**In situ Neutron Diffraction Study on Ferrite and Pearlite Transformations for a 1.5Mn-1.5Si-0.2C Steel**

Yo TOMOTA,1)* Yan Xu WANG,1) Takahito OHMURA,1) Nobuaki SEKIDO,2) Stefanus HARJO,3) Takuro KAWASAKI,3) Wu GONG4) and Akira TANIYAMA5)

1) Research Center of Structure Materials, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047 Japan. 2) Research Center of Structure Materials, National Institute for Materials Science. Now at Graduate School of Engineering, Tohoku University, 6-6-02 Aoba-yama, Sendai, 980-8579 Japan. 3) J-PARC Center, Japan Atomic Energy Agency, 2-4, Shirakata, Tokai, Naka-gun, Ibaraki, 319-1195 Japan. 4) Elements Strategy Initiative for Structural Materials, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501 Japan. 5) Advanced Technology Research Laboratories, Nippon Steel & Sumitomo Metal Corporation, 1-8 Fuso-cho, Amagasaki, Hyogo, 660-0891 Japan.

(Received on May 10, 2018; accepted on July 18, 2018)

The phase transformation behavior from austenite upon cooling in a 1.5Mn-1.5Si-0.2C steel was in situ monitored using dilatometry, X-ray and neutron diffractions. The starting temperature of ferrite transformation was in good agreement between dilatometry and neutron diffraction, whereas much higher in X-ray diffraction. Such a discrepancy in transformation temperature is attributed to the change in chemical composition near the surface of a specimen heated to elevated temperatures in a helium gas atmosphere for X-ray diffraction. In situ neutron diffraction enables us to investigate the changes in lattice constants of ferrite and austenite, which are affected by not only thermal contraction but also transformation strains, thermal misfit strains and carbon enrichment in austenite. Pearlite transformation started after carbon enrichment in austenite reached approximately 0.7 mass% and contributed to diffraction line broadening.

KEY WORDS: phase transformation; austenite volume fraction; neutron diffraction; X-ray diffraction; dilatometry; in situ measurement.

1. Introduction

It is useful to observe microstructure evolution directly during heat treatment of steels. As usual in the past, a specimen was interruptedly cooled from an elevated temperature in order to freeze microstructure and then observations were carried out at room temperature. However, in case of a low alloy steel, austenite phase at a high temperature transforms to martensite during quenching. It is also difficult to trace the microstructure change continuously at an identical position of one sample. Therefore, in situ observations or measurements of microstructural change during heat treatment have been attempted by using various techniques. For example, in situ observations or measurements using confocal scanning laser microscopy,1) transmission electron microscopy (TEM),2) scanning electron microscopy (SEM)/electron back scatter diffraction (EBSD),3) X-ray diffraction,4) etc. have been employed to track microstructure evolution during heat treatment. But it should be noticed that the surface layer of a specimen is easily damaged at elevated temperatures even in vacuum or inert gas atmosphere: oxidation, decarburization, etc. hinder to obtain the information inside a sample.

"Phase transformation is generally affected by stress. In case of martensite transformation, compressive internal stresses have been measured in the untransformed (or retained) austenite in spite of expansive and shear transformation strains, the reason of which is not made clear.5) Nakada et al. have claimed the diffusional austenite reversion from lath martensite is influenced by residual internal stress distribution near lath boundaries.6) Pearlite transformation accompanies expansive transformation strain as well as misfit strains at semi-coherent ferrite-cementite interface. Such internal stress generation has been suspected to produce complicated pearlite microstructure.7) In case of ferrite transformation, transformation strain is expansive but carbon enrichment in the untransformed austenite must compensate resulting in internal stress relaxation. Hence, to monitor such internal (phase) stresses directly during transformation must be important to understand the transformation mechanism and then to control microstructure. Employing the neutron diffraction technique, it would be possible to determine phase stresses from lattice constants of the constituents.

In this study, dilatometry measurement, in situ X-ray diffraction and in situ neutron diffraction were employed to monitor ferrite and pearlite transformations from austenite upon continuous cooling for a low alloyed Mn–Si–C steel. Concerning this steel, the results of similar experiments on heating up to 950°C were already reported in the previous paper8) and thereby ferrite and pearlite transformation...
behavior upon cooling will be discussed in this paper.

2. Experimental Procedures

The details concerning the specimen preparation were reported elsewhere and hence a brief explanation is given. The chemical compositions of the steel prepared referring to Sugimoto et al. were 0.20C-1.50Mn-1.52Si-0.009P-0.001S in mass%. Prepared steel sheets with 1.2 mm in thickness, 120 mm in length and 100 mm in width were annealed at 780°C for 300 s followed by cooling with a rate of −50°C/s down to 400°C, held there for 300 s and then cooled with a rate of −50°C/s to RT. Microstructure was observed using SEM. The details on the microstructural features of this steel were found in another paper.

