Analysis and Mapping of Detailed Inner Information of Crystalline Grain by Wavelength-Resolved Neutron Transmission Imaging with Individual Bragg-Dip Profile-Fitting Analysis

Yosuke Sakurai 1, Hirotaka Sato 1,*, Nozomu Adachi 2, Satoshi Morooka 3, Yoshikazu Todaka 2 and Takashi Kamiyama 1

Graduate School of Engineering, Hokkaido University, Kita-13 Nishi-8, Kita-ku, Sapporo 060-8628, Japan; skrineut@frontier.hokudai.ac.jp (Y.S.); takashik@eng.hokudai.ac.jp (T.K.)
Department of Mechanical Engineering, Toyohashi University of Technology, 1-1 Higariagaka, Tempaku, Toyohashi, Aichi 441-8580, Japan; n-adachi@me.tut.ac.jp (N.A.); todaka@me.tut.ac.jp (Y.T.)
Materials Sciences Research Center, Japan Atomic Energy Agency (JAEA), 2-4 Shirakata, Tokai, Naka, Ibaraki 319-1195, Japan; morooka.satoshi@jaea.go.jp
* Correspondence: h.sato@eng.hokudai.ac.jp; Tel.: +81-11-706-6679

Abstract: As a new method for evaluating single crystals and oligocrystals, pulsed neutron Bragg-dip transmission analysis/imaging method is being developed. In this study, a single Bragg-dip profile-fitting analysis method was newly developed, and applied for analyzing detailed inner information in a crystalline grain position-dependently. In the method, the spectrum profile of a single Bragg-dip is analyzed at each position over a grain. As a result, it is expected that changes in crystal orientation, mosaic spread angle and thickness of a perfect crystal can be evaluated from the wavelength, the width and the integrated intensity of the Bragg-dip, respectively. For confirming this effectiveness, the method was applied to experimental data of position-dependent Bragg-dip transmission spectra of a Si-steel plate consisting of oligocrystals. As a result, inner information of multiple crystalline grains could be visualized and evaluated. The small change in crystal orientation in a grain, about 0.4°, could be observed by imaging the Bragg-dip wavelengths. By imaging the Bragg-dip widths, both another grain and mosaic block in a grain were detected. Furthermore, imaging results of the integrated intensities of Bragg-dips were consistent with the results of Bragg-dip width imaging. These small crystallographic changes have not been observed and visualized by previous Bragg-dip analysis methods.

Keywords: wavelength-resolved neutron transmission imaging; Bragg-dip; dip profile-fitting analysis; detailed inner crystalline-grain information; crystal orientation; mosaic block

1. Introduction

There are various quantum beam methods for evaluating crystallographic information of single crystals and polycrystals. Electron microscopes [1,2], X-ray diffraction [3,4], X-ray diffraction contrast imaging [5,6], neutron diffraction [7–9] and neutron diffraction contrast imaging [10–12] are applied to crystallographic characterizations. Furthermore, recently, pulsed neutron Bragg-edge transmission imaging [13–17], one of the wavelength-resolved neutron transmission imaging methods, can evaluate crystalline microstructural information of the deep part of a sample with a high spatial resolution over a large field-of-view. This method is applied for polycrystals.

Evaluating crystalline information of single crystals and oligocrystals is important for characterizing materials such as turbine blades, electromagnetic steels and radiation scintillators. As a new method for evaluating single crystals and oligocrystals, the pulsed neutron Bragg-dip transmission analysis/imaging method [18–20] is also being developed.
The method can non-destructively evaluate the position-dependent crystallographic information of a bulk single crystal over a large area. The full pattern-fitting analysis method of the Bragg-dip neutron transmission spectrum was developed by Malamud et al. [18]. This method can evaluate detailed crystallographic information of a single crystal. However, it is not easy to visualize a real-space map of the crystalline information of a twin crystal and a sample in which crystal orientation changes significantly. Moreover, it is theoretically difficult to analyze the Bragg-dip spectrum of a crystal having unknown crystal orientation. This is because the method requires initial estimation of crystal orientation before the fitting analysis. Thus, for these reasons, it seems to be difficult for this method to analyze and visualize crystallographic information of oligocrystals. On the other hand, Sato et al. developed a method which could analyze the crystal orientation along a neutron transmission direction from the full wavelength pattern of Bragg-dips [19]. This method was applied to position-dependent Bragg-dip neutron transmission spectra measured from an oligocrystal sample, and position-dependent crystal orientations could be derived over the sample. Because this method can analyze the crystal orientation without initial estimation, it can visualize crystal orientations of each grain whose crystal orientation is unknown. However, crystalline information except for crystal orientation cannot be obtained by this method. Strickland et al. developed a method which could visualize the misorientation in single crystals [20]. In this method, the bottom of Bragg-dip, namely the wavelength where the neutron transmission was the lowest, was considered as the wavelength where Bragg-dip appears. This method can map the wavelengths where Bragg-dips appear in real space. As a result, the misorientation in a single crystal can be visualized. However, this method is not the dip profile-fitting analysis. Therefore, other Bragg-dip profile information including various crystallographic information are not utilized. Thus, it is difficult for the conventional Bragg-dip analysis methods to visualize multiple detailed crystalline information position-dependently.

Therefore, in this study, a new Bragg-dip neutron transmission spectrum analysis method was developed and applied to position-dependent oligocrystal evaluation. It is the single Bragg-dip profile-fitting analysis method. This method is applied to position-dependent Bragg-dip neutron transmission spectra. First of all, in the Bragg-dip transmission imaging experiment, neutron transmission spectra, including Bragg-dip, the profile of which reflects crystallographic information of a single crystal, are measured at each pixel of the time-of-flight (TOF) imaging detector for both wavelength analysis and imaging analysis of pulsed neutrons. Here, by the profile-fitting analysis of individual Bragg-dip in the neutron transmission spectrum, the wavelength, the width and the integrated intensity of Bragg-dip can be derived. Then, change in crystal orientation can be evaluated from change in the wavelength where Bragg-dip appears, mosaic spread angle can be evaluated from the width of Bragg-dip and change in thickness of a perfect crystal along the neutron transmission path can be evaluated from the integrated intensity of Bragg-dip. Because the method is a simple profile-fitting analysis, it is expected that the method can evaluate this detailed crystalline information position-dependently without difficult spectrum-fitting procedures.

