Stress-Strain Relationship and XRD Line Broadening in [0001] Textured Hexagonal Polycrystalline Materials

by

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1 Introduction

In this paper, the stress-strain relationship and XRD line broadening of hexagonal polycrystalline materials have been studied on the basis of the principle of stress analysis focusing on the crystal symmetries of constituent crystallites of textured materials. This is called the crystallite group method (CGM) by some groups studying the stress-strain relationships in the textured materials. As for hexagonal crystals, AlN is used as an archetypical textured crystal in the hexagonal system. Industrially, AlN is in semiconductor manufacturing because of its high heat-resistance and large mechanical strength. Another hexagonal crystal, GaN, is very famous for its blue luminescence. For these materials, it has been important matters to analyze the stress or strain incurred in the textured crystals during the fabrication. Thus, for [0001] textured hexagonal crystalline materials, Hanabus7 has proposed a technique for obtaining the stress-strain relationship under the equi-biaxial stress state. Tanaka and Akiniwa also have developed an advanced technique for obtaining the stress-strain relation under the triaxial stress state.

On the other hand, the present author has recently shown in both aspects of the theory (hereafter referred to as Y & H) and experiments that the stress-strain relationship in [111] textured cubic materials observed by X-ray diffraction (XRD) is expressed in a linear relation, where the coefficients of formulae for the relationship are given in terms of the elastic compliance constants. Those coefficients of formulae for the relationship are given in terms of the elastic compliance constants. As a result, it was shown that the average strains obtained in the crystallites for both symmetries of 6/mmm and 6/m are different from each other under the triaxial or biaxial stress field. Then, it turned out that the line width of XRD changes depending on the measurement direction.

Key words: Hexagonal, Residual stress, Fibre texture, Laue classes

2 Hexagonal polycrystalline specimen with [0001] fibre texture

Let us consider an anisotropic residual stress \( \sigma_{ij} \) (i, j = 1, 2, 3) that remains in a polycrystalline specimen with x, y and z coordinates, in which z-axis is perpendicular to the specimen surface x-y plane. The stress induces the anisotropic strain \( \varepsilon_{ij} \) (i, j = 1, 2, 3) in the specimen. Average strain, \( <\varepsilon_{ij}> \) measurable by XRD, is the average distortion of lattice spacings of the constituent crystallites along the measurement direction \( \phi \) and \( \psi \) which are represented in Laboratory Coordinates, where \( \phi \) and \( \psi \) are the angles representing the measurement direction in the polar coordinates with z-axis normal.

Referring to Y & H, strain \( <\varepsilon_{ij}> (\beta, \phi, \psi) > (i = 6/mmm, 6/m) \) is a linear function of the applied stress components \( \sigma_{ij} \) because of Hooke’s law. The coefficients are given in terms of the elastic compliance constants \( s_{ij} \). The angle \( \beta \) is half of the angle between two lat...
face. The symbols $\mathbf{a}'$ and $\mathbf{b}'$ represent the reciprocal lattice vectors of hexagonal single crystal. The projection indicates that there are twelve equivalent reflections around the [0001] axis, which are shown by double-circles. They are indexed as $h\bar{k}il$, $i\bar{k}hi$, $k\bar{h}il$, $h\bar{k}il$, $\bar{k}hi$, $\bar{h}ki$, $\bar{k}hi$, $i\bar{k}hi$, $h\bar{k}i$, $k\bar{h}i$, $\bar{h}ki$, $\bar{k}hi$ and $h\bar{k}i$, but they are not on a twofold rotation axis but on a sixfold rotation axis around the [0001] axis, where $i = -(h + k)$ is held in this expression.

The six reflections, $(a)$, $(b)$, $(c)$, $(d)$, $(e)$ and $(f)$, are in a sixfold rotation symmetry and the other six, $(a')$, $(b')$, $(c')$, $(d')$, $(e')$ and $(f')$ are also in another sixfold rotation symmetry. The six pairs of reflections, $(a)$ $(a')$, $(b)$ $(b')$, $(c)$ $(c')$, $(d)$ $(d')$, $(e)$ $(e')$ and $(f)$ $(f')$ are in a reflection symmetry each other.