As a popular experimental method, dilatometry test was performed using a dilatometer (NETZSCH TD5000SA) for a specimen with 4 mm by 15 mm by 1 mm in an argon gas atmosphere. The specimen were heated with a heating speed of 0.05°C/s from RT up to 950°C, held there for 600 s, and then cooled with a speed of −0.05°C/s down to 400°C.

X-ray diffraction specimens with 10 mm × 9 mm × 1 mm were prepared and the plane perpendicular to the normal direction (ND) was polished with emery papers and finished by buffing with alumina powder (0.1 μm in diameter). High temperature X-ray diffraction measurement was performed in a helium gas atmosphere using a multi-purpose X-ray diffractometer made by Spectris Co., Ltd. The target and filter used were Co and Fe film, respectively, and the accelerating voltage and current were 40 kV and 35 mA, respectively. The irradiation area was approximately 2.5 mm by 5 mm. The measurements were carried out for data analysis.

For in situ neutron diffraction during heating and cooling, five pieces of steel sheet with 1.2 mm in thickness, 30 mm in length and 4–6 mm in width were stacked to be nearly cylindrical shape. Such bundled specimens were set in a conventional dilatometer which was installed into an engineering dilatometer system. The viewing area was approximately 2.5 mm by 5 mm. The measurements were carried out for data analysis.

The dilatometry curve obtained is depicted in Fig. 2. During heating up to 950°C and subsequent cooling, the change in specimen length with temperature is found to deviate from thermal expansion or contraction line, indicating the occurrence of phase transformations. Here, thermal expansion coefficients of ferrite (Kf) and austenite (K′) were determined to be 13.5×10⁻⁶/°C and 21.0×10⁻⁶/°C, respectively. Upon cooling from 950°C, the deviation from the thermal contraction line of austenite was found nearly at 838°C indicating the start of ferrite transformation, i.e., Ar₃. This deviation is attributed to the expansive strain of austenite to ferrite transformation. Judging from this deviated curve with the constant cooling rate of −0.05°C/s, ferrite transformation speed was higher in the beginning, then became lower and again higher after a point P arrowed in

3. Experimental Results and Discussion

3.1. Results of Microstructure Observations and Dilatometry

Microstructures before and after heating to 950°C were presented in Fig. 1. As was reported in the previous papers, the starting microstructure was composed of ferrite, bainite and retained austenite. As is observed in Fig. 1(a), the microstructure looks to be homogeneous throughout the viewing area. On the other hand, the microstructure after heating was found to consist of ferrite and pearlite as shown in Fig. 1(b), in which the band structure related to Mn band was evolved significantly. The pearlite volume fraction determined by the linear section method for fifteen SEM micrographs like Fig. 1(b) was 26.2%.

For in situ neutron diffraction during heating and cooling, five pieces of steel sheet with 1.2 mm in thickness, 30 mm in length and 4–6 mm in width were stacked to be nearly cylindrical shape. Such bundled specimens were set in a conventional dilatometer which was installed into an engineering dilatometer system, the data slicing time can be changed freely at MLF J-PARC have employed the event-mode data acquisition system, the data slicing time can be changed freely after measurement. In the present case, the profiles obtained by every 1 min were used for data analysis.

Fig. 1. Microstructures of the specimen before heating (a) and after cooling (b).
the figure. This retardation of the transformation is believed to stem from carbon and Mn diffusions in the retained austenite (enrichment) and the point P is likely to indicate the onset of pearlite transformation.

3.2. In situ X-ray Diffraction Measurement during Cooling

Typical X-ray diffraction profiles obtained are presented in Fig. 3. A weak $11\gamma$ austenite diffraction peak was observed at RT and single austenite structure was confirmed at 950°C from the obtained diffraction profile. The diffraction peaks are observed to be split at high temperatures in Fig. 3. Since the wavelengths of $K_{\text{al}}$ and $K_{\text{a2}}$ are 0.178919 nm and 0.179321 nm, respectively, the difference in $2\theta$ for $110\alpha$ ferrite peak is 0.13°, which explains the peak split observed at an elevated temperature.

To be noted here is that no austenite peaks were found at 850°C. This is puzzling because the $A_{\text{r3}}$ temperature determined by dilatometry was 838°C, indicating that it should be still single austenite structure. Then, after finishing the high temperature X-ray diffraction measurement, the sample surface was examined using rf-GDOES measurement, the details of which was the same reported in the previous paper.8) The results presented in Fig. 4 are complicated showing serious oxidation which hinders to reveal the real Mn and C concentration profiles in the steel matrix near the specimen surface. Even though, the decarburized and oxygen-diffused zone is found to be approximately 2 μm in depth. For reference, the result for a specimen before heating is also presented in Fig. 4(b) (note the vertical scale is enlarged to show the details on C and Mn concentration profiles), in which the artificial error of this method influenced by free surface can be confirmed to be very small. Hence, the austenite in the surface layer of the specimen at high temperatures is believed to become unstable due to such a change in chemical compositions. In case of in situ EBSD measurement during heating for this steel in vacuum, a decarburized and Mn depleted layer was found by rf-GDOES measurement.9) As was discussed in the previous paper,8) information depths approximately estimated for quantum beam techniques were 100 nm for electron, a few μm for laboratory X-ray and a few cm for neutron beam. Therefore, it is concluded that the present high temperature X-ray diffraction measurement could not provide the real transformation behavior of this steel.