For this reason, in this study, we developed the single Bragg-dip profile-fitting analysis method. Then, this method was applied to experimental data of position-dependent Bragg-dip neutron transmission spectra measured from an oligocrystal material [19] to confirm the effectiveness of the new approach. As a result, a small change in crystal orientation inside a crystalline grain was detected in the real-space image. In addition, another crystalline grain and mosaic block in a crystalline grain which had not been observed by the previous data analysis method [19] could be observed in the real-space image. In this paper, the procedure of the single Bragg-dip profile-fitting analysis method and results of these new observations are reported. This paper is organized as follows. In Section 2, the outline of the wavelength-resolved neutron transmission imaging experiment using pulsed neutrons and the TOF method is described. In Section 3, the single Bragg-dip profile-fitting analysis method is
explained. In Section 4, the imaging results of single Bragg-dip profile information are described, and newly evaluated crystalline information in crystalline grains is discussed.

2. Time-of-Flight Neutron Transmission Imaging Experiment

In this study, the single Bragg-dip profile-fitting analysis method was applied to the experimental data obtained in the previous study [19]. In this section, the outline of the wavelength-resolved neutron transmission imaging experiment based on the time-of-flight (TOF) method is described.

2.1. Sample

Figure 1 shows the photograph of the sample measured in this study, and the inverse pole figure (IPF) map presented in the previous study [19]. The IPF map (Figure 1b) represents the crystal orientations parallel to the neutron transmission direction which corresponds to the normal direction of the sample plate. The sample is a 3.4 mass\% Si–steel plate of 5 mm thickness, 6.90 cm height and 6.75 cm width, which is used as electromagnetic steels. The crystal structure is body-centered cubic (b.c.c.). As shown by Figure 1a, the grain boundaries can be observed on the surface with the naked eye. It was confirmed that there were regions where two grains were stacked along the neutron transmission direction, near the grain boundaries (e.g., Figure 1 Region (α)). It can be observed on the IPF maps presented in the previous study [19]. The crystal orientations \([uvw]\) along the neutron transmission direction of Grains 1, 2 and 3 were determined in the previous study [19]. Table 1 shows its result. In this paper, furthermore, the results of the single Bragg-dip profile-fitting analysis and imaging of Grains 1, 2 and 3 are reported and discussed.

![Figure 1](image_url)

**Figure 1.** (a) Photograph of the Si–steel plate sample. The region surrounded by dashed black lines indicates the field of view (FOV). (b) IPF map of the sample, evaluated by Bragg-dip neutron transmission imaging [19]. The number indicated in the figure indicates the number of grain. The figure is reproduced with permission of the International Union of Crystallography from reference [19].

| Grain | \([uvw]\)   |
|-------|-------------|
| 1     | [100 70.52] |
| 2     | [100 66.38] |
| 3     | [100 74.26] |

2.2. Experimental

A wavelength-resolved neutron transmission imaging experiment based on the TOF method of pulsed neutrons was performed to measure the position-dependent Bragg-dip neutron transmission spectra of the sample. The experiment was performed at the
pulsed neutron instrument, the Neutron Beamline for Observation and Research Use (NOBORU) [21] constructed at BL10 at the Materials and Life Science Experimental Facility (MLF) in the Japan Proton Accelerator Research Complex (J-PARC). Figure 2 shows a schematic of the neutron beamline. The 3 GeV proton synchrotron of J-PARC was driven for the pulsed spallation neutron source, and the proton beam power changed from 400 to 500 kW during the experiment. Neutrons were produced by the spallation reaction at the Japan Spallation Neutron Source (JSNS), and moderated by the decoupled-type 20 K supercritical 100% para-H2 moderator. The moderator surface area was 10 × 10 cm2. The neutron pulse FWHM was about 50 μs for cold neutrons (0.4 nm wavelength). Therefore, the wavelength resolution could be calculated as 0.35% for cold neutrons using the neutron flight path length as described later. The neutron beam intensity and the beam angular divergence were controlled by the B4C slit. The slit size was 3 × 3 cm2, and the slit was set at 7.05 m from the neutron source. A gas electron multiplier (GEM) detector containing the 10B(n,α)7Li converter [22] with the TOF analysis function was used as a neutron TOF-imaging detector. The pixel size was 800 × 800 μm2, and 128 × 128 pixels of the imaging detector gave an active area of 10.24 × 10.24 cm2. The detector was set at 14.26 m from the neutron source, and the sample was set at 4 cm in front of the detector. Hence, the sample was set at 14.22 m from the neutron source. Therefore, the neutron collimator ratio, L/D, was about 2400, and the neutron beam angular divergence was about 0.416 mrad. We put the sample close to the detector for avoiding the blurring effect of spatial resolution due to the neutron beam angular divergence. It is no problem in terms of the diffracted neutron background for the detector. This is because longer wavelength neutrons cause back scattering according to Bragg’s law, and cannot be detected by the detector [19]. The estimated cold/thermal neutron flux during this experiment was approximately 6.5 × 104 n/cm2/s. The open beam measurement, without the sample, was about 7.2 h. The sample beam measurement was about 14.5 h. By these measurements, the neutron transmission was obtained at each wavelength position-dependently.

![Figure 2. Schematic of setup of pulsed neutron transmission imaging experiment.](image)

3. Single Bragg-Dip Profile-Fitting Analysis Method

3.1. Crystallographic Information Obtained from a Bragg-Dip Profile

In this study, the wavelength where Bragg-dip appears, the width (FWHM) of Bragg-dip and the integrated intensity of Bragg-dip were analyzed by fitting a Gaussian function to a single Bragg-dip. Bragg-dips in a neutron transmission spectrum are caused by diffraction phenomenon of neutrons in a single crystal. Generally, crystal orientation is evaluated from the wavelength where Bragg-dips appear, mosaic spread angle is evaluated from the width of Bragg-dips and crystal thickness is evaluated from the integrated intensity of Bragg-dips.