For the polycrystalline specimen, one can easily infer that those crystallites with twelve different orientations around the [0001] axis contribute to any point on Debye-Scherrer line represented by $(h\bar{k}il)$ reflections. In a similar argument to the Y & H, it is possible to distinguish the contributions of such crystallites to the $(h\bar{k}il)$ Debye-Scherrer line into two groups: the one as a contribution from crystallites with type I orientation for the reflections, $(a)$, $(b)$, $(c)$, $(d)$, $(e)$ and $(f)$, and the other as that with type II orientation for the reflections, $(a')$, $(b')$, $(c')$, $(d')$, $(e')$ and $(f')$.

Therefore, the strain $\varepsilon_{ij}(\beta, \varphi, \psi)$ induced in the crystallites of the type I orientation is different from the strain $\varepsilon_{ij}(\beta, \varphi, \psi)_{g}$ induced in the crystallites of the type II orientation. It is known that the strains in the crystallites for the type I and type II orientations can be obtained in the general Eq. (1) (Y & H), as follows:

$$
e_{ij} = \omega_{0j}\omega_{ij}\sum_{l}\sigma_{ll}\sum_{m}p_{li}p_{mj}\sigma_{ij},$$

(1)

where $\omega_{ij}$ and $\sigma_{ij}$ are the components of transformation matrices, $\omega_{ij}$ and $\sigma_{ij}$, which are expressed in Eqs. (2) and (3), for the [0001] oriented crystallites of type I and type II.
II, respectively. The components of $\omega$ and $\pi$ consist of $\beta$, $\phi$ and $\psi$, which indicate the XRD measurement direction, under a triaxial stress state ($\sigma_{ij}$). $S_{\phi\psi}$ are the elastic compliance constants expressed by the tensor notation.

$$\omega = \begin{bmatrix} \cos \phi \cos \psi & \sin \phi \cos \psi & -\sin \psi \\ -\sin \phi & \cos \phi & 0 \\ \cos \phi \sin \psi & \sin \phi \sin \psi & \cos \psi \end{bmatrix}$$

(2)

and

$$\pi = \begin{bmatrix} \cos \beta & \sin \beta & 0 \\ -\sin \beta & \cos \beta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

(3)

The two strains, $\varepsilon_{33}^{\phi\psi}(\beta, \phi, \psi)_I$ and $\varepsilon_{33}^{\phi\psi}(\beta, \phi, \psi)_II$, are obtained in Eqs.(4) and (5), as follows:

$$\varepsilon_{33}^{\phi\psi}(\beta, \phi, \psi)_I = \frac{1}{2}(s_1 - 2s_2 + (s_1 - s_2)\cos 2(\beta - \phi)\sin^2 \psi)\sigma_{11}$$

(4)

$$\varepsilon_{33}^{\phi\psi}(\beta, \phi, \psi)_II = \frac{1}{2}(s_1 + (s_1 - s_2)\cos 2(\beta + \phi)\sin^2 \psi)\sigma_{11}$$

(5)

where the $s_i$ in Eqs.(4) and (5) are the elastic compliance constants expressed by the matrix notation. By taking an arithmetic average of Eqs. (4) and (5), the average strain $<\varepsilon_{33}^{\phi\psi}(\beta, \phi, \psi)>$ in the polycrystalline specimen of the Laue class $6/mmm$ is given, as follows:

$$<\varepsilon_{33}^{\phi\psi}(\beta, \phi, \psi)> = (\varepsilon_{33}^{\phi\psi}(\beta, \phi, \psi)_I + \varepsilon_{33}^{\phi\psi}(\beta, \phi, \psi)_II)/2$$

and

where $\varepsilon_{33}^{\phi\psi}(\beta, \phi, \psi)_I$ and $\varepsilon_{33}^{\phi\psi}(\beta, \phi, \psi)_II$ are the strains obtained in Eqs.(4) and (5), respectively.

