X-RAY TRI-AXIAL STRESS MEASUREMENT OF A DIAMOND FILM

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1. Introduction

Many attempts have been made, in recent years, to apply film coatings to machine and electronic parts. Film coatings improve many properties such as wear and corrosion resistance. Diamond, the new coating film, excels in wear resistance; however, it is important to establish the optimum film deposition method and condition, and to evaluate the material strength of the film for industrial use of the diamond thin film and to avoid debonding and deformation. In addition, the film is considered to contain large residual stress such as thermal stress generated by the difference in the thermal expansion coefficient of the film and the substrate during the film deposition process, as well as intrinsic stress caused by the growth of the microstructure of the film.

X-ray diffraction methods are able to measure the residual stress and the X-ray elastic constants of the thin film for thicknesses greater than about 1 µm. Thus, it is expected that the X-ray method can be used to evaluate the properties of a diamond thin film. Ohtsuka et al. [1] made X-ray stress measurements, of a diamond thin film deposited by the CVD method and found that the diffraction angle changes non-linearly on the sin²θ diagram. Using the method of Sasaki [2], Ohtsuka obtained the X-ray elastic constants of a diamond film.

We used an X-ray method to measure the quality of a thin diamond film deposited on Si₃N₄ substrate materials with different surface structures. We determined the X-ray residual stress with the following assumptions. 1) A diamond film is considered as an elastic isotropic body. 2) The main reason for a non-linear profile of diffraction angle on the sin²θ diagram is a stress gradient in the depth direction in the film. Since the X-ray penetration depth of the diamond film is larger than in common industrial materials, we also took film thickness [3] into consideration.

2. The theory of X-ray tri-axial stress measurement of a diamond film

2.1 Penetration depth of X-rays in thin films

The X-ray penetration depth, Tp, is defined in the equation:

\[ \frac{\int_{0}^{T_p} I(z)dz}{\int I(z)dz} = R \]

where I(z) is X-ray intensity (counts) diffracted at the depth z in the film, t is film thickness, and ratio R can be often rewritten as R=1-1/c (=0.63, where c=2.71828) for bulk materials. The denominator of the left hand side of eq.(1) represents the diffracted X-ray intensity from the entire film, and the numerator represents the intensity from the surface to depth Tp of the film. When
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this equation is applied to bulk materials, the denominator should be integrated from 0 to ∞. However, in a situation where the equation is applied to a thin film, the denominator is integrated from 0 to the thickness of the film. \( I(z) \) is expressed as

\[
I(z) = K I_o \exp(-\mu L)
\]

(2)

where \( K \) is reduction ratio of X-ray intensity by diffraction, \( I_o \) is incident X-ray intensity, \( \mu \) is X-ray absorption coefficient, and \( L \) denotes the X-ray path length. \( L \) is expressed as

\[
L = \begin{cases} 
\frac{2z}{\sin \theta \cos \psi} & \text{(for } \psi \text{ goniometer)} \\
\frac{2z \sin \theta \cos \psi}{\sin^2 \theta - \sin^2 \psi} & \text{(for } \Omega \text{ goniometer)}
\end{cases}
\]

(3)

As shown in Fig.1, \( \theta \) is Bragg’s angle, \( \psi \) is the angle between the normal of the diffraction plane and the normal of the specimen surface. Solving eq.(1) for \( T_f \) we obtain

\[
T_f = \left[ \frac{\sin \theta \cos \psi}{2 \mu} : f(t) \right]
\]

(4)

Eq.(4) denotes the X-ray penetration depth when the film has a limited thickness and where \( f(t) \) represents a correction term related to the film thickness and can be expressed as

\[
f(t) = \ln \left[ \frac{1}{1 - (1 - \exp(-t/T))R} \right]
\]