3.3. Ferrite Transformation Behavior Tracked by in situ Neutron Diffraction

Changes in austenite $11\gamma$ and $200\gamma$ and ferrite $110\alpha$ peaks obtained by in situ neutron diffraction during cooling are shown in Fig. 5 together with sample temperature (see right axis) as a function of elapsed time. As seen, ferrite transformation started nearly at 850°C and finished at 620°C. Whole diffraction profiles at 725.5±3°C (60 s) during cooling obtained by the two orthogonally installed detector banks are compared in Fig. 6 at a middle state of
the transformation. As seen, the austenite and ferrite diffraction peaks were mixed, showing the existence of textures. The austenite volume fraction \( f_a \) was determined using the Z-Rietveld software.\(^{13} \) As has been discussed in the previous reports,\(^{8,14} \) the simultaneous determination of orientation distribution function (ODF) and \( f_a \) is recommended to obtain true result, but such a modification was not made in this study because texture was not so strong, statistic reliability of 60 s time for data slicing was not high and diffraction profiles could be obtained only from two directions (concerning the detailed discussion on the determination of volume fraction, see Appendix). However, in spite of such a simple data analysis using the Rietveld refinement, the transformation kinetics can be well captured. As is observed in Fig. 7 obtained from the axial diffraction profiles, the \( f_a \) decreases rapidly in the beginning, then slowly before the arrowed point P and again decreases rapidly after the point P with decreasing of temperature. Here, very important result is that the start temperature of ferrite transformation shows a good agreement with the result of dilatometry. This is because neutron diffraction enables us to monitor the bulky averaged information which is hardly influenced by surface phenomena.

Different from the dilatometry measurement, \textit{in situ} neutron diffraction provides more fruitful insights on microstructural change. For examples, lattice parameters of ferrite and austenite were determined using the Z-Rietveld analysis and the obtained results were presented in Fig. 8. The austenite lattice parameter is believed to depend on temperature \( T \), carbon concentration \( C \) (mass%), and elastic internal strain \( \epsilon \), i.e., \( a(T, C, \epsilon) \). Similarly, the ferrite lattice parameter is, hereafter, described as \( a_f(T, C, \epsilon) \) although the carbon content in ferrite is very small. Thermal expansion and contraction could be satisfactorily fitted by a linear function. In case of an austenite region from 840 to 940°C, it was expressed by

\[
a_a(T, 0.20, 0) = (0.3580 \pm 0.0005) + (7.991 \pm 0.006) \times 10^{-6} T \quad \text{nm} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cd -6 \text{ with } T_{\text{so}}.\) \end{align}

These values shows good agreements with those determined by dilatometry in Fig. 2 (see section 3.1). The obtained \( K' \) value is also close to those reported by Onink et al.\(^{15} \) and Bhadeshia et al.\(^{16} \) According to Onink et al.’s results by neutron diffraction experiments for Fe–C binary alloys, the value of \( K' \) decreases slightly with increasing of carbon content from 0.01 to 0.8 mass% (from 24.7×10\(^{-6} \) to 22.9×10\(^{-6} /\text{°C} \)).

It is found in Fig. 8(a) that the ferrite lattice parameter deviates from its thermal contraction line. This suggests that compressive internal stress generated due to the transformation strain in ferrite phase. On the other hand, in Fig. 8(b), the austenite lattice parameter deviates towards upper side.

![Fig. 5. Changes in neutron diffraction intensities for 111 austenite (γ) and 110 ferrite (α) with heating obtained in the axial direction, in which temperature history is also shown. (Online version in color.)](image)

![Fig. 6. Diffraction profiles obtained at austenite to ferrite transformation in which ycal: fitted result, yint: measured, bg: background, yphase_fcc: austenite and yphase_bcc: ferrite: (a) axial direction and (b) transverse direction. (Online version in color.)](image)

![Fig. 7. Change in austenite volume fraction during cooling determined by \textit{in situ} neutron diffraction measurement.](image)
This must be due to the internal stresses balanced with those in ferrite and another important origin for this deviation would be carbon enrichment.\(^{17,18}\)

The deviation from the thermal expansion line is attributed to (1) transformation strains, (2) thermal misfit strains and (3) carbon enrichment in austenite. These influential factors will be discussed below in order.

