Simultaneous Characterisation of Precipitates and Matrix in a Steel Using Small-Angle Neutron Scattering and Bragg-Edge Transmission Analysis

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A new technique for the quantitative characterisation of the microstructure in steels has been developed. Using a small-angle neutron scattering (SANS) instrument at a pulsed neutron source, both a SANS profile and a Bragg-edge transmission spectrum could be simultaneously measured. The SANS analysis provides structural information about the precipitates in steels, while the Bragg-edge transmission analysis reveals the crystal structure of the steel matrix. As a demonstration, Fe–C–Cu–V alloys were measured and analysed. The SANS profiles showed that nanosized precipitates were grown when the alloys were aged at 823 K. The Bragg-edge of the corresponding transmission spectra clearly revealed that the ferritic matrix was kept with the aging time. The experimental results confirmed that this new technique provides a new possibility of efficient characterisation of the steel microstructures.

KEY WORDS: small-angle scattering; SANS; precipitate; Bragg-edge transmission; crystallite.

1. Introduction

The mechanical properties of steels strongly depend on their microstructures. The precise characterisation and control of the microstructures have become increasingly important especially for advanced steels. Neutron scattering techniques such as neutron diffraction (ND) and small-angle neutron scattering (SANS) are useful to precisely characterise the microstructure of the steels. Both the ND and the SANS can measure large sample volumes because of the high penetration power of neutron, enabling a quantitative evaluation of the microstructure. ND is frequently used to determine the crystal structures, strains, and textures of the steel matrices, while SANS is typically adopted to analyse precipitates and inclusions in steels.1–5) Such microstructural information obtained with ND and SANS is closely related to the mechanical properties through dislocation motion, e.g., grain refinement strengthening and precipitation strengthening.

In order to elucidate the origin of the mechanical properties, it is desirable that both crystallographic and microstructural morphologies can be characterised with the same sample at the same time. However, until now, the microstructural information on the matrix and precipitates have been separately measured because an experimental setup for ND is different from that for SANS.

In relation to this issue, the recent progress of the Bragg-edge transmission analysis method is noteworthy.6–8) The Bragg-edge is the decrement of neutron transmission caused by the Bragg diffraction, and reflects the crystallographic information including crystal structure, strain, crystallite size, and texture. When the transmission of the crystalline materials is measured, the Bragg-edges are observed as a sawtooth pattern. At present, the Bragg-edge transmission analysis is mainly used in neutron imaging as a mapping tool of structural distributions. However, it is essentially a technique to analyse a neutron transmission spectrum, and can be applied not only to neutron imaging, but also to all the neutron-based experimental techniques measuring the transmission spectra.

Here, we focus on SANS measurements using pulsed neutrons (pulsed SANS). Generally, in SANS measurements, the neutron transmission of the sample is measured to correct the scattering intensity and subtract the background scattering. In the case of pulsed SANS, the scattering and transmission are measured using the time-of-flight (TOF) method.9) Thus, the pulsed SANS can measure the wavelength dependence of scattering and transmission including the Bragg-edge at the same time. If the Bragg-edge transmission analysis technique is applied to the data of the pulsed SANS, structural information about the steel matrix can be obtained along with the information on precipitates and inclusions provided by the SANS data. In this study, the results of this simultaneous analysis technique are presented for the first time.
To demonstrate this technique, Fe–C–Cu–V alloys (Cu–VC steel) were measured; they are regarded as model steels with precipitates. As Cu is contained in most of the recycled steels, the effective use of Cu is crucial to achieve a sustainable development in modern society. According to Senuma et al., the precipitation of VC prior to that of Cu increases the nucleation sites for Cu and decreases the size of the Cu particles by Cu and V multiple additions. This mechanism is useful for the advanced steels, as it can enhance the precipitation strengthening.

2. Experimental Procedure

The chemical composition of the Fe–C–Cu–V alloy was Fe–0.04 C–1.0 Cu–0.5 Ni–0.20 V (mass%). The samples were first casted as a 160-mm-long 120-mm-wide 140-mm-thick ingot. The ingot was then heated at 1 273 K, followed by hot rolling to a thickness of 16 mm at the finishing temperature of 1 153 K. The hot-rolled plate was directly quenched from 1 093 K to room temperature, and cut into several slabs. To form the precipitates, the slabs were aged at 823 K for 14.4, 28.8, and 43.2 ks.

The microstructures were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 1 shows the typical SEM and TEM images of the sample aged at 823 K for 43.2 ks. The matrices of the samples consist mainly of ferrite and partially pearlite. The ferrite grain size $L$ estimated from the SEM image is 29.4 μm. The TEM image confirms the formation of the spherical precipitates with an average equivalent circle diameter of 5.2 nm.

