EFFECT OF THE RESIDUAL STRESS ON THE MECHANICAL STRENGTH OF THE THIN FILMS

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ABSTRACT
The purpose of this study is to examine the effect of the residual stress on the mechanical strength of TiN and TiCN thin films with preferred orientation. TiN and TiCN thin films were deposited by the physical vapor deposition (PVD) on JIS-SKH55 steel (equivalent to AISI M35). Subsequently, the specimens were heated to 573, 798, 843, and 893K. The texture states in thin films were evaluated from the crystallite orientation distribution function (ODF) calculated from the pole figures. The pole figures and the residual stresses were measured using X-ray diffraction methodology. The pole density by the ODF changed little with the heat treatment temperature. However, as the heat treatment temperature increased, the value of the compressive stress remained nearly constant up to 573K, and decreased at temperatures higher than 573K. As for the mechanical strength test, the hardness test and the scratch test were carried out on the thin films. The dynamic hardness (DH) method was introduced to test the hardness of thin films. The change of compressive residual stress influenced the behavior of the scratch test although the hardness changed little with the heat treatment temperature.

INTRODUCTION
TiN and TiCN thin films deposited on the steel substrate materials improve the wear resistance due to the protection of the substrate surface. In the material engineering, it is well known that the residual stress in the material affects their mechanical strength of the industrial products. Further, the deposited ceramics and metals thin films show preferred orientation. It is thought that crystallite texture in the materials also influence their mechanical strength. Therefore, it is very important to know the residual stress and the preferred orientation in the film systematically. TiN and TiCN coated materials are assumed to be used at high temperature, because of their tolerance to such temperatures. It is assumed that the heat affects the residual stress and the texture state in the coated materials. In this study, the following were applied:

- The residual stress and the texture state were measured using X-ray diffraction techniques.
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The effect of the residual stress on the mechanical strength of TiN and TiCN thin films with preferred orientation was evaluated by the hardness test and the scratch test, and the effect of the texture state on the hardness was discussed.

**SPECIMENS**

*PVD conditions*

The substrate of JIS-SKH55 (AISI M35) steel has dimensions of 12 × 12 × 5 mm³. The deposited surface was polished. Thin films were deposited by the arc ion plate (AIP) technique. AIP is a kind of physical vapor deposition (PVD) technique.[1] Five samples deposited thin films were prepared under the same AIP condition for TiN and TiCN films, respectively. Processing gases used were N₂ for TiN films, and were CH₄ and N₂ for TiCN films. 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. The thickness of the TiN and TiCN films was about 3 μm.

*Heat treatments*

After deposition, one of those specimens was as-deposited, others were annealed at each temperature for TiN and TiCN thin films respectively. Heat treatment conditions for each sample are listed in Table I.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>300K(As-deposited)</th>
<th>573K</th>
<th>798K</th>
<th>843K</th>
<th>893K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>---------------</td>
<td>Air</td>
<td>Vacuum</td>
<td>Vacuum</td>
<td>Vacuum</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>(1.33Pa)</td>
<td>(1.33Pa)</td>
<td>(1.33Pa)</td>
<td></td>
</tr>
</tbody>
</table>

**EXPERIMENTS**

*Pole figures measurements and ODF calculations*

The pole figure was measured using Cu-Kα radiation with the Schulz method to calculate the ODF. 3D-orientation distribution analysis using the ODF is more quantitative than an evaluation of pole figures. For pole figures measurement, the X-ray tube voltage was 40kV and the tube current was 200mA. The inclination angle normal to the specimen surface, α, was changed from 90deg to 15deg in intervals of 15deg, and the rotation angle, β, was changed from 0deg to 355deg in intervals of 5deg, in order to calculate the ODF. Measured planes were {111}, {200}, and {220} for TiN and TiCN thin films, respectively. The ODF was calculated from three data sets of pole figures. The ODF calculator was the Standard ODF software[2].

*X-ray stress measurements*
The stresses of thin films were measured using X-ray diffraction technique. For X-ray stress measurement, Co-K\(\alpha\) was used as characteristic radiation. The X-ray tube voltage was 30kV and the tube current was 10mA. Measured plane was TiN420 and TiCN420 for each film. When the specimens have preferred orientation, the procedure for determination of residual stress should be modified orientation. The procedure for determination of residual stress for materials having \(<111>\) preferred orientation close to the specimen surface normal was obtained by Hanabusa et al. and others\[3-4\]. In our study, their method was applied.