(5)

where \( T \) is equal to \( T_f \) when \( f(t) = 1 \) (\( R = 1 - 1/c. \) Thus

\[
T = \frac{z}{\mu L} = \begin{cases} 
\frac{\sin \theta \cos \psi}{2 \mu} & \text{(for } \psi \text{ goniometer)} \\
\frac{\sin^2 \theta - \sin^2 \psi}{2 \mu \sin \theta \cos \psi} & \text{(for } \Omega \text{ goniometer)}
\end{cases}
\]

(6)

2.2 Fundamental equation for X-ray stress measurement in a thin film

By using Bragg’s law, lattice strain can be expressed by the following equation. However, when a
material has a strain gradient in the depth direction, we suppose that the equation should be rewritten as the right hand side of the equation.

\[
\langle \varepsilon_{\psi} \rangle = \frac{\langle d_{\psi} \rangle - d_0}{d_0} = (\theta - \langle \theta_{\psi} \rangle) \cot \theta_0 = \frac{\int_0^r \varepsilon_{\psi} I(z)dz}{\int_0^r I(z)dz}
\]

where \(\varepsilon\) is lattice strain, \(d\) is lattice spacing, and \(\theta\) is Bragg’s angle. \(d_0\) and \(\theta_0\) represent the \(d\) and \(\theta\) when the specimen has no strain. Subscripts \(\phi\) and \(\psi\) denote the normal direction of a diffraction plane. \(< >\) indicates an average taken over the diffracted volume. In some studies, the integration range is from the film surface to film thickness, which is equal to \(R = 1\). However, in our study, the integration range is from the film surface to the X-ray penetration depth. With stress components \(\sigma_{ij}\) (\(i,j = 1,2,3\)), \(\varepsilon_{\psi\psi}\) can be expressed as

\[
\varepsilon_{\psi\psi} = \frac{s_1}{2} \left( \sigma_{11} \cos^2 \phi + \sigma_{12} \sin 2\phi \right) \times \sin^2 \psi + \frac{s_2}{2} \sigma_{33} \cos^2 \psi + s_1 \left( \sigma_{11} + \sigma_{22} + \sigma_{33} \right)
\]

\[
+ \frac{s_2}{2} (\sigma_{13} \cos \phi + \sigma_{33} \sin \phi) \sin 2\psi
\]

where \(s_1\) and \(s_2\) are the X-ray elastic constants, and can be represented as

\[
s_1 = \frac{v}{E} \quad s_2 = \frac{2(1 + v)}{E}
\]

where \(v\) is Poisson’s ratio, \(E\) is Young’s modulus. For the next step, we write the stress components as a linear system.

\[
\sigma_{ij} = \sigma_{ij0} + A_{ij} \cdot z
\]

where \(\sigma_{ij0}\) (\(i,j = 1,2\)) are the stresses on the surface and \(A_{ij}\) (\(i,j = 1,2,3\)) are the stress gradients in the direction of depth. When stress distributions versus depth are behaving non-linearly, a polynomial of \(z\) terms can be used. From eq.(2) and (6), \(I(z)\) in eq.(7) can be substituted by \(\exp(-z/T)\). Thus, from eq.(7),(8), and (10), \(\langle \varepsilon_{\psi\psi} \rangle\) is expressed as

\[
\langle \varepsilon_{\psi\psi} \rangle = \frac{s_1}{2} \left( \sigma_{11} \cos^2 \phi + \sigma_{12} \sin 2\phi \right) \times \sin^2 \psi + s_1 \left( \sigma_{11} + \sigma_{22} + \sigma_{33} \right)
\]

\[
+ \frac{s_2}{2} (\sigma_{13} \cos \phi + \sigma_{33} \sin \phi) \sin 2\psi
\]

\[
\times \left( 1 - \exp\left\{ - \frac{z}{T_0} \right\} \right)
\]

where \(W_r\) is a weighting coefficient and is expressed as

\[
W_r = \frac{1 - \int f(t) \exp\{-f(t)\} dt}{1 - \exp\{-f(t)\}}
\]

Eq.(11) is the fundamental equation for X-ray stress measurement of a thin film and is the same as that for bulk materials except for the weighting coefficient \(W_r\). The weighting coefficient for bulk materials can be also be obtained from eq.(12) with \(t = \infty\) and \(R = 1 - 1/e\).

