Depth profile analysis of poly-crystalline layers structure and crystal grain size under surface using x-ray diffraction at small glancing angles of incidence

Yoshikazu Fujii, 1 and Takenori Nakayama 2

1Center for Supports to Research and Education Activities, Kobe University, Rokkoudai-cho, Nada-ku, Kobe 657-8501, Japan,
2Material Research Laboratory, Kobe Steel Ltd., Seishin, Nishi-ku, Kobe 651-2101, Japan
fujiiyos@kobe-u.ac.jp

Abstract. The peak profiles of the diffracted x-ray intensity were investigated as function of incidence angles at small glancing angle incidence of x-rays on a poly-crystalline surface. 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 structure of the poly-crystalline layers and the distribution of crystal grain size in the surface layers was studied. The dependence of the diffracted x-ray intensities on the glancing angle lead to the depth profile of the poly-crystalline layers of oxidized iron with accuracy of the order of nanometers. The incidence angle dependence of the peak width of diffracted x-rays lead to the depth profile of the crystal grain size of iron in the surface layer. The evaluated result is very small. It shows the crystallites size in the crystal grain under mechanically polished iron surface. Now, the analysing method for the depth profile of polycrystalline surface 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.

We measured the intensities of the diffracted x-rays on a polycrystalline iron surface at the various small glancing angles of incidence, and investigated the depth profile of the polycrystalline layers.[4] When x-rays are applied to polycrystalline, peak width of diffracted x-rays reflects the size of the crystal grain. The depth profile of the crystal grain size nearby the surface was investigated by analyzing the peak width of the diffracted x-rays at the various incidence angles.[5] Now, the analyzing method for evaluating the structure of the poly-crystalline layers and the distribution of crystal grain size in the surface layers was studied.
2. Experimental

Experimental details can be found elsewhere.[4] The polycrystalline surface of pure iron (ferrite, 99.9% purity) was mechanically polished and annealed at 400 °C for 5 minutes. The pre-heating forms a thin amorphous oxide layer on the iron surface. Small glancing angle x-ray scattering on polycrystalline iron surface was measured by using synchrotron radiation at Hyogo Prefecture beamline BL24 of SPring-8. X-rays (10keV) from a standard in-vacuum undulator are monochromatized by a double-crystal monochromator in the preceding optics hutch and then are introduced into the experimental hutch. Figure 1 shows a schematic view of the experimental arrangement. The x-ray beam irradiates upon a specimen surface at a glancing angle \( \alpha \) through slits 1 and 2, as shown in Fig. 1. The cross-section of the x-ray beam behind the slits is 0.1mm wide and 0.8mm high. Scattered x-rays from the surface at exit angle \( \beta \) from 0 ° to 0.4 ° are received in \( \theta \) direction by slits 3 and then are received by a scintillation counter. The acceptance angle of the scattered x-ray beams limited by slits 3 is 1 mrad in the \( \theta \) direction and 7 mrad in the \( \beta \) direction as shown in Fig. 1. The irradiated surface region by the x-rays is from 0.8mm*3mm to 0.8mm*14mm, which is changed by a glancing angle \( \alpha \).

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

![Figure 2. Diffraction patterns in the direction parallel to the surface at several angles of incidence](image)
Angular distributions of the scattered x-ray intensities were measured at several glancing angles of incidence. Figure 2 shows x-ray diffraction patterns at several angles of incidence. Next, peak intensities of diffracted x-rays are derived by gauss fitting of the experimental results of the peak profile with correction for a broadening due to acceptance angle. Figure 3 shows a change in the peak intensities corresponding to Fe₂O₃, Fe₃O₄, and Fe as a function of incidence angle: the peak intensity of Fe₂O₃ is high at 0.2° of incidence and low at larger incidence angles; the peak intensity of Fe₃O₄ is high at 0.3° and decreases at larger incidence angles; the peak intensity of Fe increases at a larger incidence angle. Analyzing these intensity profiles leads to the contribution of the crystals of each depth under the surface.

Figure 3. The peak intensities of diffracted x-rays as a function of the angle of incidence.

Figure 4 shows x-ray diffraction peak profiles from Fe(110) at several angles of incidence. Small shift of peak position by changing the incident angle can be seen in Fig. 4. This is the shift by deviation between θ and diffraction angle θₙ as shown in the equation; \( \cos \theta_n = \cos \theta \cos(\alpha' + \beta) \), where \( \alpha' \) is the refracted angle passing below the surface as approximately shown in the equation; \( \alpha' \approx \sqrt{\alpha^2 - \alpha_c^2} \), and the direction of the refracted x-ray is \( (\cos \alpha', 0, -\sin \alpha') \), and the direction of the detected x-ray is \( (\cos \theta \cos \beta, \sin \theta, \cos \theta \sin \beta) \), where the critical angle \( \alpha_c \) to the total external reflection is about 0.4.

