THE RESIDUAL STRESS MEASUREMENT OF TiCN PVD FILMS

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ABSTRACT
The development of titanium carbon nitride (TiCN) coating is aimed at improving wear resistance of metal cutting tools and punches. To measure the mechanical property of the TiCN coating material treated at a high temperature, it is important to improve the quality of the product used under this condition. The X-ray diffraction technique enables us to measure the internal stress through X-ray penetration depth, and is an effective method for the texture analysis of the thin-film material. In this study, TiCN thin films were deposited by the physical vapor deposition method (PVD). Subsequently, the samples were treated under various temperatures. Influences of heat treatment temperature on residual stress and texture characterization were considered [1][2]. The following conclusions were reached: (1) Residual stress of TiCN thin films is highly compressive; (2) TiCN thin films exhibit <111> fiber texture; (3) Residual compressive stress relaxes due to annealing temperature change. Residual stress decreases with increasing temperature.

INTRODUCTION
The TiCN-coating technique is used in various industries, e.g., fabrication of cutting tools and die engineering, to provide wear resistance and corrosion resistance. However, the TiCN-coating technique has several problems such as film debonding and cracking. These faults may be due to the heat effect that occurs while using and making these products. TiCN-coated materials are expected to be used at high temperature, due to their tolerance to high temperature. However, the heat may affect the residual stress in the materials and the residual stress would affect the mechanical properties [3]. In this study, the following were applied. X-ray diffraction technique for measuring the residual stress [4], and conventional analysis for the textured material. The influence of residual stress due to heat treatment in TiCN thin films is discussed.
SPECIMENS
The substrate of JIS-SKH55 steel has dimensions of $12 \times 12 \times 5$ mm$^3$. The deposited surface was polished. TiCN thin films were deposited by the arc ion plate (AIP) technique [5]. AIP is a kind of physical vapor deposition (PVD) technique. Six samples of deposited TiCN thin films were prepared under the same AIP condition. Processing gases used were CH$_4$ and N$_2$. Under this condition, the pressure in the deposition chamber was between 0.5 Pa and 10 Pa, the time for coating was between 30 min and 90 min, the substrate bias voltage was $-80$ V and the arc current was 80 A. After deposition, one of those specimens was as-deposited, four of specimens were annealed at each temperature, and the last one was treated at a subzero cooling temperature. Heat treatment conditions for each sample are listed in Table 1.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Treatment</th>
<th>Temp.</th>
<th>Atmosphere</th>
<th>Treated time</th>
</tr>
</thead>
<tbody>
<tr>
<td>143K subzero</td>
<td>Subzero cooling</td>
<td>143K</td>
<td>Air</td>
<td>1.5 hrs.</td>
</tr>
<tr>
<td>As deposited</td>
<td>As deposited</td>
<td>300K</td>
<td>-----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>573K annealed</td>
<td>Annealed</td>
<td>573K</td>
<td>Air</td>
<td>3.0 hrs.</td>
</tr>
<tr>
<td>798K annealed</td>
<td>Annealed</td>
<td>798K</td>
<td>Vacuum (1.33Pa)</td>
<td>3.0 hrs.</td>
</tr>
<tr>
<td>843K annealed</td>
<td>Annealed</td>
<td>843K</td>
<td>Vacuum (1.33Pa)</td>
<td>3.0 hrs.</td>
</tr>
<tr>
<td>893K annealed</td>
<td>Annealed</td>
<td>893K</td>
<td>Vacuum (1.33Pa)</td>
<td>3.0 hrs.</td>
</tr>
</tbody>
</table>

EXPERIMENTS
Observation of X-ray diffraction profiles
X-ray diffraction profiles of the specimen surface were measured using Cu-K$\alpha$ radiation. Figure 1 shows the setup of the X-ray experiment. Thin films such as those produced by PVD and CVD occasionally show preferred orientations. The inclination angle normal to the specimen surface, $\psi$, was changed from 0 deg to 60 deg at 15 deg intervals.

Table 2 Conditions of the pole figure measurement

<table>
<thead>
<tr>
<th>Characteristic radiation</th>
<th>Cu-K$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube voltage, kV</td>
<td>40</td>
</tr>
<tr>
<td>Tube Current, mA</td>
<td>200</td>
</tr>
<tr>
<td>Monochromator</td>
<td>Graphite (0002)</td>
</tr>
<tr>
<td>Scan speed, deg/min</td>
<td>180</td>
</tr>
<tr>
<td>Angle $\alpha$ range, deg</td>
<td>15$\sim$90</td>
</tr>
<tr>
<td>Angle $\beta$ range, deg</td>
<td>0$\sim$355</td>
</tr>
</tbody>
</table>

Pole figures
The presence of orientation texture in TiCN thin films can be confirmed by observing the pole figure. The pole figure was measured using Cu-K$\alpha$ radiation with the Schultz method. Table
shows the measurement conditions for observing the pole figure.

**Stress measurements by X-ray diffraction technique**

Concerning X-ray stress measurement, the conventional method is called the $\sin^2 \psi$ method. When specimens have orientation texture, the conventional $\sin^2 \psi$ method cannot be used because the lattice spacing $d$ vs. $\sin^2 \psi$ plots are nonlinear. If TiCN thin films have orientation texture, the $d$ vs. $\sin^2 \psi$ plots should be nonlinear. In such a case, the procedure for determination of residual stress should be modified for preferred orientation [6][7][8].