### 2.2 Specimen in the Laue class $6/m$

In Fig. 3, the projection of the reciprocal lattice of a hexagonal crystallite along the [0001] axis, which belongs to the Laue class $6/m$, is shown. There are also twelve reflections around the [0001] axis in the single crystallite and they are indexed as $hkl$, $\bar{h}k\bar{l}$, $\bar{h}kl$, $ikhl$, $\bar{h}k\bar{l}l$, $ihkl$, $h\bar{k}il$, $h\bar{k}li$, $k\bar{h}il$, $k\bar{h}li$, $h\bar{h}il$ and $h\bar{h}li$. However, all the twelve reflections are not equivalent. They are classified into two groups; one group is the six reflections, (a), (b), (c), (d), (e) and (f), for type I and the other group is another six reflections, (a'), (b'), (c'), (d'), (e') and (f'), for type II. There is no reflection symmetry between the two reflection groups, such as $hkl$ and $\bar{h}k\bar{l}$ under the condition of $h \neq k \neq 0$, because the structure factors for these two groups are different from each other, although each group is in a sixfold rotation symmetry around the [0001] axis.

For polycrystalline specimens, just as the case of $6/mmm$, the crystallites with twelve different orientations around the [0001] axis contribute to any point on Debye-Scherrer line labelled by $\{hkl\}$ or $\{\bar{h}k\bar{l}\}$ reflections with $h \neq k \neq 0$. In the case of $6/m$ symmetry, however, the $\{hkl\}$ reflections from crystallites in type I and the $\{\bar{h}k\bar{l}\}$ reflections...
from crystallites in type II should be treated independently owing to their different structure factors. The strains observed in the two types of reflections are similar to those of the symmetry $6/mmm$, given by $x'_{33}(\beta, \psi, \phi)$ and $x'_{33}(\beta, \psi, \phi)_{II}$ under the stress field, which are shown in Eqs. (4) and (5). When these two equations are compared, one can see that their contributions to the Debye-Scherrer line are also different from each other. As a result, the profile of the $\{011\}$ Debye-Scherrer line becomes asymmetric and the average strain cannot easily be defined in this case. In order to obtain individual strains, $x'_{33}(\beta, \psi, \phi)_{I}$ and $x'_{33}(\beta, \psi, \phi)_{II}$, from this Debye-Scherrer line for the symmetry $6/m$, the asymmetric line profile should be analysed by using a technique of profile fitting.

3 Line broadening under triaxial stress

3.1 Line broadening expected to a [0001] textured hexagonal specimen

As shown in a paper, the line broadening of a cubic TiN thin film with $<111>$ fibre texture occurs for specific Debye-Scherrer lines, additionally to the usual shift of diffraction angle $2\theta (h k l)$ owing to strain, where the specimen belongs to Laue class $m\overline{3}m$ or $m\overline{3}1^{13}$.

When [0001] textured hexagonal AlN is taken as a specimen for experiments of the line width of XRD, the line broadening could be easily found in the 1230 reflection by the use of CuK$\alpha$ radiation. Figure 4 shows that the (1230) reflections of the specimen have two kinds of orientations of the constituent crystallites, type I and type II. It can be seen that the two pairs of parallel lattice planes, which are one pair of 1230 and $\overline{2130}$ and the other of 2130 and $\overline{1230}$, are in a mirror relation around [0001] axis. It is notable that there exist the specific orientations of type I and type II crystallites due to the existence of [0001] fibre texture in which the two dark gray lattice planes 1230 and $\overline{2130}$ in type I and the other two dark gray planes 2130 and $\overline{1230}$ in type II will be mutually parallel. As a result, these four reflections satisfy Bragg condition observed as a Debye-Scherrer line at $\psi = 45^\circ$, if no load applied. When the specimen is loaded, the type I and type II crystallites could deform differently owing to the difference between their crystal- line orientations. Thus, the scattering angle $2\theta(1230)$ for the 1230 reflection and $2\theta(2130)$ for the 2130 reflection are no longer equivalent to each other. In other words, the 1230 and 2130 reflections would split into separate reflections under the load. However, it should be noted that the difference of the Bragg angles, $2\theta(1230) - 2\theta(2130)$, is considered to be not so large since the deformation is in terms of the elasticity. Both the peaks are not well separated but are observed as a simple line broadening of the reflection. The profile is expected to change based on the existence of triaxial or biaxial load.