(1) The \(\gamma\rightarrow\alpha\) transformation strains were estimated from the lattice parameters of austenite and ferrite at 740°C, where approximately 50% ferrite transformation was progressed. The volume fraction per Fe atom are calculated as

\[
V^\gamma = \frac{0.36370\,\text{nm}^3}{4} = 0.012027\,\text{nm}^3 \quad \text{for fcc (austenite)}
\]

\[
V^\alpha = \frac{0.28961\,\text{nm}^3}{4} = 0.012145\,\text{nm}^3 \quad \text{for bcc (ferrite)}
\]

Then, the volume strain of austenite to ferrite transformation is 0.981%. Assuming isotropic expansion, transformation strains \(\varepsilon_{ij}^{\text{trans}}\) are described as

\[
\varepsilon_{ij}^{\text{trans}} = \varepsilon_{22}^{\text{trans}} = \varepsilon_{33}^{\text{trans}} = 0.327\% \quad \text{................. (5)}
\]

If one computed transformation strains using parameters at 0°C in Eqs. (1) and (2), \(\varepsilon_0\) would become 2.3% and then \(\varepsilon_{ij}^{\text{trans}} = 0.767\%\). That is, the strain \(\varepsilon_0\) depends on transformation temperature. As will be discussed later, \(\varepsilon_{ij}^{\text{trans}}\) is also influenced by carbon concentration of austenite which increases with ferrite transformation leading to lower the value of \(\varepsilon_{ij}^{\text{trans}}\).

(2) In an austenite-ferrite temperature region, thermal misfit strain (\(\varepsilon_{ij}^{\text{ther}}(T)\)) generates due to difference in thermal expansion coefficients between austenite and ferrite, which is \(-6.4 \times 10^{-6}\,/\text{°C}\) estimated from Eqs. (3) and (4). The thermal history is dependent on elapsing time after ferrite start when carbon concentration of austenite is enriched to 0.7 mass%. This seems to be reasonable in comparison with the point P in Fig. 7.

The lattice expansion strain due to carbon enrichment \(\varepsilon_{ij}^{\text{C}}\) was evaluated as follows,

\[
\varepsilon_{ij}^{\text{C}} = \frac{0.0033 \times C\,(\text{mass}\%)}{a^i(\text{RT,0,0})} \quad \text{................. (9)}
\]

In case of 0.7 mass% C, \(\varepsilon_{ij}^{\text{C}}\) becomes 0.647%, which is also a kind of eigen strain to induce internal stresses.

If one estimated the austenite fraction at P by the so-called lever rule in Fig. 2 using the drawn thermal contraction lines for ferrite and austenite, it would be about

\[0.20\text{mass\% (bulk average)}\]

\[0.26 = 0.763\text{mass\%}.\]

Therefore, pearlite transformation would be concluded to start when carbon concentration of austenite is enriched to be approximately 0.7 mass%. This seems to be reasonable in comparison with the point P in Fig. 7.

The lattice expansion strain due to carbon enrichment \(\varepsilon_{ij}^{\text{C}}\) was evaluated as follows,

\[
\varepsilon_{ij}^{\text{C}} = \frac{0.0033 \times C\,(\text{mass}\%)}{a^i(\text{RT,0,0})} \quad \text{................. (9)}
\]

In case of 0.7 mass% C, \(\varepsilon_{ij}^{\text{C}}\) becomes 0.647%, which is also a kind of eigen strain to induce internal stresses.

If one estimated the austenite fraction at P by the so-called lever rule in Fig. 2 using the drawn thermal contraction lines for ferrite and austenite, it would be about

\[0.20\text{mass\% (bulk average)}\]

\[0.26 = 0.763\text{mass\%}.\]

Therefore, pearlite transformation would be concluded to start when carbon concentration of austenite is enriched to be approximately 0.7 mass%. This seems to be reasonable in comparison with the point P in Fig. 7.

The lattice expansion strain due to carbon enrichment \(\varepsilon_{ij}^{\text{C}}\) was evaluated as follows,

\[
\varepsilon_{ij}^{\text{C}} = \frac{0.0033 \times C\,(\text{mass}\%)}{a^i(\text{RT,0,0})} \quad \text{................. (9)}
\]

In case of 0.7 mass% C, \(\varepsilon_{ij}^{\text{C}}\) becomes 0.647%, which is also a kind of eigen strain to induce internal stresses.

If one estimated the austenite fraction at P by the so-called lever rule in Fig. 2 using the drawn thermal contraction lines for ferrite and austenite, it would be about

\[0.20\text{mass\% (bulk average)}\]

\[0.26 = 0.763\text{mass\%}.\]
10% which is much smaller than 26.2% determined from microstructure in Fig. 1. This is because the drawn line is for austenite with 0.2 mass% C not 0.7 mass% C. With increasing of carbon concentration in austenite, its thermal contraction line shifts towards the upper side, resulting in the estimation of higher austenite volume fraction. It also indicates that the value of $\varepsilon^{\text{trans}}_{ij}$ decreases with increasing of the carbon concentration of austenite.