In this case, residual stress can be determined by

$$\sigma^s = -\frac{\sin \theta_2 - \sin \theta_1}{S_2 \sin \theta_2 - S_1 \sin \theta_1} \quad [\text{Pa}]$$  \(1\)

where $\theta_1$ and $\theta_2$ are diffraction angles obtained from the experiment, and $S_1$ and $S_2$ are elastic constants obtained using the following equations for the ideal $<111>$ orientation.

$$\frac{\varepsilon_{ii}^c}{\sigma^s} = \frac{2}{3} S_{0}^c + 2S_{12}^c + \frac{1}{2} S_{44}^c \sin^2 \psi \equiv S'_i \quad (i = 1, 2)$$  \(2\)

$$S_0^c \equiv S_{11}^c - S_{12}^c - \frac{1}{2} S_{44}^c$$

where $S_{ij}^c$ is elastic compliance of the TiN single crystal,

$$S_{11}^c = 2.17, \quad S_{12}^c = -0.83, \quad S_{44}^c = 5.95 \quad [\text{TPa}^{-1}]$$  \(3\)

In this study, as shown in Fig. 1, $\sigma_{11}^s$ is defined as residual stress $\sigma^s$ in the longitudinal direction (LD) on the specimen surface. The values of $\psi$ of fcc materials with $<111>$ texture show comparatively strong intensities at $\psi_1=39$ deg and $\psi_2=75$ deg. The determination of angle $\psi$ is detected from the intensity distribution of near-ideal angle $\psi$. Thus, residual stress was determined from $\psi_1, \psi_2, 2\theta_1$ and $2\theta_2$ obtained from the experiment. Table □ shows the conditions for X-ray stress measurement.

<table>
<thead>
<tr>
<th>Table □ X-ray stress measurement conditions for TiCN thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic radiation</td>
</tr>
<tr>
<td>Tube voltage, kV</td>
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<tr>
<td>Tube current, mA</td>
</tr>
<tr>
<td>Radiation filter</td>
</tr>
<tr>
<td>Diffraction plane</td>
</tr>
<tr>
<td>Diffraction angle $2\theta$, deg</td>
</tr>
<tr>
<td>Measured angle $\psi$, deg</td>
</tr>
<tr>
<td>Scan method</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Change of the diffraction intensity with angle $\psi$

Figure 2(a) shows the relationship between the angle $\psi$ and the X-ray diffraction intensity. As angle $\psi$ increased, the peak intensity of diffraction from the TiCN111 decreased. Similarly, the TiCN222 peak diffraction intensity behaved the same as the TiCN111 one. Figure 2(b) shows the detailed distribution of X-ray diffraction intensity with angle $\psi$. The TiCN111 peak diffraction intensity decreased with increasing angle $\psi$. On the other hand, the TiCN200 peak diffraction intensity increased with increasing angle $\psi$. These significant changes did not occur only for this sample but for all samples. Here the Fe110 peak diffraction intensity also decreased with increasing angle $\psi$, but the rate of decrease was smaller than that of the TiCN111 one. The reason why the Fe110 peak diffraction intensity had this tendency is thought to be that the X-ray penetration depth became shallower as angle $\psi$ increased. These results indicate that TiCN thin films have anisotropy and <111> a preferred orientation might be formed parallel to the specimen surface. To further advance is study, pole figures were investigated to evaluate the state of orientation texture in TiCN thin films.

Confirmation of the fiber texture by pole figures

Figure 3 illustrates the {111} pole figure of the <111>-oriented single crystal, and the {111}, {200} and {220} incomplete pole figures of as-deposited TiCN coated samples are shown in Fig. 4. LD and TD are abbreviations for longitudinal direction and transverse direction, respectively.
ND is the normal direction of the specimen surface. In the TiCN-coated sample, almost all crystals have a \{111\} axis close to the substrate normal. The pole densities have approximately the symmetry of the major fiber axis. Therefore, the \{111\} fiber texture model was assumed in the X-ray analysis.

![Fig.4 Pole figure of the TiCN-as deposited](image)

**Change of the residual stress due to heat treatment**

Figure 5 shows the diffraction profiles of the TiCN420 at $\psi_1=39$ deg, which were used for X-ray stress analysis. These profiles have a tendency to form a sharp peak as annealing temperature increases. Figure 6 shows the relationship between residual stress and heat treatment temperature.

![Fig.5 Relation the shape of X-ray profile and heat treatment condition ($\psi=39$ deg)](image)

![Fig.6 Relation between residual stress and heat treatment temperature](image)

The TiCN thin films had high and compressive residual stress. The AIP technique provides a high-energy state with accelerated Ti, C and N ions. TiCN is then deposited on the substrate. Many lattice defects occurred in the TiCN thin films in the high-energy state. At the same time, the C or N ion was shot among the lattice plane, so that the lattice constant was shortened. Subsequently, these films were fixed to the substrate. As a result, compressive...
stress may have occurred as a result of the lattice spacing contraction.
The reasons for the change in the residual stress value with the heat treatment were also
considered. As heat treatment temperature increased, the value of compressive stress
remained nearly constant up to 573K, and then the value decreased at temperatures higher
than 573K. The decrease in compressive stress with increasing annealing temperature may
occur due to the diffusion of C and N ions into the TiCN thin films. Annealing diffused C and
N ions. They may disappear during the occurrence of an atomic defect, or they may change
into carbon and N\textsubscript{2} gas and disappear into the grain boundary, so that the compressive residual
stress can relax as a result of the lattice constant expansion. Thus, the tendency to form a
sharp peak in Fig. 5, may indicate the change in the chemical components of TiCN thin films.

CONCLUSIONS
(1) Residual stress of TiCN thin films was highly compressive; (2) The X-ray diffraction
profile of the TiCN thin films were obtained, and the stress state and the pole density in TiCN
thin films were measured. As a result, the TiCN thin films exhibit $<111>$ fiber texture; (3)
After PVD, the compressive stress was changed with changes in annealing temperature. As
heat treatment temperature increased, compressive stress remained nearly constant up to 573K,
and then decreased at temperatures higher than 573K.

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