These relations between the crystallographic information and the Bragg-dip profiles are explained as follows. Bragg-dips appear as the attenuations of neutron transmission
intensities caused by single crystal diffractions. Diffracted neutrons causing Bragg-dips satisfy Bragg’s law:

\[ \lambda = 2d_{hk} \sin \theta_{hk} (0^\circ \leq \theta \leq 90^\circ) \]  

Here, \( \lambda \) is the neutron wavelength, \( d_{hk} \) is the crystal lattice spacing of \((hkl)\) plane and \( \theta_{hk} \) is the Bragg angle. According to Equation (1), the wavelength \( \lambda \), where Bragg-dip appears, depends on the lattice spacing \( d_{hk} \) and the Bragg angle \( \theta_{hk} \). Therefore, the information relating to the macro-strain depending on \( d_{hk} \), and the change in crystal orientation relating to \( \theta_{hk} \), can be evaluated from the Bragg-dip wavelength \( \lambda \).

The width of Bragg-dip, \( \Delta \lambda \), depends on the width of the crystal lattice spacing distribution \( \Delta d_{hk} \) which relates to the micro-strain and the crystallite size, and the fluctuation of Bragg angle \( \Delta \theta_{hk} \) which relates to the mosaic spread angle of the crystal. Therefore, the information relating to the crystal defect such as micro-strain and mosaic can be evaluated from the width of Bragg-dip. Here, the other parameters which can affect the width of Bragg-dip, \( \Delta \lambda \), are discussed. The width of Bragg-dip, \( \Delta \lambda \), is also affected by the instrumental resolution, such as the wavelength resolution and the beam angular divergence. The wavelength resolution depends on the neutron wavelength. Moreover, when the neutron supermirror guide tube is used in the neutron beamline, the beam angular divergence also depends on the wavelength. Hence, the width of Bragg-dip, \( \Delta \lambda \), can also change depending on the wavelength. However, actually, the change in the wavelength of a certain Bragg-dip is small in a certain crystal because the changes in macro-strain and crystal orientation are small in the same crystal. Therefore, the width of Bragg-dip, \( \Delta \lambda \), is not affected by the change in the instrumental resolution so much because the Bragg-dip wavelength is not changed. Thus, it is generally considered that the change in the width of Bragg-dip represents the changes in crystal defect and mosaic spread angle.

Finally, the information evaluated from the integrated intensity of a Bragg-dip is explained. In the neutron diffraction experiment, the diffracted intensity is proportional to the crystal volume. In the Bragg-dip neutron transmission method, the integrated intensity of Bragg-dip is proportional to the diffracted intensity along the neutron transmission path. Thus, this type of diffracted intensity is proportional to the crystal thickness where neutrons are transmitted. Therefore, the information of the crystal thickness can be evaluated from the integrated intensity of Bragg-dip. However, because of the extinction effect, the integrated intensity of Bragg-dip is not simply proportional to the crystal thickness. The principle of the extinction effect is described in Section 3.3.

### 3.2. Profile-Fitting Function

\( Tr(\lambda) \), called the neutron transmission spectrum, is expressed as the following equation:

\[ Tr(\lambda) = \exp[-N\sigma_{tot}(\lambda)]. \]  

Here, \( \lambda \) is the neutron wavelength, \( N \) is the projected atomic number density of the crystal and \( \sigma_{tot}(\lambda) \) is the microscopic neutron total cross-section that represents the probability of the interaction between neutron and nucleus. The negative value of the natural logarithm of transmission is calculated as the following equation:

\[ -\ln(Tr(\lambda)) = N\sigma_{tot}(\lambda), \]  

and this value is proportional to the neutron total cross-section. \(-\ln(Tr(\lambda))\) is usually used in this study for the following reasons. The neutron total cross-section includes the neutron coherent elastic scattering cross-section. The neutron coherent elastic scattering cross-section, as described later, is proportional to the diffracted intensity. The diffracted intensity is proportional to the crystal volume. Therefore, by evaluating the neutron transmission spectrum in the dimension of a cross-section like \(-\ln(Tr(\lambda))\), the crystallographic information can be evaluated more quantitatively.
The neutron total cross-section $\sigma_{\text{tot}}(\lambda)$ is expressed as the following equations:

$$\sigma_{\text{tot}}(\lambda) = \sigma_{\text{Bragg}}(\lambda) + \sigma_{\text{nonBragg}}(\lambda),$$  
$$\sigma_{\text{tot}}(\lambda) = \sigma_{\text{coh}}(\lambda) + \sigma_{\text{incoh}}(\lambda) + \sigma_{\text{elas}}(\lambda) + \sigma_{\text{abs}}(\lambda).$$

$\sigma_{\text{Bragg}}(\lambda)$ and $\sigma_{\text{nonBragg}}(\lambda)$ satisfy the following equations:

$$\sigma_{\text{Bragg}}(\lambda) = \sigma_{\text{coh}}(\lambda),$$
$$\sigma_{\text{nonBragg}}(\lambda) = \sigma_{\text{incoh}}(\lambda) + \sigma_{\text{elas}}(\lambda) + \sigma_{\text{abs}}(\lambda).$$

Here, $\sigma_{\text{Bragg}}(\lambda)$ is the Bragg scattering cross-section, $\sigma_{\text{nonBragg}}(\lambda)$ is the non-Bragg scattering cross-section, $\sigma_{\text{coh}}(\lambda)$ is the coherent elastic scattering cross-section, $\sigma_{\text{incoh}}(\lambda)$ is the incoherent elastic scattering cross-section, $\sigma_{\text{elas}}(\lambda)$ is the inelastic scattering cross-section and $\sigma_{\text{abs}}(\lambda)$ is the absorption cross-section. Figure 3a shows the neutron transmission spectrum of Grain 3, one of the crystalline grains in the sample measured in the experiment. Figure 3b shows the negative value of the natural logarithm of transmission, $-\ln(\text{Tr}(\lambda))$. Figure 3c shows the procedure of the profile fitting and the Bragg-dip profile information obtained through the profile fitting. In Figure 3b, the peak indicated by the Bragg scattering component is caused by the Bragg scattering cross-section, $\sigma_{\text{Bragg}}(\lambda)$, and the baseline indicated by the non-Bragg scattering component is caused by the non-Bragg scattering cross-section, $\sigma_{\text{nonBragg}}(\lambda)$. The profile of the non-Bragg scattering cross-section, $\sigma_{\text{nonBragg}}(\lambda)$, can be approximated by the following linear function (see Figure 3c left):

$$\sigma_{\text{nonBragg}}(\lambda) = a\lambda + b.$$  

Here, $a$ and $b$ are the parameters refined by the fitting. Furthermore, the Bragg scattering cross-section, $\sigma_{\text{Bragg}}(\lambda)$, is added to the non-Bragg scattering cross-section. In this study, the Gaussian function is fitted to the Bragg scattering cross-section, $\sigma_{\text{Bragg}}(\lambda)$, to analyze the wavelength where Bragg-dip appears, the width and the integrated intensity of Bragg-dip. The probability density function which is used for the profile fitting follows a Gaussian distribution, and it is expressed as the following equation:

$$\sigma_{\text{Bragg}}(\lambda) = S \times \exp\left(-\frac{(\lambda - \lambda_{hkl})^2}{2\sigma^2}\right) / \sqrt{2\pi\sigma^2}. $$

