A proposal of depth profile analysis method of strain distribution in surface layer using x-ray diffraction at small glancing angles of incidence

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Abstract. Diffracted x-rays at small glancing angle of incidence on surface materials were investigated as function of incidence angles for the studies of residual stresses of surface layers. The intensity of x-ray propagation in surface layer materials characterized by a complex refractive index that changes continuously with depth was derived, and with use of the result, an analyzing method for evaluating the depth profiles of the strain distribution in the surface layer was studied. The derived analyzing method can be applied to the residual stress distribution analysis of the surface layer materials of which densities change continuously in depth as multi thin films, compound plating layers. Now, the analyzing method for the depth profile of the strain distribution in the surface layer using x-ray diffraction at small glancing angles of incidence was discussed with correction on some errata of equations in the previous studies.

1. Introduction
X-rays scattered from a material surface at a glancing angle provide useful information on the structure of the surface layer.[1-3] When x-rays are applied to a material surface at a small glancing angle of incidence, the intensity of x-rays scattered on the surface is the sum of the x-rays that scattered by atoms only on the surface, and the contribution of the atoms at each depth to the x-rays intensity varies with the glancing angle, so the depth profile of the surface layers can be found by analyzing the incidence angle dependence of the scattered x-rays.

Compound plating is used for the purpose of the strength improvement on the surface of the material, and accurately knowing the residual stress in the compound plating becomes important. Residual stresses in poly-crystalline materials were measured using the glancing incidence x-ray diffraction. In the previous studies, the in-depth distribution of residual stresses was estimated with the use of the term of penetration depth.[4,5] These estimations cannot be applied to the residual stress distribution analysis of the surface layer materials as multi thin films and compound plating layers with rough surface and rough interfaces because densities of the surface layer materials change continuously in depth. We therefore derived the x-ray intensity propagating during the surface layer materials of which density changes continuously in depth, and calculated the dependence of the diffracted x-ray intensity on the glancing angle.[6,7] With the use of the analyzing method, the depth profiles of the strain distribution in the surface layer were studied.[8] The derived analyzing method
can be applied to the strain distribution analysis of the surface layer materials of which densities change continuously in depth as the surface with roughness and layers structure. Now, the analyzing method for the depth profile of the strain distribution in the surface layer was discussed with correction on some errata of equations in the previous studies.

2. Experimental
Experimental details can be found elsewhere.[9] Intensities of the diffracted x-rays on the chromium coating steel were measured at several glancing angles $\alpha_0$ of incidence with Synchrotron radiation at SPring-8 BL24XU. Thickness of chromium layer is about 2 $\mu$m. Figure 1 shows a schematic view of the experimental arrangement. Figure 2 shows the intensity distributions of diffracted x-rays by polycrystalline chromium in the surface layer.

![Figure 1. The schematic view of the experimental arrangement](image)

![Figure 2. Intensity distributions of scattered x-rays at several glancing angles of incidence.](image)

![Figure 3. Observed scattering angle of diffracted x-rays from Cr(310).](image)
The scattering angles of x-rays diffracted by poly-crystalline chromium in the surface layer are shown in Fig. 3. The increase in the scattered angle $\theta_s$ at smaller incident angle $\theta_0$ includes the effect of refraction as shown in Fig. 4. Analyzing the incidence angle dependence of the diffraction angle, the depth profiles of the strain distribution in the surface layer can be derived.

![Figure 4. The schematic of glancing incidence x-ray diffraction at incident angle $\alpha_0$.](image)

3. Analysis

In the condition of small glancing angle of incidence, most of the x-rays are scattered by only shallow regions near the surface. In the region, the stress $\sigma_z$ in the direction $z$ normal to the surface can be neglected, i.e. $\sigma_z = 0$. Here the isotropic stress, i.e. $\sigma_x = \sigma_y = \sigma$ is assumed, the strain $\varepsilon_z = -\nu E \sigma / E$, where $\nu$ is the Poisson’s ratio and $E$ is the Young’s modulus.