3.4. Estimation of Phase Stresses and Strains in Austenite and Ferrite

Lattice parameter is influenced by hydrostatic component of elastic strains. During ferrite transformation on continuous cooling, three kinds of eigen strains $({\varepsilon}_i^j)$ appear as mentioned above. They include: (1) transformation strain (about 0.327%), (2) thermal misfit strain (about 0.032%), and (3) carbon enrichment in austenite (0-0.647%). The internal stresses are caused by $\varepsilon^a_{ij}$, but high local internal stresses must be relaxed by diffusion and/or dislocation motion at elevated temperatures. The plastic relaxation is too difficult to take into consideration quantitatively here because its mechanism is uncertain. However, the unrelaxed state could be evaluated using the Eshelby inclusion theory. The averaged long range internal stresses, i.e., phase stresses caused by $\varepsilon^a_{ij}$ can be written as:

$$\sigma^a_{ij} = -f_a C_{ijkl} (S_{\text{full}} - I) \varepsilon^a_{nm}$$ ................................ (10)

$$\sigma^a_{ij} = (1 - f_a) C_{ijkl} (S_{\text{full}} - I) \varepsilon^*_{nm}$$ ................................ (11)

where $C_{ijkl}$ and $I$ refer to elastic moduli and unit tensor, respectively. Assuming spherical grain and the Poisson ratio of 0.30, the Eshelby tensor, $S_{\text{full}}$, are expressed as $S_{1111} = S_{2222} = S_{3333} = 7 - 5v, S_{2233} = S_{3311} = S_{1122} = S_{1332} = S_{1133} = S_{1221} = 5v - 1, S_{1212} = S_{2322} = S_{3131} = -(4 - 5v) 15(1 - v)$, and $S_{1133} = -0.238$. Here, three kinds of origins for $\varepsilon^a_{ij}$ can be regarded to have isotropic feature, $\varepsilon^a_{ij} = q$ when $i=j$ and $\varepsilon^a_{ij} = 0$ when $i\neq j$. Employing the general isotropic Hooke’s equation for $C_{ijkl}$, the next simple relation can be obtained in the present case.

$$\sigma^a_{11} = \sigma^a_{22} = \sigma^a_{33} = -f_a \times (3.57 Eq)$$ ................................ (12)

where $E$ stands for Young modulus. Needless to say, the sum of phase stresses is zero and then,

$$\sigma^a_{ij} \times f_j + \sigma^a_{ij} \times f_a = 0$$ ................................ (13)

The elastic internal strain contributing to diffraction peak shift is described by

$$\beta_{ij} = \frac{1 - 2v}{E} \sigma_{ij}$$ .................................................. (14)

where $\beta_{ij} = \beta_{22} = \beta_{33} = \beta$. Stress or strain condition is hydrostatic in the present case. Paying attention to austenite phase, tensile hydrostatic strain increases in the beginning of ferrite transformation caused by transformation strain and thermal misfit strain. With increasing of $f_a$, it would be expected that the influence of carbon enrichment $\beta$ becomes larger, which must cancel out the influence of (1) and (2). That is, the value of $\beta$ is postulated to become larger in the beginning and then decrease with progressing of ferrite transformation. In conclusion, the lattice parameter of austenite could be expressed by

$$a' (T, C, \varepsilon) = \left( a' (RT, 0, 0) + 0.0033C \right) \left( 1 + K' T \right) (1 + \beta)$$ ................................ (15)

The elastic strain in ferrite was calculated from Fig. 8(a) and the results were plotted in Fig. 9. Using Eq. (13) of the equilibrium balance for phase stresses, the elastic strains of austenite were computed and the results were also plotted in Fig. 9. As was discussed above, at the early stage of ferrite transformation, the stress partitioning is remarkably observed which is mainly caused by (1) and (2). The interpretation of Fig. 9 could be made by these three contributing factors.