Here, $S$ is a scale factor of the peak height which includes the effect of projected atomic number density $N$ during the analysis. In addition, $\sigma$ is the standard deviation of the Gaussian function. The standard deviation, $\sigma$, is related to the full width at half maximum (FWHM) of the Gaussian distribution, $w$, by the following equation:

$$w = 2\sqrt{2\ln 2} \times \sigma \approx 2.35\sigma.$$  

The wavelength where Bragg-dip appears, $\lambda_{hkl}$, is determined from the wavelength where the Gaussian function is the maximum. The FWHM of Bragg-dip, $2.35\sigma$, is determined from the standard deviation, $\sigma$. The height of Bragg-dip is determined as $\sigma_{\text{Bragg}}(\lambda_{hkl}) = S / \sqrt{2\pi\sigma^2}$. This profile information is shown in Figure 3c, right.
In this section, the principle of extinction effect is described. The extinction effect is the effect when the diffracted neutrons are diffracted again in the same crystallite or other crystallites. As a result, the intensity of diffracted neutrons should be considered when the integrated intensity information of Bragg-dip is evaluated.

The extinction effect is the effect when the diffracted neutrons are diffracted again in the same crystal condition. Because the total integration of the probability density function (Equation (9)), which follows a Gaussian distribution, has a negative dependence on the width and the height of Bragg-dip. On the other hand, the probability density function (Equation (9)) as the following equation:

\[ \text{Integrated Intensity} = \text{Height} \times \text{Width} \]

It turns out that the product of the height and the width is constant. Here, \( S \), the scale factor of the height, is settled on one value under the same instrumental condition and the same crystal condition. Because the total integration of the probability density function which follows a Gaussian distribution is also constant, the value which is calculated by multiplying the height and the width of Bragg-dip can be considered as the integrated intensity of Bragg-dip.

\[ c_{\text{Bragg}}(\lambda_{\text{Bd}}) \times 2.35\sigma = \left( \frac{S}{\sqrt{2\pi\sigma^2}} \right) \times 2.35\sigma = 2.35S / \sqrt{2\pi} \]  

(11)

\( \frac{c_{\text{Bragg}}(\lambda_{\text{Bd}})}{\sqrt{2\pi}} \) (constant).

**Figure 3.** (a) The neutron transmission spectrum of Grain 3. (b) The negative value of the natural logarithm of transmission. (c) The procedure of the profile fitting and the Bragg-dip profile information obtained by the profile fitting.

Next, the analysis method of the integrated intensity, which is related to the crystal thickness, is explained. The value which is proportional to the integrated intensity of Bragg-dip is calculated by multiplying the FWHM and the height of Bragg-dip. The reason why the product of the FWHM and the height of Bragg-dip can be treated as the integrated intensity of Bragg-dip is described as follows. The integrated intensity of Bragg-dip is proportional to the crystal thickness. Hence, the integrated intensity should not change depending on the width and the height of Bragg-dip. On the other hand, the probability density function (Equation (9)), which follows a Gaussian distribution, has a negative correlation between the width and the height. In other words, under the condition that the integrated intensity is constant, the height decreases when the width increases, and the height increases when the width decreases. The constant value which is proportional to the integrated intensity is calculated by multiplying the height and the width of the probability density function (Equation (9)) as the following equation:

\[ c_{\text{Bragg}}(\lambda_{\text{Bd}}) \times 2.35\sigma = \left( \frac{S}{\sqrt{2\pi\sigma^2}} \right) \times 2.35\sigma = 2.35S / \sqrt{2\pi} \]  

(11)

It turns out that the product of the height and the width is constant. Here, \( S \), the scale factor of the height, is settled on one value under the same instrumental condition and the same crystal condition. Because the total integration of the probability density function which follows a Gaussian distribution is also constant, the value which is calculated by multiplying the height and the width of Bragg-dip can be considered as the integrated intensity of Bragg-dip.
3.3. Principle of Extinction Effects

In this section, the principle of extinction effect is described. The extinction effect should be considered when the integrated intensity information of Bragg-dip is evaluated. The extinction effect is the effect when the diffracted neutrons are diffracted again in the same crystallite or other crystallites. As a result, the intensity of diffracted neutrons decreases and the neutron transmission increases. In other words, because of the extinction effect, the coherent elastic scattering cross-section decreases; the microscopic cross-section does not really change, but the observed macroscopic cross-section is reduced due to the multiple diffraction. Here, the crystallite means the perfect crystal block or the mosaic block. The crystalline grain consists of plural crystallites or mosaic blocks. There are two kinds of extinction effects. One is the primary extinction effect, and it is the effect when the diffracted neutrons are diffracted again in the same crystallite. The other is the secondary extinction effect, and it is the effect when the diffracted neutrons are diffracted again in other crystallites. The occurrence probability of the primary extinction effect depends on the crystallite size. In contrast, the occurrence probability of the secondary extinction effect depends on the crystalline grain size. In polycrystals, only the primary extinction effect should be considered. However, in single crystals, not only the dominant primary extinction effect but also the secondary extinction effect should be considered [23]. Here, there are some considerable issues concerning the secondary extinction effect. Firstly, both extinction effects cannot be separately evaluated currently. In addition, if we use a high-spatial resolution detector, neutrons re-diffracted at the different crystallite may be detected by the different neighboring pixel from a pixel positioned along the direction of incident neutrons. Such a considerable phenomenon has not been investigated yet at all. Therefore, the secondary extinction effect cannot be quantitatively evaluated in the present study.