2.3 Method of stress calculation

In order to obtain the stress components with high accuracy from the X-ray measurement, the sum or the difference of the strain at each angle \(\phi\) are given by:
substituting these equations in eq.(11) we obtain:

\[
\begin{align*}
(c_1) &= u_1 X_1 + u_2 X_2 + u_3 X_3 \\
(c_2) &= u_4 X_4 + u_5 X_5 \\
(c_3) &= u_6 X_6 + u_7 X_7
\end{align*}
\]

where \( u_1 \) to \( u_7 \) are

\[
\begin{align*}
&u_1 = \sigma_{110} + \sigma_{220} \\
&u_2 = A_{11} + A_{22} \\
&u_3 = A_{33} \\
&u_4 = \sigma_{110} - \sigma_{220} \\
&u_5 = A_{11} - A_{22} \\
&u_6 = 2\sigma_{120} \\
&u_7 = 2A_{12}
\end{align*}
\]

and \( X_1 \) to \( X_7 \) are

\[
\begin{align*}
X_1 &= \frac{s_2}{2} \sin^2 \psi + 2s_i \\
X_2 &= X_1 W/T \\
X_3 &= 2\left(\frac{s_2}{2} \cos^2 \psi + s_i\right) W/T \\
X_4 &= \frac{s_2}{2} \sin^2 \psi \\
X_5 &= X_4 W/T
\end{align*}
\]

All the stress components except \( A_{13} \) and \( A_{23} \) can be calculated by applying a least square method to eq.(11). In order to calculate \( A_{13} \) and \( A_{23} \), the deviation \( \langle a_2 \rangle \) of the lattice strains is used.

\[
\langle a_2 \rangle \phi = \left< \epsilon_{\phi \psi} \right> \phi - \left< \epsilon_{\phi \psi} \right> \phi=180 \bigg/ 2
\]

These deviations in the positive and the negative direction of the angle \( \psi \) are

\[
\begin{align*}
\langle a_2 \rangle \phi=0 &= A_{13} \cdot X_6 \\
\langle a_2 \rangle \phi=90 &= A_{23} \cdot X_6
\end{align*}
\]

where \( X_6 \) is expressed as

\[
X_6 = \frac{s_2}{2} W/T \sin 2\psi
\]

\( A_{13} \) can be obtained with \( \psi=0 \), and \( A_{23} \) can be obtained with \( \psi=90 \). Thus, when we want to obtain all the tri-axial stress components, we need to have \( \sin^2 \psi \) diagrams of \( \phi=0^\circ, \pm 45^\circ, \pm 90^\circ, \pm 135^\circ \) and \( \pm 180^\circ \).
2-4. Determination of the X-ray elastic constants of a thin film.

Supposing the thin film has a tri-axial state of residual stress as shown in eq.(10), and the sample is subjected to uniform loading in the direction of $\phi=0^\circ$, eq.(11) can be rewritten as

\[
\langle \varepsilon_{\psi} \rangle = \sigma_{\psi_{0}} \left( \frac{1}{2} \cos^2 \phi \sin^2 \psi + s_{1} \right) + \frac{s_{2}}{2} \left( \sigma_{\psi_{0}} \cos^2 \phi + \sigma_{\psi_{0}} \sin \phi \sin 2\phi + \sigma_{\psi_{0}} \sin^2 \phi \right) \sin^2 \psi + s_{1} \left( \sigma_{\psi_{0}} + \sigma_{\psi_{2}} \right)
\]

\[+ \left( \frac{s_{2}}{2} \left( A_{\psi}^2 \cos^2 \phi + A_{\psi}^2 \sin \phi \sin 2\phi + A_{\psi} \sin \phi \sin 2\phi \right) \sin^2 \phi \right) \sin 2\phi \psi \right) - \Delta \cdot T \]

where superscripts R denote residual stress and A denote applied stress. When $\phi=0^\circ$, differentiating eq.(20) with respect to $\sin^2 \phi$ gives eq.(21):

\[
\left( \frac{\partial \langle \varepsilon_{\psi} \rangle}{\partial \sigma_{110}^A} \right)_{\phi=0} = \frac{s_{2}}{2} \sin^2 \psi + s_{1}
\]