3.5. Pearlite Transformation and Change in Ferrite Diffraction Profile

The lattice strains caused by carbon enrichment in austenite were evaluated by subtracting the internal elastic strains given in Fig. 9 from the strains directly determined in Fig. 8. The obtained results are presented in Fig. 10 which figures out the behavior of carbon enrichment. From this figure, the carbon concentration increases with increasing of $f_a$ and ceases increasing after the point P where pearlite transformation starts to take place. As discussed above, the pearlite transformation was considered to occur after the carbon concentration reached to approximately 0.7 mass% where $f_r$ was about 0.26. The signal concerning the onset of pearlite transformation was found in transformation kinetics in Figs. 2 and 7 and the strain related to carbon enrichment in Fig. 10. The cementite diffraction peaks could not clearly be
detected in a 60 s time-sliced profile because of its small amount, but FWHMs of ferrite peaks were found to change after the point P, i.e., the start of pearlite transformation. As examples, the FWHMs of 110α and 200α diffraction peaks determined are shown in Fig. 11 as a function of fP, the decrease of which means the lowering of temperature. Here, FWHM is shown by TOF as well as the inverse of lattice spacing (d). In general, FWHM decreases with decreasing of temperature, so that the results in Fig. 11 are unusual. Diffraction line broadening is influenced by dislocation density, character and arrangement, crystallite size (coherently diffracting mosaic size) and planar defects like stacking fault.26) The present line broadening related to pearlite transformation is believed mainly due to the coherent interface misfit strain.27) According to high resolution TEM studies,28) the interface between ferrite and cementite in pearlite structure is semi-coherent having a certain crystal orientation relationship, where the interface coherent strain/stress is partially relaxed by introducing misfit dislocations and interface ledges. Recently, Nakada and Kato have evaluated such interface stress generation and its relaxation by introducing of misfit dislocations using a micro-mechanics model.29)

4. Conclusions

The phase transformation behavior from austenite during cooling for a 1.5Mn-1.5Si-0.2C steel was in situ monitored using dilatometry, X-ray diffraction and neutron diffraction. The main conclusions obtained would be summarized as follows.

(1) The ferrite and pearlite transformation kinetics showed excellent agreements between dilatometry and neutron diffraction, whereas the ferrite formation was observed to start at a much higher temperature in X-ray diffraction measurement. Such discrepancy in transformation temperature is attributed to the change in chemical composition near the surface of a specimen heated to elevated temperatures; oxidation and changes in Mn and C concentrations were found at near surface layer after the measurement.

(2) In situ neutron diffraction measurement enables us to investigate the changes in lattice constants of ferrite and austenite, showing not only thermal contraction but also carbon enrichment in austenite and phase stresses.

(3) The transformation strains, thermal misfit strains, carbon enrichment in austenite and generation of phase stresses during ferrite transformation were discussed from the neutron diffraction data using the Eshelby inclusion theory.

(4) The carbon concentration for the onset of pearlite transformation was estimated and diffraction profile line broadening caused by pearlite formation was presented.

Acknowledgements

This paper is based on the results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO). Discussion and advice given by members of Innovative Structural Materials Association (ISMA) are highly acknowledged. Specimens used in this study were prepared as a round robin test for NEDO as well as the ISIJ research project on the microstructure evaluation using compact neutron source. The in situ neutron diffraction measurements were performed at J-PARC MLF under a user program 2015A0153.

REFERENCES

1) For example, H. Shibata, Y. Arai, M. Suzuki and T. Emi: Metall. Mater. Trans. B, 31B (2000), 981.
2) For example, T. Tomota, Y. Morioaka and W. Nakagawara: Acta Mater., 46 (1998), 1419.
3) For example, T. Shinozaki, Y. Tomota, T. Fukino and T. Suzuki: ISIJ Int., 57 (2017), 533.
4) For example, X-ray diffraction: H. J. Stone, M. J. Peet, H. K. D. H. Bhadeshia, P. J. Withers, S. S. Babu and E. D. Specht: Proc. R. Soc. A, 464 (2008), 1009.
5) For example, M. Villa, F. Niessen and M. A. J. Somers: Metall. Mater. Trans., 49A (2018), 28.
6) N. Nakada, T. Tsuchiyama and S. Takaki: Proc. 5th Int. Symp. on Steel Science (ISSS 2017), ISIJ, Tokyo, (2018), 35.
7) For example, N. Nakada and M. Kato: ISIJ Int., 56 (2016), 1866.
8) Y. Tomota, N. Sekido, S. Harjo, T. Kawasaki, W. Gong and A. Taniyama: ISIJ Int., 57 (2017), 2240.
9) Y. Tomota, N. Sekido, P. G. Xu, S. Harjo, M. Tanaka, T. Shinohara, Y. H. Su and A. Taniyama: Tetsu-to-Hagane, 103 (2017), 2237.
10) K. Sugimoto, N. Usai, S. Kobayashi and S. Hashimoto: Tetsu-to-Hagane, 78 (1992), 1480.
11) A. Moriai, S. Torii, H. Suzuki, S. Harjo, Y. Morii, M. Arai, Y. Tomota, T. Suzuki, Y. Akinwai, H. Kimura and K. Akita: Physica B, 385–386 (2006), 1043.
12) S. Harjo, T. Ito, K. Aizawa, H. Arima, J. Abe, A. Moriai, T. Ishigaki, T. Morishima, K. Mori and T. Kamiyama: Mater. Sci. Forum, 681 (2011), 443, doi: 10.4028/ www.sctiflnc.net/MSF.681.443.
13) R. Oishi, M. Yonemura, Y. Nishimaki, S. Torii, A. Hoshikawa, T. Ishigaki, T. Morishima, K. Mori and T. Kamiyama: Nucl. Instrum. Methods Phys. Res. A, 600 (2009), 94, doi: 10.1016/j. nima.2008.11.056.
14) P. G. Xu, Y. Tomota, Y. Arakaki, S. Harjo and H. Sueyoshi: Mater. Charact., 127 (2017), 104.
15) M. Onink, C. M. Brakman, F. D. Tichelaar, E. J. M. Temmerman, S. van der Zwaag, J. H. Root and N. B. Konyer: Scr. Metall. Mater., 29 (1993), 1011.
16) H. K. D. H. Bhadeshia, S. A. David, J. M. Vitek and R. W. Reed: Mater. Sci. Technol., 7 (1991), 686.
17) Y. Tomota, P. G. Xu, E. C. Oliver and A. Paradokova: In-situ Studies with Photons, Neutrons and Electrons Scattering, ed. by T. Kannengiesser et al., Springer, Berlin, (2010), 175.
18) P. G. Xu, Y. Tomota, S. C. Vogel, T. Suzuki, M. Yonemura and T. Kamiyama: Rev. Adv. Mater. Sci., 33 (2015), 389.
19) C. S. Roberts: Trans. AIME, 197 (1953), 203.
20) L. Cheng, A. Böttger, T. H. de Keijser and J. Mittereijer: Scr. Mater., 24 (1990), 509.
21) R. C. Ruhl and M. Cohen: Trans. Metall. Sci. AIME, 245 (1969), 241.