Figure 4. Peak profiles of diffracted x-rays from Fe(110) at several angles of incidence.
The peak width $\delta\theta$ of diffracted x-rays as a function of incident angle is shown in Fig. 5. The experimental results of the peak width $\delta\theta$ of diffracted x-rays are broaden due to acceptance angle; $\left[ (\alpha' + \beta') / \tan \theta \right] \Delta\beta + \Delta \theta$, where $\beta = 3.5 \text{mrad}$, $\Delta\beta = 7 \text{mrad}$ and $\Delta \theta = 1 \text{mrad}$. The peak width $\delta\theta_d$ of diffracted x-rays shows the data of which a broadening due to acceptance angle was corrected as the following, $\delta\theta_d = \sqrt{\delta\theta^2 - \left[ (\alpha' + \beta') / \tan \theta \right] \Delta\beta + \Delta \theta}^2$.

The peak width is corresponding to the size of Fe crystal grain in the surface layer. Wide peak at smaller incidence angle show that Fe crystal grain is smaller nearby the surface, because the contribution from the surface top layer is large at a smaller glancing angle. Analyzing these peak profiles leads to the depth profile of the crystal grain size under the surface.

![Figure 5. FWHM of the diffracted x-ray peaks from Fe(110) at several glancing angles.](image)

3. Analysis

The intensity of x-rays, i.e., the electric and magnetic field propagating in the material, can be obtained using Maxwell’s equations.[6] 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 $N$ layers. Figure 6 is a multilayer representation of the calculation of refractive x-ray intensity. The vacuum is denoted as $j = 0$ and $n_0 = 1$. The thickness of one layer is $d$ and only the thickness of the bottom layer is assumed to be infinite.

![Figure 6. Multilayer representation for calculation of refractive x-ray intensity](image)

The reflectance of multiplayer system, consisting of $N$ layers can be calculated using the recursive formalism given by Parratt.[7] Let $n_j$ be the refractive index of the $j$-th layer, defined as $n_j = 1 - \delta_j - i\beta_j$, (1)
where \( \delta_j \) and \( \beta_j \) are the real and imaginary parts of the refractive index. These optical constants related to the atomic scattering factor and electron density of the \( j \)-th layer material. For x-rays of wavelength \( \lambda \), the optical constants of the \( j \)-th layer material consisting of \( N_{ij} \) atoms per unit volume can be expressed as

\[
\delta_j = \frac{\lambda^2 r_e}{2\pi} \sum_i f_{1i} N_{ij}, \quad \beta_j = \frac{\lambda^2 r_e}{2\pi} \sum_i f_{2i} N_{ij},
\]

where \( r_e \) is the classical electron radius and \( f_{1i} \) and \( f_{2i} \) are the real and imaginary parts of the atomic scattering factor of the \( i \)-th element atom, respectively.

The electric field of x-ray radiation at glancing angle of incidence \( \alpha \) is expressed as

\[
E_o(z) = A_0 \exp\left\{ i (k_o \cdot r - \omega t) \right\}.
\]  

Incident radiation is usually decomposed into two geometries to simplify the analysis, one with incident electric field \( E \) parallel to the plane of incidence (p-polarization) and one with \( E \) perpendicular to that plane (s-polarization). An arbitrary incident wave can be represented in terms of these two polarizations. \( E_{ox} \) and \( E_{oz} \) are p-polarization, and \( E_{oy} \) is s-polarization, and those components of the amplitude’s electric vector are expressed as

\[
A_{ox} = -A_{oy} \sin \alpha, \quad A_{oy} = A_{ox}, \quad A_{oz} = A_{oy} \cos \alpha.
\]

The components of wave vector of incidence x-rays are

\[
k_{ox} = \frac{2\pi}{\lambda} \cos \alpha, \quad k_{oy} = 0, \quad k_{oz} = \frac{2\pi}{\lambda} \sin \alpha.
\]

The electric field of x-rays propagating in the \( j \)-th layer material is shown as

\[
E_j(z) = A_j \exp\left\{ i (k_j \cdot r - \omega t) \right\}.
\]