Differentiating eq.(21) with respect to $\sin^2 \phi$ gives eq.(22)

\[
\frac{s_{2}}{2} = \frac{\partial}{\partial \sin^2 \phi} \left( \frac{\partial \langle \varepsilon_{\psi} \rangle}{\partial \sigma_{110}^A} \right)_{\phi=0}
\]

Substituting $\psi=0^\circ$ in eq.(21) we obtain:

\[
s_{1} = \left( \frac{\partial \langle \varepsilon_{\psi} \rangle}{\partial \sigma_{110}^A} \right)_{\phi=0}
\]

Eq.(21) shows that the gradient of the relation between $\langle \varepsilon_{\psi} \rangle$ and $\sigma_{110}$, $\partial \langle \varepsilon_{\psi} \rangle / \partial \sigma_{110}$, is a linear function with respect to $\sin^2 \psi$, and the X-ray elastic constants, $(1+\nu)/E$ and $-\nu /E$, can be determined from the gradient and the intercept with the axis respectively.

3. Experimental Procedure

3-1. The Substrate Material and Test Piece.

The substrate material for the experiment was sintered silicon nitride ceramic, Si$_3$N$_4$. The chemical composition (wt. %) was as follows: 2.04Mg, 3.54Ce, 0.71Sr, 0.016Al, 0.042Fe, 0.031Y, 4.94 Total-oxide and Bal. Si$_3$N$_4$. The mechanical properties of the substrate were as follows: bending strength 920MPa, mechanical Young's modulus 265GPa, bulk density 3.21g/cm$^3$ and coefficient of expansion 3.71$\times10^{-6}$. The shape and dimensions of the specimen are: a rectangular beam with a length of 50mm, a width of 8mm and a thickness of 4mm. The surfaces of the substrates were machined by lapping and grinding (three different types; grinding wheel no. #80, #200, #600).

3-2. Deposition of the diamond thin film.

Fig.2 shows the schematic illustration of a thermal-filament CVD device used for diamond film coating. CVD conditions are shown in Table.1. \( \text{CH}_3\text{OH} + \text{H}_2 \) gas (mixing ratio 1:9) was gas-phased with a W filament. Temperature of the substrate during the process was 1173K~1273K. The film thickness of the diamond was 10\( \mu \)m.
3-3. X-ray diffraction conditions

X-ray diffraction exposure conditions were: Cr-\(\kappa\alpha\) radiation, the C-220 diffraction plane in the diamond film was measured, diffraction angle \(2\theta\) was about 131.5 deg., all the measurements were made with a Rigaku MSF-2M X-ray stress measurement device. The parallel beam method and iso-inclination method (\(\Omega\) goniometer) were used for the optical system. Table 2 shows the main X-ray diffraction conditions for this experiment.

4. Results and discussion

4-1. \(\sin^2 \psi\) diagram
Fig. 4 2θ vs. sin²ψ plot obtained from the diamond film deposited on Si₃N₄ ground with a #200 grinding wheel.

Fig. 5 Diffraction intensity as a function of sin²ψ obtained from a diamond film deposited on Si₃N₄ ground with a #200 grinding wheel.