Fig. 11. Changes in FWHMs of 110 (a) and 200 (b) ferrite diffraction peaks with cooling as a function of austenite volume fraction.
Appendix on the Determination of Austenite Volume Fraction (\(f_\gamma\))

In a two-phase alloy like the present austenite-ferrite system, it is recommended to use hkl diffraction peaks as many as possible to determine the volume fractions of the constituents. The Rietveld refinement method has been used for multi-peak analysis. As discussed in the previous reports in details,\(^8,14\) it is not easy to obtain the reliable value for a textured steel. In the Z-Rietveld code, the March-Dollase function has been adopted to correct the influence of texture, but it does not work for engineering steels in our experience. It seems to be applicable to powders with a weak texture but it does not work for engineering steels in our experience.

Therefore, one easy method is to assume a random texture case of Bragg edge spectrum analysis as reported in ref. 8. It was also true in the case of Bragg edge spectrum analysis as reported in ref. 8. Therefore, one easy method is to assume a random texture as was done in the present study for Fig. 7.

In the Z-code, the peak position and intensity can be made variable, which is convenient to obtain individual hkl peak position and intensity. The examples of such fitting were presented in Fig. 6. In diffraction methods using either X-ray or neutron, the volume fraction of austenite (\(f_\gamma\)) is determined from hkl diffraction intensities of austenite and ferrite. Because hkl diffraction intensities are influenced by texture, the following correction has usually been applied\(^{A1,A2}\)

\[
f_\gamma = \frac{1}{n} \sum \frac{I_{hkl}}{F_{hkl}^2} = \left( \frac{1}{m} \sum \frac{I_{hkl}}{F_{hkl}^2} + \frac{1}{n} \sum \frac{I_{hkl}}{F_{hkl}^2} \right)
\]  

(A1)

Here, \(n\) and \(m\) refer to number of hkl peaks of austenite (subscript \(\gamma\)) or the matrix (subscript \(\alpha\): ferrite, bainite and martensite) used for \(f_\gamma\) calculation, respectively; \(I_{hkl}\) and \(F_{hkl}\) stand for measured integrated intensities of hkl peaks of the two constituents \(\gamma\) and \(\alpha\), respectively while \(R\) stands for the theoretical intensities of corresponding diffraction peaks of random or non-textured sample, which was obtained by the simulation mode of Z-code. In ASTM E975-13,\(^{A3}\) it was written that “this method should be applied to steels with near random crystallographic orientations of ferrite and austenite phases because preferred crystallographic orientations can drastically change these measured intensities from theoretical values”, so that the application of Eq. (A1) is limited. In our studies on steels containing the retained austenite like low-alloyed TRIP steels,\(^8,14\) the influence of texture could not be removed satisfactorily. Hence, we rotated a sample and obtained diffraction profiles from 525 directions and put them into the MAUD software\(^A3\) to obtain orientation distribution function (ODF) and \(f_\gamma\) simultaneously. We believe this method can be recommended if one want to have a reliable value of \(f_\gamma\) in a textured steel.

