N, but the film debonded at L=30N. All specimens exhibited similar fracture forms by the scratch test, and had similar critical load L_C, 25-30N. The areas of scratch section determined in Fig. 9 were compared for all specimens at L=25N because of detail investigation on abrasive wear. Penetration depth of intender was also about 1μm, it was same with the indentation depth of hardness test. Figure 10 shows the relation between the area of scratch section and the negative applied bias voltages. As bias voltages increased, the area of section increased except –150V. As a result, the trend in the scratch area graph corresponds to a trend in Fig. 5. Therefore, crystalline preferred orientation affects the abrasive wear for the thin film materials. In spite of the increase in compressive residual stress due to negative bias voltages, the scratch strength became weak because of preferred orientation. In our previous study, it was confirmed that the residual stress of thin films having preferred orientation affected the scratch strength. Therefore, it is thought that the scratch area at –50V is contained the influence of residual stress. Because the residual stress at –50V is smaller than that at –80V, the scratch area at –50V also could become large. In other words, the scratch strength at –50V could become weak. However, FWHM also decreased as negative bias voltage increased in Fig. 6(b). The decrease of FWHM indicates not only the change of orientation, but also the change of crystal grain size in films generally. Change of grain size could cause hardening of materials. In this specimen, both effects should be occurred.

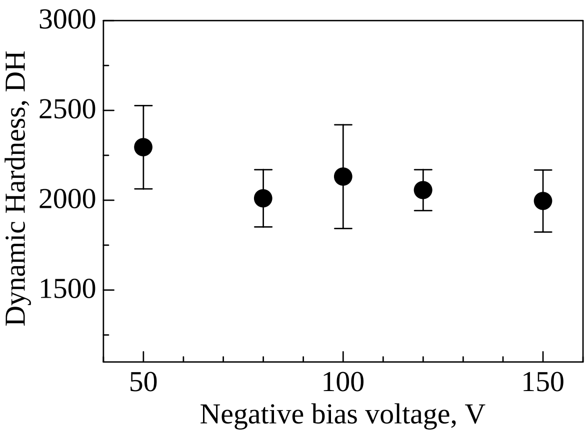


Fig. 7 Dynamic hardness

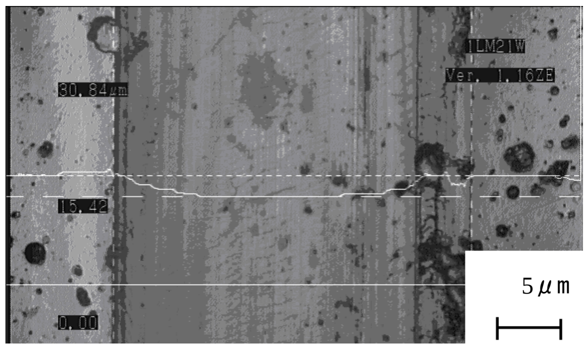


Fig. 8 Scratch surface observation

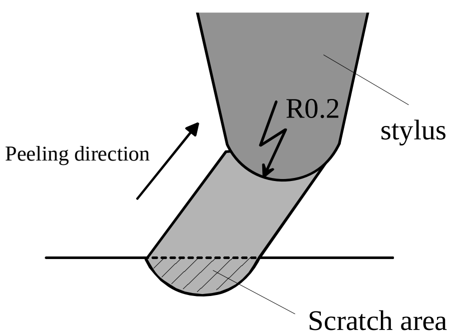


Fig. 9 Definition of scratch area

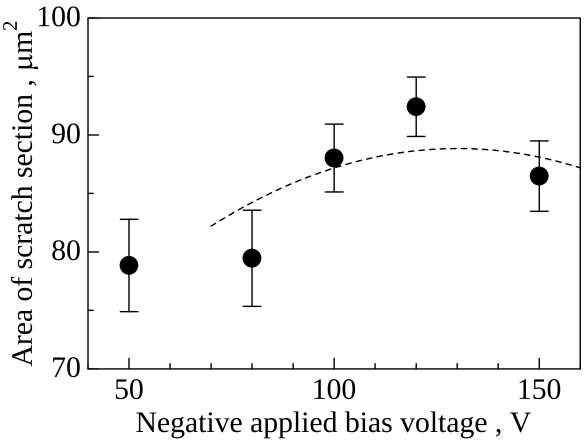


Fig. 10 Relation between area of scratch section and negative bias voltage

Summary

(1) TiCN thin films exhibited <111> preferred orientation close to the specimen surface normal. Orientation density was changed with the negative bias voltages, and the orientation density at –120V was the highest of all specimens. (2) Residual stress increased to high compressive gradually, but its tendency was not rapid. (3) Residual stress and preferred orientation did not affect the hardness of thin films. However, the preferred orientation influenced abrasive wear using the scratch test. The value of scratch section area at –120V was the largest of all specimens. Therefore, only the residual stress estimation is not enough about the mechanical evaluation of thin films. The evaluation of the preferred orientation is also necessary.

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