![Fig. 4 Schematic drawing of two types of orientations in hexagonal crystallites both of which [0001] direction is perpendicular to the surface of this page, showing that they are in [0001] fibre texture. However, the two crystallites are oriented in such a way that the (1230) and (2130) lattice planes (dark gray) of type I crystallite are parallel to the (2130) and (2130) lattice planes (dark gray) of type II so that these four lattice planes satisfy Bragg condition along the direction $\psi = 45^\circ$. The dark gray lattice planes and light gray ones are in reflective symmetries to (1120) plane in both crystallites. However, the shapes of the two crystallites could be deformed differently under a biaxial stress load since the two reflections, (1230) and (2130), and the other two reflections, (2130) and (1230), are not in a rotation symmetry, respectively.](image-url)
3.2 Line broadening inferred from stress-strain relationship

According to the paper proposed by Yokoyama et al. (2009), the separation of two Bragg peaks, \( \Delta \theta(I) - \Delta \theta(II) \), is given in Eq.(7), where \( \Delta \theta(I) \) is the shift of diffraction angle owing to strain in the type I crystallites and \( \Delta \theta(II) \) is that for type II.

\[
\Delta \theta(\beta, \varphi, \psi) = \frac{\Delta a \theta(\beta, \varphi, \psi)}{2} = \frac{1}{2} \tan(\theta_{0}) \Delta \theta_{(I, II)}(\varphi, \psi), \tag{7}
\]

where \( 2 \theta_{0} \) is the diffraction angle for undistorted crystallites and \( \Delta \theta_{(I, II)}(\varphi, \psi) \) is the residual strain between the type I and type II crystallites.

The peak separation can be expressed as the residual strain caused by the difference of orientations for type I and type II crystallites. Thus, it is given by subtracting Eq.(4) from Eq.(5), as follows:

\[
\Delta \varepsilon_{12,\beta,\varphi,\psi} = \varepsilon_{12}^{(I)}(\beta, \varphi, \psi) - \varepsilon_{12}^{(II)}(\beta, \varphi, \psi) \nonumber = \sin \beta \varepsilon_{(I)}(\varphi, \psi) \cos \varphi + \sin \varphi \varepsilon_{(I)}(\varphi, \psi) \cos \varphi \nonumber = \sin \beta \varepsilon_{(II)}(\varphi, \psi) \cos \varphi + \sin \varphi \varepsilon_{(II)}(\varphi, \psi) \cos \varphi. \tag{8}
\]

If the shearing stresses \( \sigma_{12} \) and \( \sigma_{23} \) are small enough to be neglected, Eq.(8) shows that the split \( \Delta \theta(\beta, \varphi, \psi) \) consists of two terms: there is a term, proportional to the deviation from the homogeneous stress, \( \varepsilon_{12} - \varepsilon_{11} \), depending on \( \sin 2 \psi \theta \psi \), and there is a contribution from the shearing stress component, \( \varepsilon_{12} \), depending on \( \cos 2 \psi \theta \psi \). It is interesting that the first term does not contribute at \( \varphi = 0 \) and \( \varphi = 90^\circ \) even under loading and also the other term similarly does not contribute at \( \varphi = 45^\circ \). Since the separation of two Bragg reflections \( \Delta \theta(\beta, \varphi, \psi) \) is induced by the elasticity, it is generally less than the full width at half maximum (FWHM) of reflections used for the inspection. Thus, the reflections will not be observed as two separate peaks but simply as a line broadening, where the line width changes depending on the measurement direction, \( \varphi \) and \( \psi \).