**Dynamic hardness tests**

Dynamic hardness tests were used to study the effect of residual stress and texture state on hardness of the thin films. Hardness was measured by DUH-W201 (Shimadzu co.). This is a new material strength systems for materials that cannot be handled by regular testers, such as semiconductors, LSI, ceramics, hard disks, evaporated thin films, and coating layers. The mechanism of dynamic hardness measurement is as same as universal hardness, which is prescribed in DIN (Deutsches Institut für Normung e.V.). DH is given by

\[
DH \equiv \alpha \frac{P}{D^2}
\]  

where \( P \) mN is test force, \( D \) m is indentation depth. \( \alpha \) is constant value determined by the shape of indentation. In Berkovich indenter made by triangular diamond pyramid width tip angle of 115deg, value \( \alpha \) is \( \alpha = 3.8584 \). Figure 1 shows the diagram of the hardness test cycle, and Table II lists the condition of test.

<table>
<thead>
<tr>
<th>Table II. DH test conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test mode</td>
</tr>
<tr>
<td>Test force, mN</td>
</tr>
<tr>
<td>Loading speed, mN/sec</td>
</tr>
<tr>
<td>Hold time, sec</td>
</tr>
</tbody>
</table>

**Scratch tests**

Scratch tests were examined to study the effect of residual stress and texture state on abrasive wear of the thin films. In this test, abrasive strength of the thin films was examined. Scratch tester was TUS-10 (Toshiba Tungaloy Co., Lid.). Tip of indenter made by diamond had R0.2mm. After
the stylus stuck in the thin films with constant normal load, the specimen was displaced at constant speed. Scratch speed was 10mm/min. As it 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, Japan) observations.

RESULTS AND DISCUSSION

Changes of preferred orientation in thin films due to annealing temperature

Figure 3(a) is the position of ideal orientation for ODF on $\phi_2 = 45$ deg, defined by Euler angles shown in Figure 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 of $\phi_2 = 45$ 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. Variation of the orientation distribution with annealing temperature was examined by comparison of $\phi_1$ sections. The $\phi_1 = 45$ deg sections of ODF for all specimens are shown in Figure 4. As a result, there was little change of the orientation density with annealing temperature.
Changes of residual stress in thin films due to annealing temperature

Figure 5(a) shows the relation between residual stress in thin films and annealing temperatures. As annealing temperature increased, the value of compressive residual stress remained nearly constant up to 573K, and decreased at temperature higher than 573K. The relation between the full-width at half maximum (FWHM) of X-ray profile and annealing temperature was shown in Figure 5(b). The value of FWHM remained nearly constant up to 573K, and decreased at temperature higher than 573K. This tendency was somewhat similar to that of residual stress. The third kind stresses are deviation from the average of stresses within smaller regions than a grain, and the strength of stress is about the atomic force. They are caused by lattice defects, dislocation and so on. Presence of the third kind stress is evaluated by changes of FWHM of X-ray profiles qualitatively. A decrease of FWHM results from a decrease of the third kind residual stress in the film due to annealing. The relaxation of compressive residual stress in films may be related to the relaxation of the third kind of residual stress in grains[5].

![Residual stress vs. Annealing temperature](image1)

![FWHM vs. Annealing temperature](image2)

(a) Residual stress

(b) FWHM

Figure 5. Relation between the X-ray stress measurement parameter and annealing temperature

Changes of mechanical strength in thin films due to annealing temperature

Figure 6 shows the relation between dynamic hardness of thin films and annealing temperature. The hardness little changed at all temperatures for all specimens. It is generally reported that TiCN is harder than TiN, however such tendency was not observed. The fiber texture of specimens may affect the hardness.[6] Because the fiber texture is like the single crystal, the mechanical strength must be different with the direction of action of force. This mechanism should affect the hardness test. Figure 7 shows observations of scratch surface using the laser microscope. The flaking was not observed at normal load L=20N, but the film debonded at L=30N. All specimens exhibited similar fracture forms by the scratch test, and had similar critical load L_c, 20-30N. However the investigation by a more detail load was not carried out because of a lack of weight for test load. Therefore the areas of scratch section determined in Fig.8 were compared for all specimens at L=20N. Figure 9 shows the relation between the area of scratch section and annealing temperature. As annealing temperature increased, the area of section...
increased. As a result, the tendency to increase of the scratch area corresponds to a tendency to decrease of the residual stress. Residual stress affects the abrasive wear for the film materials.

![Figure 6. Dynamic hardness of TiN and TiCN thin films](image)

![Figure 7. Laser microscope observations of surface conditions and roughness in scratch test.](image)

![Figure 8. Definition of scratch area](image)

![Figure 9. Change in abrasive wears with increasing annealing temperature](image)

**CONCLUSIONS**

Main results in this study are summarized as following:

1. TiN (TiCN) thin films exhibited <111> fiber texture. There was little change of orientation density with annealing temperature.
2. As annealing temperature increased, compressive residual stress was relaxed at high temperature than 573K for TiN (TiCN) thin films.
3. The residual stress did not affect the hardness. However the residual stress influenced the behavior of the scratch test. Abrasive wears decreased by high compressive residual stress.

**REFERENCES**