In any case, the integrated intensity should be constant in a crystalline grain ideally. However, in actuality, it changes due to the extinction effects. In this study, by considering the extinction effect, the existence of a new mosaic block reflecting crystal defects was observed finally.

4. Imaging of Bragg-Dip Profiles and Evaluation of Detailed Inner-Grain Information

4.1. Measured Neutron Transmission Spectra of Three Evaluated Grains

Figure 4 shows the results of neutron transmission imaging at each wavelength measured in the experiment and the neutron transmission spectra of three crystalline grains, Grains 1, 2 and 3, evaluated in this study. Figure 4a,c,e are neutron transmission images of Grains 1, 2 and 3 at the wavelength where (110) Bragg-dip appears. The darker regions in the images indicate that the neutron transmission intensity is lower, and it means that (110) Bragg-dip appears at the wavelength. The grain shapes can be observed in the neutron transmission images. In the neutron transmission images and IPF maps presented in the previous study [19], each grain is observed as a single crystal. In this study, for the investigation of inner defects in each grain, the single Bragg-dip profile-fitting analysis method was applied to Bragg-dips in the neutron transmission spectra of Grains 1, 2 and 3. For each grain, two Bragg-dips, indicated in Figure 4b,d,f, which are respectively caused by (110) plane and (101) plane, were analyzed. By the analysis, the Bragg-dip wavelengths, the widths of Bragg-dips and the integrated intensities of Bragg-dips were mapped at each pixel.
4.2. Imaging of Appearance Wavelength of Bragg-Dip and Evaluation of Small Change in Crystal Orientation in a Grain

Figure 5 shows the results of imaging the wavelengths where Bragg-dips of Grains 1, 2, and 3 appear. For each grain, two Bragg-dip wavelengths, $\lambda_{hkl}$, were mapped in real space. Each Bragg-dip is caused by (110) plane and (101) plane. Here, imaging of the Bragg-dip wavelength of Grain 3 (Figure 5e,f) is discussed as an example. In Grain 3, (110) Bragg-dip appears at a relatively longer wavelength, whereas (101) Bragg-dip appears at a relatively shorter wavelength (e.g., Region (1)). In addition, (110) Bragg-dip appears at a relatively shorter wavelength, whereas (101) Bragg-dip appears at a relatively longer wavelength (e.g., Region (2)). These relations mean that the interval between the two Bragg-dips changes. This tendency was also observed in the other grains. Such a change in the interval between two Bragg-dips represents the change in the crystal orientation [13]. Here, it is considerable that the macro-strain and the residual-strain can also change the interval of the two Bragg-dips. However, the changes in the wavelengths of (110) and (101) Bragg-dips of Grains 1, 2 and 3 are about 0.1–0.6%, and these values are too large to be the changes in the wavelengths caused by the elastic-strain, such as the macro-strain and the
residual-strain. Therefore, in the present case, the change in the interval between the two Bragg-dips is considered as representing the change in the crystal orientation.

Figure 5. (a) Imaging of (101) Bragg-dip wavelength of Grain 1. (b) Imaging of (110) Bragg-dip wavelength of Grain 1. (c) Imaging of (101) Bragg-dip wavelength of Grain 2. (d) Imaging of (110) Bragg-dip wavelength of Grain 2. (e) Imaging of (101) Bragg-dip wavelength of Grain 3. (f) Imaging of (110) Bragg-dip wavelength of Grain 3.

Figure 6 shows imaging of the interval between the two Bragg-dips, \( \lambda_{110} - \lambda_{101} \), of Grains 1, 2 and 3, and the neutron transmission spectra of the regions where the Bragg-dip interval is wide or narrow (Regions (1)–(6)). Incidentally, in Figure 6d, a Bragg-dip appears at the wavelength of 0.39 nm on the neutron transmission spectrum at Region (5). It is the (110) Bragg-dip of Grain 3. This is because Grain 2 and Grain 3 are stacked along the neutron transmission direction in this region (see Figure 1, Region (α)). As shown in Figure 6a,c,e, the interval of Bragg-dips certainly changes in the same grain. Nevertheless, as shown in Figure 6b,d,f, the changes in the interval of Bragg-dips are slight. Hence, such small changes in the crystal orientation were not observed in the Bragg-dip neutron IPF map presented in the previous study [19]. Here, the difference in the crystal orientation between Regions (1) and (2), where the difference in the interval of Bragg-dips is relatively
large, was calculated as an example. The crystal orientation at each region was evaluated with the database of Bragg-dip wavelength pattern used in the previous study [19]. As a result, the angular difference between Regions (1) and (2) was evaluated as 0.4°. Thus, such a small change in the crystal orientation in each crystalline grain, which had not been observed by the previous method, could be newly observed by the single Bragg-dip profile-fitting analysis method.

Figure 6. (a) Imaging of the interval between (110) Bragg-dip wavelength and (101) Bragg-dip wavelength of Grain 1. (b) Neutron transmission spectra of Regions (3) and (4). (c) Imaging of the interval between (110) Bragg-dip wavelength and (101) Bragg-dip wavelength of Grain 2. (d) Neutron transmission spectra of Regions (5) and (6). (e) Imaging of the interval between (110) Bragg-dip wavelength and (101) Bragg-dip wavelength of Grain 3. (f) Neutron transmission spectra of Regions (1) and (2).

4.3. Imaging of Width (FWHM) of Bragg-Dip and Identification of Grains with Small Orientation Differences

The changes in the crystal defect, such as the micro-strain and the mosaic spread angle, can be observed by analyzing the width of Bragg-dip. However, in this study, the crystal defect was observed as a mosaic block and another crystalline grain whose crystal orientation was slightly different.
Figure 7a,b shows the results of imaging the width (FWHM) of (101) Bragg-dip and (110) Bragg-dip of Grain 3. We found that the FWHM of each Bragg-dip was broader at Region (7), indicated by white circles in Figure 7a,b. In particular, (101) Bragg-dip width drastically changed in Region (7). Figure 7c–e show the comparison of three neutron transmission spectra of Mini Regions A, B in Region (7) and entire Grain 3. Mini Regions A and B consist of $3 \times 3$ pixels of the detector. We found that the Bragg-dip widths/profiles evaluated at Mini Regions A and B in Region (7) were different. It is discussed in the following sections.