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

\[
A_i = \Phi_i A_0, \quad A_j = \Phi_j A_{j-1} \exp\{i(k_{j-1,z}d)\},
\]

the Fresnel coefficient tensor for refraction on the interface between \( j-1 \) and \( j \) layer is given by

\[
\Phi_{j,xx} = \frac{2k_{j-1,z} k_{j,1} \cdot k_{j,1}}{k_{j-1,z} + k_{j,z}}, \\
\Phi_{j,xy} = \Phi_{j,yx} = \frac{2k_{j-1,z} k_{j,1} \cdot k_{j,1}}{k_{j-1,z} + k_{j,z}}, \\
\Phi_{j,yy} = \Phi_{j,yy} = \frac{2k_{j-1,z} k_{j,1} \cdot k_{j,1}}{k_{j-1,z} + k_{j,z}}, \\
\Phi_{j,zz} = \Phi_{j,zz} = \Phi_{j,zz} = \Phi_{j,zz} = \Phi_{j,zz} = \Phi_{j,zz} = \Phi_{j,zz} = \Phi_{j,zz} = 0.
\]

The wave vector \( k_j \) of the \( j \)-th layer is related to the refractive index \( n_j \) of the \( j \)-th layer as shown in the following

\[
k_j = \sqrt{\frac{n_j^2 k_o^2}{c^2}} = \text{const},
\]

and the x,y-direction components of wave vector are constant, then the z-direction component of wave vector of the \( j \)-th layer is shown as

\[
k_{j,z} = \sqrt{n_j^2 k_o^2 k_{oz}^2},
\]

and the Fresnel coefficient for refraction on the interface between \( j-1 \) and \( j \) layer is given by
\[ \Phi_{j,xx} = \frac{2k_{j,1}n_{j,1}^2}{k_{j,1}n_j^2 + k_{j,1}n_{j,1}^2} \]
\[ \Phi_{j,yy} = \frac{2k_{j,1}k_{j,2}n_{j,1}^2}{k_{j,1}n_j^2 + k_{j,2}n_{j,1}^2} \]
\[ \Phi_{j,zz} = \frac{2k_{j,1}n_{j,1}^2}{k_{j,1}n_j^2 + k_{j,2}n_{j,1}^2} \]

By the condition of incident x-ray, the z-direction component of wave vector of the j-th layer is shown as
\[ k_{j,z} = \frac{2\pi}{\lambda} \sqrt{n_j^2 \cos^2 \alpha} = \frac{2\pi}{\lambda} (a_j + ib_j). \]  

Using these equations, the electric field of x-ray propagating in j-th layer is expressed as
\[ E_j(z) = (\prod_{j=1}^{j} \Phi_j) A_j \exp \left[ i(k_{j,0}x + d \sum_{j=1}^{j-1} k_{j,2} + k_{j,1}(z - (j-1)d) \cot \omega_0) \right], \]
and the intensity of the refractive x-ray in j-th layer at depth z is shown as
\[ I(z) = (\prod_{j=1}^{M} \Phi_j) A_j (\prod_{j=1}^{M} \Phi_j) A_j \exp \left\{ id \frac{4\pi}{\lambda} \sum_{j=1}^{M} b_j - \frac{4\pi}{\lambda} b_j(z - (j-1)d) \right\}. \]

3.1. Depth profiling of poly-crystalline layers structure

We assume that the diffraction peak intensities corresponding to Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\) and Fe are in proportion to the sum of the refractive x-ray intensity in each layer of the polycrystalline specimen, as shown in the following equation
\[ I_M = \int_0^\infty \rho_M(z) I(z) \, dz, \]
where \( \rho_M(z) \) is the density of the polycrystalline M at the depth z. The surface and interface of the polycrystalline specimen have a roughness characterized with the root mean square deviation \( \sigma \) of the surface or interface with respect to a flat surface or interface. The structural diagram of polycrystalline oxide layers on the iron surface is shown in Fig. 7.

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Figure 7. Structural diagram of polycrystalline oxide layers on the iron surface.
A schematic diagram of the depth profile of the density of the polycrystalline specimen is shown in Fig. 8. The density of the polycrystalline \( M \) at depth \( z_1 \) to \( z_1 + D \) with interface roughness \( \sigma_1 \) and \( \sigma_2 \) and thickness of \( D \) is expressed as

\[
\rho_M(z) = \int_{-\infty}^{z} f(x - z_i, \sigma_i) dz \cdot \left[ 1 - \int_{-\infty}^{z} f(x - z_i - D, \sigma_2) dz \right],
\]

(16)

\[
f(x, \sigma) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{x^2}{2\sigma^2}\right).
\]

(17)

Figure 8. Schematic diagram of the depth profile of the density of the polycrystalline specimen.