For comparison, a piece of slab was not aged. The samples for the SANS measurements were cut from the aged slabs; their dimensions were about 15 mm in width, 15 mm in height, and 2 mm in thickness. At this thickness, the transmission of typical steel is about 80% at a wavelength of 0.6 nm, which is sufficient for the SANS measurements. To normalise the data of the neutron experiments, the thickness of the samples was accurately measured by a micrometre.

The simultaneous measurements of the SANS and Bragg-edge were performed with the SANS instrument TAIKAN installed at the Japan Proton Accelerator Research Complex (J-PARC). The incident neutron beam entered in a direction normal to the rolling plane. The SANS patterns were measured using a small-angle detector bank consisting of $^3$He linear-position-sensitive detectors. The transmission spectra were recorded using the transmission nitrogen neutron monitor. The wavelength $\lambda$ between 0.20 and 0.76 nm was used with a time-of-flight method. Ferritic and martensitic steels generally have large magnetic moments and show significant magnetic scatterings. To separate the magnetic scattering from the nuclear scattering contribution, a magnetic field of 1 T, which is enough to align the magnetic moments in the samples, was applied using an electromagnet. In the present study, only the nuclear scattering contributions were analysed. For the Bragg-edge transmission analysis, a value of $\lambda$ between 0.2 and 0.7 nm was used. To avoid the contamination of the SANS scattering intensity with Bragg diffraction, SANS patterns with $\lambda$ longer than 0.42 nm were used. Since the Bragg cut-offs of the typical steel matrices are 0.40 nm for ferrite and 0.41 nm for austenite, longer wavelengths do not generate Bragg diffraction. Under this condition, the $q$ range of SANS was between 0.1 and 3 nm$^{-1}$. Here, $q$ is a momentum transfer and is equal to $(4\pi\lambda)\sin\theta$, where $\theta$ is half the scattering angle. The obtained SANS intensities were normalised by the sample thickness and converted into absolute units using the scattering of the glassy carbon standard characterised at the Argonne National Laboratory.

3. Results and Discussion

As shown in Fig. 2(a), all the SANS profiles of the aged samples exhibit a shoulder below $q \approx 1$ nm$^{-1}$; the shoulder is conversely absent in the profile of the as-quenched sample. This result indicates that nanosized particles are formed in the samples subjected to aging. The SANS profile of the as-quenched sample is generated by the scattering of structural features larger than the precipitates, such as surface roughness, or cementite. Only the scattering due to the nanosized precipitates was extracted by subtracting the SANS profile of the as-quenched sample from those of the aged samples (Fig. 2(b)). In all the profiles, a plateau is observed for $q < 0.5$ nm$^{-1}$. The plateau, which is the so-called Guinier region and reflects the size of the scatterer, shifts to lower $q$ with the increase of the aging time, suggesting that the precipitates become larger with the aging time.

From the SANS profiles, the size distribution of the precipitates was analysed using a curve fit. The scattering of the precipitates dispersed in the steel matrix is given by

$$I(q) = d_\nu \Delta \rho^2 \int_0^\infty V^2 F^2(q,r)N(r)dr,$$

where $d_\nu$ and $\Delta \rho$ are the number density of the precipitates

![Fig. 1. (a) Scanning electron microscopy and (b) transmission electron microscopy images of Fe–C–Cu–V alloy aged at 823 K for 43.2 ks.](image)
and scattering contrast, respectively; $r$ and $V$ are the radius and the volume of the particles, respectively; $F(q,r)$ is the form factor, which reflects the particle shape and size. Based on the TEM result, the precipitates are assumed as having a spherical shape. The form factor of the spherical particles is described as

$$F(q, r) = \frac{3\sin(qr) - qr\cos(qr)}{(qr)^3}.$$  

The function $N(r)$ indicates the size distribution. A form-free distribution function that is not restricted to an existing function such as a Gaussian function and that can take any non-negative value was used as $N(r)$. The values of $N(r)$ were treated as the fit coefficients. The ranges and steps of the fit coefficients were determined with reference to a previous study.\(^{18}\)

The results of the fitting are shown in Fig. 2(b). The fit curves coincide with the experimental results. The bars in Fig. 3(a) shows the size distribution obtained with the form-free fitting. In the samples aged for 28.8 and 43.2 ks, the obtained size distributions are skewed towards the large particles, in agreement with the characteristics of a log-normal size distribution rather than with those of the

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**Fig. 2.** (a) Small-angle neutron scattering (SANS) profiles of Fe–C–Cu–V alloys. (b) SANS profiles of the aged samples after subtraction of that of the as-quenched sample. The solid, dotted, and gray curves show the results of the fitting for the Fe–C–Cu–V alloys aged for 43.2, 28.8, and 14.4 ks, respectively.