**Figure 7.** (a) Imaging of FWHM of (101) Bragg-dip in Grain 3. (b) Imaging of FWHM of (110) Bragg-dip in Grain 3. (c) Comparison of neutron transmission spectra at Mini Regions A, B and entire Grain 3. (d) Comparison of (101) Bragg-dip profiles at Mini Regions A, B and entire Grain 3. (e) Comparison of (110) Bragg-dip profiles at Mini Regions A, B and entire Grain 3.

4.3.1. Mosaic Block Detection through the Observation of Bragg-Dip Broadening

Firstly, the widths of Bragg-dip at entire Grain 3 and Mini Region A were compared. The FWHM of each Bragg-dip, shown in Figure 7d,e was evaluated. The FWHM of (101)
Bragg-dip at entire Grain 3 was 0.0021 nm. The FWHM of (101) Bragg-dip at Mini Region A was broader, 0.0033 nm. On the other hand, the FWHM of (110) Bragg-dip at entire Grain 3 was 0.0017 nm. The FWHM of (110) Bragg-dip at Mini Region A was also 0.0017 nm. The Bragg-dip pattern at entire Grain 3 corresponded to that of Mini Region A. However, at Mini Region A, the width of only (101) Bragg-dip was broad. In contrast, the width of (110) Bragg-dip did not change.

This suggests the possibility of the existence of another mosaic block with slightly different crystal orientation. This is because around the crystal orientation of [100 74 26], which is the crystal orientation of entire Grain 3, (110) Bragg-dip wavelength did not change so much depending on the change in the crystal orientation, according to the database presented in the previous study [19]. At entire Grain 3, which has the crystal orientation of [100 74 26], (101) and (110) Bragg-dips appeared at the wavelength of 0.2842 and 0.3925 nm, respectively. On the other hand, in the case of the crystal orientation of [100 74 27], (101) and (110) Bragg-dips appeared at the wavelength of 0.2860 and 0.3918 nm. The difference between the (101) Bragg-dip wavelengths was 0.0018 nm, and the difference between (110) Bragg-dip wavelengths was 0.0007 nm. Thus, the difference in (110) Bragg-dip wavelengths was smaller than that of (101) Bragg-dip wavelengths. Therefore, at Mini Region A, it is considered that the change in the width of (110) Bragg-dip was not observed, and the change in the width of (101) Bragg-dip was observed. This can be caused by another mosaic block with slightly different crystal orientation.

4.3.2. Different Crystalline Grain Detection through the Observation of Bragg-Dip Split

Next, the widths of Bragg-dip at entire Grain 3 and Mini Region B were compared. At entire Grain 3, (101) Bragg-dip appeared at the wavelength of 0.284 nm on the neutron transmission spectrum. However, at Mini Region B, two Bragg-dips appeared around the wavelength of 0.284 nm, as shown by Figure 7d. Thus, the Bragg-dip appearance pattern changed at Mini Region B. The wavelengths of these two Bragg-dips were 0.2828 and 0.2869 nm. The FWHM of each Bragg-dip were 0.0011 and 0.0013 nm. These values were smaller than that of entire Grain 3, 0.0021 nm. On the other hand, the FWHM of (110) Bragg-dip at Mini Region B was 0.0024 nm. This value was larger than that of entire Grain 3, 0.0017 nm (see Figure 7e). The separation of (101) Bragg-dip and broadening of (110) Bragg-dip are considered to be caused by another crystalline grain at Mini Region B. The reason is explained as follows. The separation of (101) Bragg-dip at Mini Region B is considered to represent the existence of two crystalline grains which have different crystal orientations. On the other hand, (110) Bragg-dip does not separate because the difference in (110) Bragg-dip wavelengths between two crystalline grains is not large. Hence, it is considered that two (110) Bragg-dips are overlapping, and they are observed as a broad (110) Bragg-dip. Here, we considered a possibility that the Bragg-dip pattern at Mini Region B, which had three Bragg-dips at the wavelengths of 0.2828, 0.2869 and 0.3931 nm, may be caused by one crystalline grain. However, such a crystal orientation does not exist according to the database presented in the previous study [19]. Therefore, it was a more reliable conclusion that these three Bragg-dips were caused by two crystalline grains.

The crystal orientations along the neutron transmission path of these crystalline grains were evaluated as [100 74 26] and [100 75 28] by using the database [19]. The (101) Bragg-dip at shorter wavelength was caused by the crystalline grain of [100 74 26], and the (101) Bragg-dip at longer wavelength was caused by that of [100 75 28]. The angular difference between these crystal orientations was about 0.9°. Based on the above considerations, two crystalline grains, which are overlapping along the neutron transmission path, could be observed at Mini Region B. In the region where the angular difference is smaller compared with Mini Region B (e.g., Mini Region A), the Bragg-dips were just broad but not split, and such a region existed near Mini Region B. Therefore, at these regions, the crystal turned out to be imperfect. Mosaic blocks existed at Mini Region A as discussed in the former paragraph, and different crystalline grain existed at Mini Region B.
4.4. Imaging of Integrated Intensity of Bragg-Dip

4.4.1. Crystal Thickness Evaluation from the Integrated Intensity of Bragg-Dip

In this section, the information of the crystal thickness, obtained by analyzing the integrated intensity of Bragg-dip, is discussed. Figure 8a,b show the results of imaging ($\sigma_{\text{Bragg}}(\lambda_{hkl}) \times 2.35\sigma$) of Grain 3. Figure 8c,d show the neutron transmission spectra at entire Grain 3, Region (8) around Region (a) and Mini Region A. Here, the integrated intensity of Bragg-dip is $\sigma_{\text{Bragg}}(\lambda_{hkl}) \times 2.35\sigma$, the product of the height and the FWHM of Bragg-dip.