A simulation of the XRD line broadening in a [0001] textured hexagonal polycrystalline sample of AlN is shown for CuK\( \alpha \) radiation as an application of the theory of line broadening. The elastic stiffness constants of AlN are given as \( c_{11} = 3.398 \), \( c_{12} = 0.140 \), \( c_{13} = 0.127 \), \( c_{33} = 0.382 \), \( c_{44} = 0.096 \) TPa in the literature.\(^{15}\) The line broadening in Eq.(7) of a reflection 123, for which \( 2 \theta = 127.373^\circ \), \( \beta = 40.89^\circ \), and \( \varphi = 58.471^\circ \), is calculated as \( \Delta \theta = 0.026\% \) for \( \varphi = 0^\circ \) and \( \Delta \theta = 0.065\% \) for \( \varphi = 45^\circ \) under the stress state of \( \varepsilon_{12} = 100 \), \( \varepsilon_{23} = 200 \), \( \varepsilon_{12} = 20 \), and \( \varepsilon_{23} = 0 \) MPa. Thus the difference angle, 0.04\(^\circ \), between these two line broadenings is enough large to be observed by laboratory instrument.

4 Discussion and Conclusions

In a hexagonal specimen in the Laue class 6/mmm or 6/m with [0001] fibre texture, the strains induced in the lattice planes of the specific reflections (hkl) in type I and type II crystallites are originally not equivalent to each other under load, if the reflections satisfy the requirement of \( h \neq k \neq 0 \), such as 1250 and 2150. A single XRD profile comes from each of the two crystallite types, type I and type II, which are called logical profiles. These logical profiles separated by the elastic deformation are located at their own scattering angles estimated by the strains of type I and type II (Eq.(4) or Eq.(5)), respectively. In fact, it is impossible to observe one of these two logical profiles independently but they are observed as one XRD profile, which is the superposition of the two.

As for logical profiles in a hexagonal specimen with 6/mmm, they take the same shape at each of their scattering angles, since all the twelve reflections contributing to the diffraction along \( \varphi = 0^\circ \) in type I and type II crystallites are equivalent. In other words, they have the same structure factors (see Fig.2). Thus, the XRD profile observed is reproduced by superposing the logical profiles of type I and type II. As a result, it is reasonable to take the arithmetic average of the strains in both types of crystallites for obtaining the average strain.

On the other hand, although both sets of six reflections for the two types of crystallites in a hexagonal specimen with 6/m are observed at the same scattering angles if the specimen is not loaded. However, their structure factors are different from each other (see Fig. 3). Thus, if the specimen is loaded, the average strain is not obtained in a similar way to 6/mmm since their logical profiles take the different shapes at their scattering angles. It can be given by taking a treatment of profile fitting for the observed XRD profile with the two logical profiles.

Since the peak separation in the [0001] textured hexagonal specimens occurs just due to the difference, 2\( \beta \), of type I and type II orientations, the line broadening is independent of the crystal symmetries, 6/mmm and 6/m. It has been shown by a simulation of a specimen of AlN that the XRD line broadening in [0001] textured hexagonal materials is observable by using laboratory instrument.

The strain analysis for type I and type II crystallites explains one reason for elastic inhomogeneities in the textured materials. As a result, it is known that the strain is observed by XRD through reflections with the same indices or same diffraction angles in crystallites differently oriented on the basis of the crystal symmetry. However the plastic inhomogeneity is not known in this analysis because the elastic and plastic strains cannot be distinguished in this theory. In the future, since the Reuss model is only taken into account in this study, another grain interaction model, such as the Voigt or Kröner model, would be applied to our theory.
5 References