**Fig. 3.** (a) Size distributions of the precipitates obtained from the curve fitting. For visibility, the distribution of the samples aged for 14.4 and 28.8 ks are shifted to +100 and +40, respectively. The bars are obtained with the form-free size distribution analysis. The solid and broken curves are the results of the fitting using log-normal and Lifshitz-Slyozov-Wagner size distribution functions, respectively. (b) Aging time dependence of the volume-weighted average diameter of the precipitates.
size distribution predicted by the Lifshitz-Slyozov-Wagner (LSW) theory of Ostwald ripening.\(^{19}\) For comparison, the additional curve fittings of the SANS profiles using the log-normal function and the LSW function were carried out. The size distributions obtained with the log-normal function (solid lines) and the LSW function (broken lines) are also shown in Fig. 3(a). For the samples aged for 28.8 and 43.2 ks, the log-normal size distribution accurately describes the experimental results, while the LSW function overestimates the large precipitates. Meanwhile, in the sample aged for 14.4 ks, the log-normal size distribution differs considerably from the negatively skewed distribution obtained with the form-free fitting. This results show that the validity of the conventional analyses assuming a simple LSW or log-normal size distribution was carefully examined. Figure 3(b) shows the aging time dependence of the average diameter of the precipitates estimated from the form-free size distributions shown as the bars in Fig. 3(a). Notably, the precipitate diameters tend to increase with the aging time. The average diameter of the sample aged for 43.2 ks is consistent with the value obtained from the TEM results.

Next, the transmission spectra \(T_r(\lambda)\) of the same samples will be discussed. For comparison, \(T_r(\lambda)\) were converted into the attenuation coefficients \(\sigma(\lambda)\) and normalised by the sample thickness \(t\) based on the Beer-Lambert law described as:\(^{20}\)

\[
T_r(\lambda) = \exp[-\sigma(\lambda)t]. \quad \text{(3)}
\]

**Figure 4** shows \(\sigma(\lambda)\) for all the samples. Between \(\lambda = 0.40\) and 0.42 nm, a sharp change of \(\sigma(\lambda)\) is observed. This wavelength corresponds to the Bragg-edge of the \{110\} planes in ferrite, shown by a broken line in Fig. 4.\(^6,8\) Small edges are also observed at the \{200\} and \{211\} Bragg-edges. Therefore, we successfully observed the Bragg-edges using the pulsed SANS instrument. The gradual increase of \(\sigma(\lambda)\) for \(\lambda > 0.42\) nm is attributed to the form-free scattering and absorption. In contrast to the SEM observation, no cementite features were observed, probably because of the substantially small amount present. Furthermore, the Bragg-edges scarcely change with the aging, indicating that the ferrite crystallites retain almost the same morphology during the aging at 823 K.

The detailed analysis of the Bragg-edges using a curve fit was performed. According to a previous study, \(\sigma(\lambda)\) consists of elastic coherent scattering \(\sigma_e(\lambda)\), elastic incoherent scattering \(\sigma_i(\lambda)\), inelastic coherent scattering \(\sigma_{ic}(\lambda)\), inelastic incoherent scattering \(\sigma_{inc}(\lambda)\), and absorption \(\sigma_{abs}(\lambda)\).\(^{6,8}\)

\[
\sigma(\lambda) = \sigma_e(\lambda) + \sigma_i(\lambda) + \sigma_{ic}(\lambda) + \sigma_{inc}(\lambda) + \sigma_{abs}(\lambda). \quad \text{(4)}
\]

The term \(\sigma_e(\lambda)\) provides the sawtooth pattern of the Bragg-edges. For the ferrite, the other scattering terms contribute only marginally to the attenuation spectra between \(\lambda = 0.2\) and 0.4 nm.\(^8\) The absorption coefficient is proportional to \(\lambda\), andbecomes the main component for \(\lambda\) values higher than the \{110\} Bragg-edge. The term \(\sigma_i(\lambda)\) is described as,

\[
\sigma_i(\lambda) = \frac{\lambda^2}{2V_0} \sum_{hkl} |F_{hkl}|^2 P_{hh}(\lambda, d_{hh}) P_{kk}(\lambda, d_{kk}) E_{hh}(\lambda, d_{hh}),
\]