Figure 8. (a) Imaging of the integrated intensity of (101) Bragg-dip in Grain 3. (b) Imaging of the integrated intensity of (110) Bragg-dip of Grain 3. (c) Comparison of the neutron transmission spectra at entire Grain 3 and Region (8). (d) Comparison of the neutron transmission spectra at entire Grain 3 and Mini Region A.
At Region (8), the integrated intensities of both (101) and (110) Bragg-dip were small. Region (8) is the region where Grains 2 and 3 were found to be overlapping in the IPF map presented in the previous study [19]. In actuality, on the neutron transmission spectrum at Region (8) shown by Figure 8c, Bragg-dips of both Grains 2 and 3 appeared. Here, we note that the sample thickness was constant, 5 mm. Hence, overlapping of Grains 2 and 3 at Region (8) means that the thickness along the neutron transmission path of Grain 3 was smaller than 5 mm here. Therefore, the reduction in the integrated intensity of two Bragg-dips at Region (8) indicates that the thickness of Grain 3 became smaller. In other words, the reduction in the integrated intensities of Bragg-dips which are observed at Region (8) in Figure 8a,b indicate that Grain 3 became thinner. This means that the information of crystal thickness can be evaluated from the integrated intensity of Bragg-dip.

4.4.2. Extinction and Mosaicity Evaluation from the Integrated Intensity of Bragg-Dip

In this section, the mosaicity information in the crystalline grain, obtained by analyzing the integrated intensity of Bragg-dip, is explained. Figure 8a,b,d show that the integrated intensity of Bragg-dip was larger at Mini Region A. The increase in the integrated intensity of Bragg-dip indicates the increase in the crystal thickness or the reduction in the extinction effect. However, in this case, the sample thickness was constant at 5 mm. Hence, we deduced that the increase in the integrated intensity of Bragg-dip at Mini Region A meant the reduction in the extinction effect. The reduction in the extinction effect indicates that the crystallite size was smaller. Because the neutron transmission path length in the sample was constant at 5 mm, the small crystallite size means that multiple crystallites (mosaic blocks) exist along the neutron transmission path. This is consistent with the consideration of the existence of another mosaic block at Mini Region A, described in Section 4.3.1. In other words, imaging of the integrated intensity of Bragg-dip also indicates the existence of another mosaic block at Mini Region A, as well as imaging the width of Bragg-dip.

5. Conclusions

In this study, the single Bragg-dip profile-fitting analysis method was developed. This method can evaluate and visualize detailed crystalline information of single crystals and oligocrystals. This method was applied to experimental data of position-dependent Bragg-dip neutron transmission spectra measured from an oligocrystal material to confirm the effectiveness. In the analysis, the Gaussian function was fitted to an individual Bragg-dip profile on the neutron transmission spectrum. By using this method, the wavelength where Bragg-dip appears, the width of Bragg-dip and the integrated intensity of Bragg-dip were deduced at each pixel of the neutron TOF-imaging detector.

From the results of imaging of the Bragg-dip wavelengths, the slight changes in the pattern of Bragg-dip wavelengths and the slight change in the crystal orientation in the crystalline grain, about 0.4°, could be observed. From the results of imaging the broadening of Bragg-dip, a mosaic block could be observed in the crystalline grain. Moreover, another crystalline grain, whose crystal orientation was different by about 0.9°, could be observed in this crystalline grain through the observation of the Bragg-dip split. In the results of imaging of the integrated intensity of Bragg-dip, the integrated intensity became larger at the region where the aforementioned mosaic block existed. This is because the extinction effect reduced. This was caused by the decrease in the crystallite size. This means some mosaic blocks exist along the neutron transmission path. Thus, imaging of the integrated intensity of Bragg-dip also shows the existence of the mosaic block as well as imaging of the width of Bragg-dip. Furthermore, the change in the crystal thickness could also be visualized. Thus, the fluctuation of the crystal orientation and the existence of mosaic blocks in a crystalline grain could be observed in the real-space image. This crystalline information could not be observed in the previous method.

As explained above, this method can visualize detailed crystalline information which has not been visualized by previous analysis methods. The significant feature of the proposed method is the simplicity of the data analysis. By combining this method with the
full pattern-fitting analysis [18] and the wavelength pattern analysis [19], more detailed crystalline information evaluation of single crystals and oligocrystals will be realized in the imaging mode.

**Author Contributions:** Conceptualization, H.S., N.A., S.M., Y.T. and T.K.; methodology, Y.S., H.S., S.M. and T.K.; software, Y.S. and H.S.; validation, Y.S., H.S., N.A., S.M., Y.T. and T.K.; formal analysis, Y.S. and H.S.; investigation, Y.S., H.S., N.A., S.M., Y.T. and T.K.; resources, H.S., S.M., Y.T. and T.K.; data curation, Y.S. and H.S.; writing—original draft preparation, Y.S.; writing—review and editing, H.S., N.A., S.M., Y.T. and T.K.; visualization, Y.S. and H.S.; supervision, H.S., N.A., S.M., Y.T. and T.K.; project administration, H.S., Y.T. and T.K.; funding acquisition, H.S., S.M., Y.T. and T.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by JSPS KAKENHI Grant Number 16K20876.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Acknowledgments:** The authors would like to thank Y. Shiota (Metal Technology Co., Ltd.), K. Oikawa (J-PARC), M. Harada (J-PARC), Y. H. Su (J-PARC) and S. Y. Zhang (CROSS) for experimental assistance at J-PARC MLF BL10 NOBORU. The neutron experiment at J-PARC MLF BL10 NOBORU was performed under a user program (proposal No. 2014P0601). This work was partially supported by the ISIJ research group “steel microstructure analysis using compact neutron sources”.

**Conflicts of Interest:** The author declares no conflict of interest.

**References**

1. Humphreys, F.J. Characterisation of fine-scale microstructures by electron backscatter diffraction (EBSD). *Scr. Mater.* **2004**, *51*, 771–776. [CrossRef]

2. Groeber, M.A.; Haley, B.K.; Uchic, M.D.; Dimiduk, D.M.; Ghosh, S. 3D reconstruction and characterization of polycrystalline microstructures using a FIB–SEM system. *Mater. Charact.* **2006**, *57*, 259–273. [CrossRef]

3. Delhez, R.; de Keijser, T.H.; Mittemeijer, E.J. Determination of crystallite size and lattice distortions through X-ray diffraction line profile analysis. *Fresenius Z. Anal. Chem.* **1982**, *312*, 1–16. [CrossRef]

4. Vanasupa, L.; Joo, Y.C.; Besser, P.R.; Pramanick, S. Texture analysis of damascene-fabricated Cu lines by x-ray diffraction and electron backscatter diffraction and its impact on electromigration performance. *J. Appl. Phys.* **1999**, *85*, 2583. [CrossRef]