### References

\(^{22}\) J. D. Eshelby: *Proc. R. Soc. Lond.*, A241 (1957), 376.
\(^{23}\) T. Mori and K. Tanaka: *Acta Metall.*, 21 (1973), 571.
\(^{24}\) Y. Tomota, K. Kuroki, T. Mori and I. Tamura: *Mater. Sci. Eng.*, 24 (1976), 85.
\(^{25}\) S. Harjo, Y. Tomota and M. Ono: *Acta Mater.*, 47 (1999), 353.
\(^{26}\) Y. Tomota, S. Sato and S. Harjo: *Tetsu-to-Hagané*, 103 (2017), 73.
\(^{27}\) N. Nakada, N. Koga, T. Tsuchiyama and S. Takaki: *Scr. Mater.*, 61 (2009), 133.
\(^{28}\) For example, D. S. Zhou and G. J. Shiflet: *Metall. Mater. Trans. A*, 23A (1992), 1259.
\(^{29}\) N. Nakada and M. Kato: *ISIJ Int.*, 56 (2016), 1866.

### Table A1. Debye-Waller factors at typical temperatures.

| Temperature (°C) | BCC_Fe Mean | BCC_Fe Error |
|------------------|-------------|--------------|
| 770              | 0.79301     | 0.002936     |
| 750              | 0.653048    | 0.004920     |
| 700              | 0.407143    | 0.003567     |

### Table A2. Influence of determination methods on \(f_\gamma\) at three representative temperatures.

| Temperature (°C) | \(f_\gamma\) MAUD | \(f_\gamma\) Z-Rietveld |
|------------------|-------------------|------------------------|
| 770              | 0.79301           | 0.822686               |
| 750              | 0.653048          | 0.693033               |
| 700              | 0.407143          | 0.456607               |

In case of high temperature measurement, another influential parameter is the Debye-Waller factor. According to refs. A4 and A5, the Debye-Waller factors for BCC Fe and FCC Fe at typical temperatures were calculated as shown in Table A1. In the computation for Fig. 7, we employed a multi-histogram analysis procedure keeping the Debye-Waller factor as 0.3 which has usually been used so far.

Therefore, to check the influence of texture and Debye-Waller factor on \(f_\gamma\), several methods were examined and compared for the profiles obtained at three typical temperatures (sliced numbers of 374, 381 and 397 which were related to approximately 770, 750 and 700°C, respectively).

Main results were tabulated in Table A2. In case of Trial A (Fig. 7), \(f_\gamma\) showed a little lower value compared with other cases taking texture and Debye-Waller factor into account.

Trial B is the case assuming random texture and temperature dependent Debye-Waller factor. Probably, Trial C is considered to be more appropriate, where Eq. (A1) was used for the individual hkl diffraction intensities obtained as shown in Fig. 6. We recommend the Trail D but diffraction profiles obtained only from two directions are not be enough. If we can obtain in situ diffraction profiles with enough statistic reliability using many detectors, we would be able to obtain more reliable results using the Trial D method. In the text, the results by Trial A were plotted for simplicity.

### Table A1.

| Temperature (°C) | BCC_Fe Mean | BCC_Fe Error |
|------------------|-------------|--------------|
| 770              | 0.79301     | 0.002936     |
| 750              | 0.653048    | 0.004920     |
| 700              | 0.407143    | 0.003567     |

### Table A2. Influence of determination methods on \(f_\gamma\) at three representative temperatures.

| Temperature (°C) | \(f_\gamma\) MAUD | \(f_\gamma\) Z-Rietveld |
|------------------|-------------------|------------------------|
| 770              | 0.79301           | 0.822686               |
| 750              | 0.653048          | 0.693033               |
| 700              | 0.407143          | 0.456607               |

In case of high temperature measurement, another influential parameter is the Debye-Waller factor. According to refs. A4 and A5, the Debye-Waller factors for BCC Fe and FCC Fe at typical temperatures were calculated as shown in Table A1. In the computation for Fig. 7, we employed a multi-histogram analysis procedure keeping the Debye-Waller factor as 0.3 which has usually been used so far.

Therefore, to check the influence of texture and Debye-Waller factor on \(f_\gamma\), several methods were examined and compared for the profiles obtained at three typical temperatures (sliced numbers of 374, 381 and 397 which were related to approximately 770, 750 and 700°C, respectively).

Main results were tabulated in Table A2. In case of Trial A (Fig. 7), \(f_\gamma\) showed a little lower value compared with other cases taking texture and Debye-Waller factor into account. Trial B is the case assuming random texture and temperature dependent Debye-Waller factor. Probably, Trial C is considered to be more appropriate, where Eq. (A1) was used for the individual hkl diffraction intensities obtained as shown in Fig. 6. We recommend the Trail D but diffraction profiles obtained only from two directions are not be enough. If we can obtain in situ diffraction profiles with enough statistic reliability using many detectors, we would be able to obtain more reliable results using the Trail D method. In the text, the results by Trial A were plotted for simplicity.