On the stress estimation by using x-ray diffraction at small glancing angle incidence, $\sin^2 \psi$ diagram method is useful, but becomes difficult to apply the method due to its nonlinearity when a sample has stress gradient in the surface, i.e. the co-axial stress $\sigma$ becomes $\sigma(z)$; the in-depth distribution of residual stresses. This difficulty is due to the changing strain with depth dependence to the surface, i.e. the strain $\varepsilon_z = \varepsilon_z(z)$. In the previous studies, the residual stresses $<\sigma>$ was estimated with the use of the term of x-ray penetration depth $T$ as the following equation, [4,5]

$$<\sigma> = \frac{1}{T} \int_0^T \sigma(z) \exp(-z/T) dz$$

(1)

The strain $\varepsilon_\psi$ in the direction normal to the diffraction plane is

$$\varepsilon_\psi(z) = -\frac{1 + \nu}{2\nu} \varepsilon_z(z) \sin^2 \psi + \varepsilon_z(z)$$

(2)

Scattered angle $\theta_s$ of the diffracted x-ray is

$$\theta_s = 2(\theta_0 - \varepsilon_\psi(z) \tan \theta_0)$$

(3)

where $\theta_0$ is the Bragg angle at stress free and the effect of refraction was neglected. Using above relation, the residual stresses $<\sigma>$ in the previous studies was estimated as the following equation,

$$\theta_s = 2\theta_0 + 2 \tan \theta_0 \left( \frac{2\nu}{E} - \frac{1 + \nu}{E} \sin^2 \psi \right) \frac{1}{T} \int_0^T \sigma(z) \exp(-z/T) dz$$

(4)

where the penetration depth $T$ was approximately shown as $\sin(\alpha_0)/\mu$, where $\mu$ is a linear absorption coefficient. These estimations cannot be applied to the surface layer materials of which densities change in depth $z$ as the surface with roughness and layers structure because $T$ is not constant.

We therefore characterized the refractive index of the surface layer materials with complex refractive index, which changes continuously in depth, and derived the x-ray intensity propagating during the surface layer materials. The intensity of x-rays, i.e., the electric and magnetic field propagating in the material, can be obtained using Maxwell’s equations.[10] The effects of x-rays on
the material are characterized by complex refractive index $n$, which changes continuously with depth. The material for which the density changes continuously with depth is divided into thin $N$ layers. The reflectance of multi-layer system, consisting of $N$ layers can be calculated using the recursive formalism given by Parratt.[11] Derivation of the electric field of x-ray propagating in $j$-th layer is explained in another paper in this proceeding.[12]

The electric field of x-ray radiation at glancing angle of incidence $\alpha_0$ is expressed as

$$E_\alpha(z) = A_j \exp\{i(k_{0z} \cdot \hat{r} \cos \alpha)\}. \quad (5)$$

The amplitude $A_j$ of $j$-th layer is derived from continuity equations for the interface between the $j-1$ and $j$ layer as shown by

$$A_j = \Phi_j A_0, \quad A_j = \Phi_j A_{j-1} \exp\{ik_{j-1}d\}, \quad (6)$$

By the condition of incident x-ray, the $z$-direction component of wave vector of the $j$-th layer is shown as

$$k_{jz} = \frac{2\pi}{\lambda} \sqrt{n_j^2 \cos^2 \alpha_0} = \frac{2\pi}{\lambda} (a_j + ib_j).$$

The Fresnel coefficient tensor for refraction on the interface between $j-1$ and $j$ layer is given by

$$\Phi_{j,x\!x} = \frac{2n_{j-1}^2 \sqrt{n_{j-1}^2 \cos^2 \alpha_0}}{n_j \sqrt{n_{j-1}^2 \cos^2 \alpha_0} + n_{j-1} \sqrt{n_j^2 \cos^2 \alpha_0}} = \frac{2(n_j^2(a_{j-1} + ib_{j-1}) + n_{j-1}^2(a_j + ib_j))}{n_j^2(a_{j-1} + ib_{j-1}) + n_{j-1}^2(a_j + ib_j)}.$$

Using these equations, the electric field of x-ray propagating in $j$-th layer is expressed as

$$E_j(z) = (\prod_{j=1}^{j} \Phi_j \cdot A_j \exp\{i(k_{0z} \cdot \hat{r} \cos \alpha)\}, \quad (8)$$

and the intensity of the refractive x-ray in $j$-th layer at depth $z$ is shown as

$$I(z) = \left| \prod_{j=1}^{j} \Phi_j \cdot A_j \right|^2 \exp\left\{ -4\pi^2 \frac{1}{\lambda} \sum_{h=0}^{\infty} b_h \cdot \delta(z - (j-1)d) \right\}. \quad (9)$$

On the other hand, scattered angle $\theta_s$ of the diffracted x-ray from the crystal plane at the depth $z$ is

$$\theta_s = 2\theta_0 - 2\varepsilon_\alpha(z) \tan \theta_0 + \alpha(z) \cdot (z - (j-1)d). \quad (10)$$

where $\theta_0$ is the Bragg angle at stress free and $\alpha(z)$ is the refracting angle at the depth $z$.