We calculated the diffraction intensities corresponding to \( \text{Fe}_2\text{O}_3 \), \( \text{Fe}_3\text{O}_4 \) and \( \text{Fe} \) for this model with a rough surface and rough interfaces between each layer. In the calculation, the thickness \( d \) of one layer of multilayer is 0.01nm. Parameters of the fit are the thickness \( D_1 \) of \( \text{Fe}_2\text{O}_3 \), \( D_2 \) of \( \text{Fe}_3\text{O}_4 \), and surface roughness \( \sigma_1 \), the interface roughnesses \( \sigma_2 \) and \( \sigma_3 \).

Figure 9 shows the calculated intensities of x-rays from top layer and from 2nd layer at changing the thickness \( D_1 \) of top layer, when surface and interface roughnesses \( \sigma \) are 5nm. X-ray intensities from 2nd layer at the angle of incidence smaller than the critical angle decrease rapidly when the thickness \( D_1 \) of top layer is larger. This character is shown as same in the experimental results of incident angle dependence of the diffracted x-ray intensities for \( \text{Fe}_3\text{O}_4 \) (220). Then it was found that the \( \text{Fe}_3\text{O}_4 \) layer is 2nd layer and is below the \( \text{Fe}_2\text{O}_3 \) layer.

The calculated results of the incident angle dependence of the intensity for \( \text{Fe}_2\text{O}_3 \), \( \text{Fe}_3\text{O}_4 \) and \( \text{Fe} \) are compared with each experimental result. The contribution from the thin top layer is large at a smaller glancing angle, and contribution from the substrate \( \text{Fe} \) becomes large with increasing incident angle.
The analytical results that show the best fit with the experimental results are shown in the Fig. 10. The fitting parameters are shown in Table 1.

![Comparison between the calculated and experimental results of the diffracted x-ray intensities for Fe₂O₃ (104), Fe₃O₄ (220), and Fe (110)](image)

**Table 1. Parameters of the fit on depth profile of polycrystalline oxide layers on the iron surface**

| Thickness D (nm) | Roughness □ (nm) |
|------------------|------------------|
| Fe₂O₃            | 4.0              | □₁ = 0.3       |
| Fe₃O₄            | 8.5              | □₂ = 2.0       |
|                  |                  | □₃ = 1.0       |

The fitting accuracy with an error ratio 10% is ~ 1nm on the thickness of each layer. It was found that the thickness of each layer effects the ratio of the intensities at the small and large glancing angles. The fitting accuracy of surface roughness σ₁ and the interface roughness σ₂ is ~ 0.2nm. It was found that the roughness affects the ratio of the intensities at the critical angle and the large glancing angle. Thus the thickness and interface roughness of the surface oxidized iron layers (Fe₂O₃ and Fe₃O₄) were determined by analyzing the dependency of the diffracted x-rays intensities on the incidence. The depth profile of the polycrystalline layers of oxidized iron was evaluated to accuracy of the order of nanometers. Because the refractive indices of Fe₂O₃ and Fe₃O₄ are close to each other, this structure cannot be measured in good precision by the usual x-ray reflectivity measurement. The incidence angle dependence of the diffracted x-rays on polycrystalline specimen gives good information for investigating the depth profile of the surface structure of such material.

### 3.2. Depth profiling of the crystal grain size

The peak width of diffracted x-rays of Fe(110) is corresponding to the size of Fe crystal grain in the surface layer. Wide peak at smaller incidence angle shows that Fe crystal grain is smaller nearby the surface. Analyzing these peak profiles leads to the depth profile of the crystal grain size under the surface. The analysis was done on the supposition that the forms of the crystal grains and the direction of the crystal grains are distributed uniformly even in a surface, because x-rays are irradiating the over million crystal grains, and because there is no report that the direction of the crystal grain of the iron is not distributed uniformly in a surface.

When x-rays are applied to a crystal of lattice constant a₀ and grain size L₀, intensity distribution of diffracted x-rays in θ₀ direction from the crystal is shown by Laue function as
\[
\sin^2\left(\frac{KL}{2}\right)
\sin^2\left(\frac{Ka}{2}\right), \quad (18)
\]

where
\[
K = 2k_s \sin\left(\frac{\theta_s}{2}\right). \quad (19)
\]