5. Ludwig, W.; Schmidt, S.; Lauridsen, E.M.; Poulsen, H.F. X-ray diffraction contrast tomography: A novel technique for three-dimensional grain mapping of polycrystals. I. Direct beam case. *J. Appl. Crystallogr.* **2008**, *41*, 302–309. [CrossRef]

6. Johnson, G.; King, A.; Honnicke, M.G.; Marrow, J.; Ludwig, W. X-ray diffraction contrast tomography: A novel technique for three-dimensional grain mapping of polycrystals. II. The combined case. *J. Appl. Crystallogr.* **2008**, *41*, 310–318. [CrossRef]

7. Wenk, H.-R.; Lutterotti, L.; Vogel, S. Texture analysis with the new HIPPO TOF diffractometer. *Nucl. Instrum. Methods Phys. Res. Sect. A* **2003**, *515*, 575–588. [CrossRef]

8. Santisteban, J.R.; Daymond, M.R.; James, J.A.; Edwards, L. ENGIN-X a third-generation neutron strain scanner. *J. Appl. Crystallogr.* **2006**, *39*, 812–825. [CrossRef]

9. Gutmann, M.J.; Kockelmann, W.; Chapon, L.C.; Radaelli, P.G. Phase imaging using time-of-flight neutron diffraction. *J. Appl. Crystallogr.* **2006**, *39*, 82–89. [CrossRef]

10. Peetemans, S.; King, A.; Ludwig, W.; Reischig, P.; Lehmann, H. Cold neutron diffraction contrast tomography of polycrystalline material. *Analyst* **2014**, *139*, 5765–5771. [CrossRef]

11. Cereser, A.; Strobl, M.; Hall, S.A.; Steuwer, A.; Kiyanagi, R.; Tremssin, A.S.; Knudsen, E.B.; Shinozara, T.; Willendrup, P.K.; da Silva Fanta, A.B.; et al. Time-of-Flight Three Dimensional Neutron Diffraction in Transmission Mode for Mapping Crystal Grain Structures. *Sci. Rep.* **2017**, *7*, 9561. [CrossRef]

12. Samothrakis, S.; Ravenstós, M.; Čapek, J.; Larsen, C.B.; Grünzweig, C.; Tovar, M.; García-Gonzalez, M.; Kopeček, J.; Schmidt, S.; Strobl, M. Grain morphology reconstruction of crystalline materials from Laue three-dimensional neutron diffraction tomography. *Sci. Rep.* **2020**, *10*, 3724. [CrossRef]

13. Sato, H. Deriving Quantitative Crystallographic Information from the Wavelength-Resolved Neutron Transmission Analysis Performed in Imaging Mode. *J. Imaging* **2018**, *4*, 7. [CrossRef]

14. Santisteban, J.R.; Edwards, L.; Fitzpatrick, M.E.; Steuwer, A.; Withers, P.J.; Daymond, M.R.; Johnson, M.W.; Rhodes, N.; Schooneveld, E.M. Strain imaging by Bragg edge neutron transmission. *Nucl. Instrum. Methods Phys. Res. Sect. A* **2002**, *481*, 765–768. [CrossRef]
15. Sato, H.; Kamiyama, T.; Kiyanagi, Y. A Rietveld-Type Analysis Code for Pulsed Neutron Bragg-Edge Transmission Imaging and Quantitative Evaluation of Texture and Microstructure of a Welded $\alpha$-Iron Plate. *Mater. Trans.* **2011**, *52*, 1294–1302. [CrossRef]

16. Woracek, R.; Penumadu, D.; Kardjilov, N.; Hilger, A.; Boin, M.; Banhart, J.; Manke, I. 3D Mapping of Crystallographic Phase Distribution using Energy-Selective Neutron Tomography. *Adv. Mater.* **2014**, *26*, 4069–4073. [CrossRef]

17. Sato, H.; Iwase, K.; Kamiyama, T.; Kiyanagi, Y. Simultaneous Broadening Analysis of Multiple Bragg Edges Observed by Wavelength-resolved Neutron Transmission Imaging of Deformed Low-carbon Ferritic Steel. *ISIJ Int.* **2020**, *60*, 1254–1263. [CrossRef]

18. Malamud, F.; Santisteban, J.R. Full-pattern analysis of time-of-flight neutron transmission of mosaic crystals. *J. Appl. Crystallogr.* **2016**, *49*, 348–365. [CrossRef]

19. Sato, H.; Shiota, Y.; Morooka, S.; Todaka, Y.; Adachi, N.; Sadamatsu, S.; Oikawa, K.; Harada, M.; Zhang, S.; Su, Y.; et al. Inverse pole figure mapping of bulk crystalline grains in a polycrystalline steel plate by pulsed neutron Bragg-dip transmission imaging. *J. Appl. Crystallogr.* **2017**, *50*, 1601–1610. [CrossRef]

20. Strickland, J.; Tassenberg, K.; Sheppard, G.; Nenchev, B.; Perry, S.; Li, J.; Dong, H.; Burca, G.; Kelleher, J.; Irwin, S. 2D single crystal Bragg-dip mapping by time-of-flight energy-resolved neutron imaging on IMAT@ISIS. *Sci. Rep.* **2020**, *10*, 20751. [CrossRef]

21. Oikawa, K.; Maekawa, F.; Harada, M.; Kai, T.; Meigo, S.; Kasugai, Y.; Ooi, M.; Sakai, K.; Teshigawara, M.; Hasegawa, S.; et al. Design and application of NOBORU—NeutrOn Beam line for Observation and Research Use at J-PARC. *Nucl. Instrum. Methods Phys. Res. Sect. A* **2008**, *589*, 310–317. [CrossRef]

22. Uno, S.; Uchida, T.; Sekimoto, M.; Murakami, T.; Miyama, K.; Shoji, M.; Nakano, E.; Koike, T.; Morita, K.; Satoh, H.; et al. Two-dimensional Neutron Detector with GEM and its Applications. *Phys. Procedia* **2012**, *26*, 142–152. [CrossRef]

23. Sabine, T.M. Extinction in Polycrystalline Materials. *Aust. J. Phys.* **1985**, *38*, 507–518. [CrossRef]