Fig. 4 shows an X-ray diffraction profile. As can be seen from this figure, the distribution of the diffraction angle (2θ) falls convex on a curve which is in the downward direction. Moreover, the curve is steeper when sin²ψ is 0-0.1. In addition, whether ψ is preceded by a minus or plus sign, both 2θ data were the same. Thus, this specimen did not show a ψ-splitting, which means residual stresses such as σ₁₃ and σ₂₃ did not exist in this film. It also can be seen that the profile has a few undulations. Fig. 5 shows the intensity distribution of the diffraction peak versus sin²ψ. Peak intensity was the weakest at ψ = 0°. In figure 5, the peak intensity reached a maximum value at sin²ψ = 0.13 and 0.3. In figure 4, in general, the peak intensity distribution as seen in Fig. 5 suggests the existence of a textured structure in the diamond film. However, the diffraction intensity of the thin film is also influenced by the incident angle of the X-ray beam. Both influences can be superimposed in the result shown in Fig. 4. In this study, we assumed that the curvature in the sin²ψ plots was due to the stress gradients with depth since the diamond film is isotropic. The method in which stress gradients and film thickness are both considered was applied to the diffraction data in order to obtain the stress gradient. In addition, the mean tri-axial stresses in the diamond film were also analyzed using the Dölle-Hauk method.

4-2. Determination of the diffraction angle in a stress free state (2θ₀)

For the analysis of the X-ray tri-axial stress as well as stress gradients, an accurate value of 2θ₀ for the diamond film is required. In this paper, the value was calculated using the Hauk method⁶ and the sin²ψ plots obtained from the diamond films. It was assumed that Poisson's ratio is equal to be 0.5.

4-3. Result of a stress analysis by means of the Dölle-Hauk method

Fig. 6 shows the result of a tri-axial stress calculation in a diamond film obtained using the Dölle-Hauk method⁶. We see from the result that both σ₁₁ and σ₂₂ are almost at the same stress level, and are large and tensile. Also σ₃₃ is negative. The three other shear stress components, σ₁₂, σ₁₃ and σ₂₃, are small compared to the normal stresses. It was found that
residual stresses show only slight differences as a result of process used to produce the surface of the specimens.

Fig. 6 Results of a stress calculation by using the Döllc-Hauk method.

4-4. Result of a stress analysis by means of the method considering a stress gradient

Fig. 7 shows a depth profile in a diamond film obtained by the method when the
existence of a stress gradient was considered. Results show that a huge tensile residual stress exists on the surface of the diamond film, and the tensile stress increases with depth, so that the stress at the boundary between the film and the substrate is larger than that on the surface. The residual stresses in the film do not balance, which means that compressive stress in the substrate is needed for equilibrium of the total cross-sectional area of the specimen.

![Diagram showing stress distribution in a diamond film](image)

Fig. 7 An example of depth profile in the diamond film obtained from present study.
Fig. 8 shows a comparison of the components of stress gradients calculated for each specimen. We see the tendency that larger surface stresses and stress gradients emerge due to heavier surface processing, and saturation can also be seen in the range of #200 and #80. However, the condition of the surface does not seriously affect the residual stress in diamond films. In addition, the steep stress gradient with depth, nonlinear $\sin^2 \psi$ plots in X-ray diffraction experiments are also possibly due to, for example, elastic anisotropy based on the preferred orientation of grains in the film and composition gradients with depth. Our X-ray data (the relation between the peak intensity and specimen tilt angles) showed some oscillations, which suggests the existence of a texture in the film. In order to carry out a more accurate stress analysis, the residual stress should be analyzed using a method in which the above factors, as well as a stress gradient, are considered with depth.

5. Conclusions

(1) From X-ray diffraction experiments for diamond films deposited on Si$_3$N$_4$
ceramics, nonlinear (curved) sin² plots were obtained. The diffraction peak intensities showed oscillations.

(2) The conditions used to produce a surface on the Si₃N₄ substrate do not seriously affect X-ray diffraction data, but there is some relation between tri-axial residual stress or stress gradients with depth and the conditions used to produce substrate surfaces.

6. References