When x-rays are applied to polycrystalline in a surface layer, the diffraction intensity is the sum of the diffracted x-rays from the polycrystalline in each layer. Then the peak profile of the diffracted x-rays is shown in the following equation
\[
I_M(K) = \int_0^\infty S_M(z) \sin^2\left(\frac{KL(z)}{2}\right) I(z) dz \sin^2\left(\frac{Ka}{2}\right), \quad (20)
\]

where \(S_M(z)\) is the density of the polycrystalline M at the depth z. The grain size at the depth z was supposed to be \(L(z)\). \(I_M(K)\) has diffraction peaks as Laue function like. \(I(z)\) is function of the incidence angle \(\alpha\). Therefore when \(L(z)\) is not constant in depth, \(I_M(K)\) becomes function of \(\alpha\). The incident angle dependence of the peak width of diffracted x-rays gives good information to investigate the depth profile of the crystal grain size in the surface layer. The investigated iron specimen surface in this study has polycrystalline oxide layers. The thickness of the surface oxidized iron layers (Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) ) were evaluated 4.0nm and 8.5nm, respectively. In the case that some materials exist in the surface layer, the refractive index \(n(z)\) change with the density in the depth z, and the intensity \(I(z)\) of the refractive x-rays in depth z is calculated with using the refractive index \(n(z)\).

In Fig. 5, wide peak at smaller incidence angle shows that Fe crystal grain is smaller nearby the surface, because the contribution from the surface top layer is large at a smaller glancing angle. Then the size of the crystal grain in the surface top layer is made \(L_s\), the size of the crystal grain in deep layer is made \(L_D\), and the characteristics depth of the surface condition is made D. With using these characteristic parameters we express the crystal grain size \(L(z)\) of each depth under the surface as shown in the following equation,
\[
L(z) = L_s + (L_s - L_D) \exp\left(-\frac{z}{D}\right). \quad (21)
\]

The peak profile of the diffracted x-rays, which simulates the observation, is calculated by eq. (20) with the using the grain size model of eq. (21), and the calculated results of the incident angle dependence of the peak width are compared with the experimental result.

![Figure 11](image-url)
Figure 11 shows comparison between the calculated and experimental results of the peak width of diffracted x-rays for Fe(110), where the experimental results show the peak width $\delta \theta_d$ of which a broadening due to acceptance angle was corrected. Parameters that reproduce the experimental result were $L_D=85\text{nm}$, $L_S=17\text{nm}$ and $D=150\text{nm}$, respectively. The evaluated result shows that the crystal grain under surface is very small. This result is consistent that the grain size in mechanically polished surface is usually smaller than those in bulk, but this analyzed results seems too small. It is said industrially that a crystal grain in the neighborhood on the surface breaks and becomes small multiple grains as so called crystallitles, when surface is made smoothly by mechanically polishing. The result in this study agrees with what is said industrially, and those contents were proved. But, it is big still in comparison with the scale of the surface roughness. These results show that, though a crystal grain around the surface is broken, a crystal grain itself is shaved, and it is being made smooth by mechanically polishing the surface. The result in this study agrees with what is said industrially, and those contents were proved. But, it is big still in comparison with the scale of the surface roughness. These results show that, though a crystal grain around the surface is broken, a crystal grain itself is shaved, and it is being made smooth by mechanically polishing the surface. The result of evaluated grain size $L_D$ in deep layer was smaller than those of bulk. It shows that the evaluated results from x-ray diffraction shows the crystallites size in the crystal grain under mechanically polished iron surface.

4. Conclusions
Intensities of diffracted x-rays on a polycrystalline iron surface were measured at various incidence angles, and the dependency of the incidence angle was investigated. The thickness and interface roughness of the surface oxidized iron layers (Fe$_2$O$_3$ and Fe$_3$O$_4$) were evaluated to accuracy of the order of nanometers by analyzing the dependency of the diffracted x-rays intensities on the incidence. Because the refractive indices of Fe$_2$O$_3$ and Fe$_3$O$_4$ are close to each other, this structure cannot be measured in good precision by the usual x-ray reflectivity measurement. The incidence angle dependence of the diffracted x-rays on polycrystalline specimen gives good information for investigating the depth profile of the surface structure of such material.

The incidence angle dependence of the peak width of diffracted x-rays lead to the depth profile of the crystal grain size in the surface layer. By the calculation reproducing the experimental result, the depth profile of the crystal grain size in the surface polycrystalline layers was evaluated. The evaluated result shows that the crystal grain under mechanically polished iron surface is very small. The result in this study agrees with what is said industrially, and those contents were proved. The result of evaluated grain size in deep layer was smaller than those of bulk. The evaluated results from x-ray diffraction in this experiments show the crystallites size in the crystal grain under the surface.

These analysis are performed also with the use of a compact UHV x-ray diffractometer for surface glancing scattering using a rotating-anode source at Kobe university.[8]

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