where \(V_0\), \(F_{hkl}\), and \(d_{hh}\) are the unit cell volume, a crystal structure factor, and the lattice spacing, respectively. The functions \(R_{hh}(\lambda, d_{hh})\), \(P_{hh}(\lambda, d_{hh})\), and \(E_{hh}(\lambda, d_{hh})\) are a resolution function, preferred orientation function, and primary extinction function of the lattice planes \(\{hkl\}\), respectively. This expression is basically identical to that used for the ND analysis. In this study, since the change in \(d_{hh}\) was not examined, \(R_{hh}(\lambda, d_{hh})\) has been ignored. The crystal structure was fixed as body-centered cubic, and the lattice spacing of bcc Fe was used to replace \(d_{hh}\). For \(P_{hh}(\lambda, d_{hh})\), the modified March-Dollase preferred orientation distribution function was adopted.\(^{6,21}\) This involves the texture information, and provides the March-Dollase coefficient \(R\), which indicates the degree of crystallographic anisotropy. The value \(R = 1\) indicates a random structure, while \(R = 0\) and \(R = \infty\) indicate a single crystal. When the texture becomes developed, \(R\) differs from 1. In the current experimental setting, the information on the rolling direction is not obtained because the transmission spectra do not reflect the azimuthal information in the sample plane. The texture in the rolling plane can be analysed from \(P_{hh}(\lambda, d_{hh})\). The function \(E_{hh}(\lambda, d_{hh})\) represents the extinction effect caused by the multiple Bragg diffraction, and is related to the crystallite size \(S\). The Sabine function was used as \(E_{hh}(\lambda, d_{hh})\).\(^{6,22,23}\) The terms \(\sigma_{ic}(\lambda)\), \(\sigma_i(\lambda)\), and \(\sigma_{inc}(\lambda)\) were calculated from the
chemical composition based on Granada’s expressions.\textsuperscript{6,24)} The absorption term was also calculated from the chemical composition.

Before analysing the curve fitting, the preferred orientation will be discussed. Figure 5 shows the simulated attenuation coefficients for the ferritic steels with the current chemical composition and the possible rolling planes as the preferred orientations. In ferrite, the \{100\}, \{110\}, \{211\}, \{311\}, and \{332\} planes are typically developed.\textsuperscript{25,26)} Among these rolling planes, only the \{110\} rolling plane is suited for the concave curve of the experimentally obtained \{110\} Bragg-edge.

Figure 4 shows the fitting results as solid curves. The curves are in good agreement with the \{110\}, \{200\}, and \{211\} Bragg-edges of the experimental results as well as the absorption at $\lambda > 0.42$ nm. The March-Dollase coefficient and crystallite size obtained are shown in Fig. 6. The parameters are almost constant with the aging, indicating that the texture and crystallite size are stable, and almost no recovery, recrystallisation, or grain growth occurs during the aging at 823 K.

A value of $R$ different from 1 indicates the presence of the texture. The formation of the \{110\} rolling plane is a characteristic of the recrystallisation texture in austenite. Therefore, the present samples probably undergo recrystallisation in the austenite phase during the hot rolling; subsequently, the inherited texture remains in the ferrite. The crystallite size $S$ estimated from the Bragg-edge is about 1/10 of the ferrite grain size $L$ obtained by SEM. The crystallite size reflects the size of a coherent scattering region in which the neutron holds enough coherence to generate diffraction. On the other hand, the present SEM analysis provides the size of the ferrite grain, which is limited by the grain boundaries and probably composed of subgrains and stacking faults. Therefore, the reason of the discrepancy between $S$ and $L$ can be explained by the subgrains structure which may exist in ferrite grains. This is consistent with the present results. From the comparison of $L$ and $S$, the number of crystallites in a ferrite grain is estimated to be $(L/S)^3 = 1.9 \times 10^3$.

According to the results of both the SANS and Bragg-edge analyses, the evolution of the microstructure with the aging can be summarised as follows. With the aging, the SANS profiles change, while the Bragg-edge spectra remain unaltered, suggesting that the precipitates coarsen, whereas the crystallites are stable during the aging at 823 K.
The new technique presented here and based on the use of SANS and Bragg-edge transmission analyses will provide a remarkably effective way to obtain in-situ observations of microstructures in steels. The high penetration power of the neutron allows the use of various sample environments such as furnaces and tensile testing machines. This means that the change of the microstructures in the steels can be characterised in real time, opening new frontiers in the research and development of steels.

4. Conclusion

In conclusion, the microstructures of low carbon ferritic steels were investigated using simultaneously the SANS and Bragg-edge transmission measurements. We successfully observed the SANS profile of the precipitates and the Bragg-edges of the ferrite crystallites at the same time using the pulsed SANS instrument. Furthermore, the curve fitting analyses of the SANS profiles and the Bragg-edge spectra were performed. The results show that the precipitates coarsened during the aging at 823 K, whereas the ferrite crystallite size and texture remained unaffected.

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