The diffraction peak intensities are in proportion to the sum of the refractive x-ray intensity in each layer of those polycrystalline. Then the peak angle of the diffracted x-rays is shown in the following equation,

$$\theta_3(\alpha_0) = 2\theta_0 + \alpha_0 + \int_0^h \left[ 2 \tan \left( \frac{\theta_0 (1 + \nu \sin^2 \psi - 1) \varepsilon_\alpha(z) - \alpha(z)}{2\nu} \right) - \alpha(z) \right] I(z) dz,$$  

where $I(z)$, $\alpha(z)$ and $\nu$ are function of the incident angle $\alpha_0$, therefore $\theta_3$ is function of $\alpha_0$. The incident angle dependence of the scattered angle $\theta_s(\alpha_0)$ of the diffracted x-rays can give good information to investigate the depth profile of the strain distribution in the surface layer materials of which densities change continuously in depth as the surface with roughness and layers structure. The refractive index $n(z)$ change with the density $\rho(z)$ in the depth $z$, and the intensity $I(z)$ of the refractive
x-ray in depth \( z \) is calculated with using the refractive index \( n(z) \). In the case that some materials \( M \) exist in the surface layer, the peak angle of the diffracted x-rays from the material is

\[
\theta_s^z (\alpha_o) = 2 \theta_o + \alpha_o + \frac{\int_0^h [2 \tan \theta_o (\frac{1+\nu}{2\nu} \sin^2 \psi - 1) \epsilon (z) - \alpha (z)] \rho_M (z) I(z) dz}{\int_0^h \rho_M (z) I(z) dz}, \tag{12}
\]

where \( \rho_M(z) \) is the density of the polycrystalline material \( M \) in the depth \( z \).

In the calculation of scattered angle \( \theta_s \) from the chromium coating, we considered the surface roughness. The surface roughness is characterized with the root mean square deviation \( \sigma \) of the surface with respect to a flat surface. The density \( \rho_M(z) \) of the polycrystalline chromium coating in the depth \( z \) with the surface roughness of \( \sigma \) is expressed as

\[
\rho_M(z) = \frac{1}{\sqrt{2\pi\sigma}} \exp \left( -\frac{x^2}{2\sigma^2} \right) dx \tag{13}
\]

Then the effect of the surface roughness is reflected in the refractive index \( n(z) \) and the intensity \( I(z) \) of the refractive x-ray. The estimation with using the term of penetration depth \( T \) in the previous studies cannot be applied to such material with the surface roughness since \( T \) depend on the incident angle. The calculation for the depth profiling of the strain is performed with using eq. (12).

At first, the incidence angle dependence of scattered angle is calculated with the constant strain \( \epsilon_z \) as shown in Fig. 5. By comparison with calculated and observed scattering angle, the strain seems to decrease at smaller angle of incidence.

![Figure 5. Incidence angle dependence of calculated and observed scattering angle. The solid lines are calculated result with the constant strain \( \epsilon_z \).](image)

From the calculations for several models of the strain distribution, the strain distribution that reproduces the experimental results of the incidence angle dependence was derived. The strain distribution in the surface layer of the chromium coating is found as the following

\[
\epsilon_z = -0.019 \left\{ 1 - \exp \left( -\frac{z}{r} \right) \right\}, \tag{14}
\]

where \( r \) is 80nm, and in the calculation the surface roughness \( \sigma \) of 100nm in eq.(13) is considered. This roughness corresponds to the roughness of substrate steel surface. The same level depth into which the strain changes as the surface roughness consents. Comparison between calculated and observed scattering angle of Cr(310) is shown in Fig. 6. The solid line is calculated result. The calculated result reproduces the experiment result, and the depth profile of the strain distribution in the surface poly-crystalline layers was evaluated with a high accuracy.
4. CONCLUSIONS
The strain distribution in the surface layer of the chromium coating steel is investigated with the use of x-ray diffraction at small glancing angle of incidence. Analyzing the incidence angle dependence of the scattered angles of diffracted x-rays, the depth profile of the strain in the surface layer is derived. The depth profile of the strain is accurately obtained with surface roughness. The derived analyzing method can be applied to the residual stress distribution analysis of the surface layer materials of which densities change continuously in depth as the surface with roughness and layers structure.

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