Microscopic stress characterisation of functional iron-based alloys by white X-ray microbeam diffraction

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Abstract. Microscopic residual stress evolution in an austenite (γ) grain during a shape-memory process in an Fe–Mn–Si–Cr alloy was investigated using the white X-ray microbeam diffraction technique. The stresses were measured on a coarse grain, which had an orientation near <144>, parallel to the tensile loading direction with a high Schmid factor for a martensitic transformation. The magnitude of the residual stresses in a grain of the sample, which was subjected to a 23 % tensile strain and subsequent shape-recovery heating, was found to be very small and comparable to that prior to tensile deformation. Measurements of the recovery strain and microstructural analyses using electron backscatter diffraction suggested that the low residual stresses could be attributed to the significant shape recovery caused by a highly reversible martensitic transformation in the grain with a particular orientation.

1. Introduction

Iron-based alloys are utilised not only for structural materials but also for functional materials. These functional materials include Fe–Mn–Si-based shape-memory alloys [1], in which the shape-memory effect appears through a stress-induced martensitic transformation by deformation and a reverse transformation by subsequent heating. It is known that the shape-memory effect depends on the geometrical relationship between the crystallographic orientation of grains and the external loading direction [2]. The orientation dependence of the shape-memory effect is observed in both single crystals and polycrystalline alloys [1, 2].

Recent studies [3-5] have suggested that residual stress developed during a stress-induced martensitic transformation is an important factor contributing to the improvement of the shape-memory effect. Tomota et al. [6] insisted that the effects of solid-solution hardening and training treatments in shape-memory alloys can be understood from the viewpoint of back stress, i.e., internal stress built up by a stress-induced γ (fcc) → ε (hcp) martensitic transformation. According to a study by Tomota and Maki [4], the back stress forms in the γ phase around the growing ε martensite plate tips, and it serves an important role in promoting the reversible motion of the partial dislocation in the shape-recovery process on heating, thereby improving the recovery strain of the alloys. The evolution of internal stress would depend on the grain orientation because of the orientation...
dependence of the martensitic transformation. Although the macroscopic strain change has been commonly examined to evaluate the shape-memory effect, almost no systematic studies on the evolution of microscopic stress in iron-based shape-memory alloys have been performed thus far. For a more comprehensive understanding of the relationship between the residual stress and shape-memory effect, the evolution of residual stress during the shape-memory deformation process must be characterised.

Recently, white X-ray microbeam diffraction has emerged as a powerful tool for measuring the microscopic stress within grains [7-9]. The recently developed microstructure visualisation technique, coupled with energy spectra measurements with a solid-state detector at the BL28B2 beamline of SPring-8, enables the measurement of strain/stress on the local area of interest in materials [10]. In our previous study, this technique was applied to investigate the stress in individual grains in a Cu-Al-Mn superelastic alloy, and the results showed an inhomogeneous stress distribution, both at the granular and intragranular scales [11]. This technique was also applied to analyse the stress distribution in Fe–Mn–C twinning-induced plasticity steels [12].

In the present study, we investigated the microscopic stress evolution within a grain during the shape-memory behaviour of an Fe–Mn–Si–Cr shape-memory alloy using the white X-ray microbeam diffraction technique. The diffraction experiments were performed on a grain with a specific crystallographic orientation undergoing a highly reversible martensitic transformation.

2. Experimental procedures

2.1. Materials
The material used in this study was a polycrystalline Fe-28%Mn-6%Si-5%Cr (mass%) shape-memory alloy produced by centrifugal casting [13]. The microstructure of the alloy consisted of large columnar grains. The alloy was annealed at 1,000 °C for 8 h to coarsen the grains. Small tensile samples were cut from the cast along a specific direction so that the gauge part contained a coarse columnar grain with a specific crystallographic orientation. The tensile samples were additionally annealed at the austenite temperature range (900 °C) for 30 min to eliminate any deformed microstructures formed during sample preparation. To use the samples in white X-ray microbeam diffraction experiments, the thickness (t) was reduced to about 200 µm by electropolishing with a solution of acetic acid and 20 vol% perchloric acid. The diffraction experiments were carried out on a measurement area of 1.5 mm × 0.5 mm in the sample gauge region (3.0 mm × 0.6 mm), as shown in figure 1a.

![Figure 1. Schematic of tensile sample used for X-ray microbeam diffraction experiments.](image)

For recovery strain measurements, two marks with an initial distance of 1 mm were indented on the gauge part of the sample with microindentation. The recovery strain was calculated by measuring the change in the distance after deformation and recovery heating. Recovery heating was conducted at 350 °C for 10 min.
2.2. White X-ray microbeam diffraction experiments

White X-ray microbeam diffraction experiments were conducted using high-energy synchrotron radiation at the SPring-8 BL28B2 beamline (Hyogo, Japan). Figure 2 shows a schematic diagram of the X-ray microbeam diffraction experiments. The incident beam with a size of 25 × 25 µm was illuminated on the tensile sample and the diffracted beams generated from the tensile sample in the transmission (Laue) geometry were collected on the image detector. X-ray energy spectra for several Laue reflection regions were measured using a Ge solid-state detector. The obtained X-ray energy spectra were used to calculate the lattice spacing of the \((hkl)\) planes, \(d_{hkl}\) [10]. White X-ray microbeam diffraction experiments were performed during a shape-memory cycle, i.e., before deformation (0 % strain) \(\rightarrow\) tensile deformation (23 % strain, unloaded) \(\rightarrow\) after recovery heating. Details of the experimental setup and experimental procedures are given in reference [15].

![Figure 2. Schematic diagram showing the X-ray microbeam diffraction experiments.](image)

Prior to the X-ray diffraction experiments, the microstructure of the sample was investigated using electron backscatter diffraction (EBSD). Then, the sample with a particular grain orientation was selected to use in the X-ray diffraction experiments. EBSD patterns were obtained using a Nordlys II EBSD detector mounted on a Hitachi SU-6600 scanning electron microscope operating at an acceleration voltage of 20 kV. EBSD data were processed using HKL CHANNEL 5 Flamenco software to obtain the microstructural information. To analyse the microstructural evolution during the shape-memory process, the microstructure of the sample, which was used in the X-ray diffraction experiments, was observed at some strain levels and after recovery heating.

The sample used in the present study had an orientation near \(<144>\), parallel to the loading direction (LD) in tensile tests (\(<144>/<\text{LD})\), which is among the most preferential orientations for a martensitic transformation. The EBSD orientation map of figure 3a, taken from the undeformed gauge region of the tensile sample, shows that the microstructure consisted of a coarse \(\gamma\) grain with a specific orientation as confirmed by the green colour. Low-angle grain boundaries with misorientations less than 10° were observed, indicating the presence of sub-grains. The image (figure 3b) obtained by X-ray microbeam diffraction from the similar area with the EBSD orientation image shows a somewhat blurred structure because of the presence of sub-grains. The X-ray diffraction experiments were performed on three positions as marked with P1, P2, and P3 in figure 3b.

The EBSD inverse pole figure shown in figure 4a indicates that the grain is oriented near \(<144>/<\text{LD}\), which has a high Schmid factor (value of 0.5) for a martensitic transformation, as shown in the contour map of figure 4b. We therefore expect a martensitic transformation to be very favourable in that grain. In addition, the transformation strain by martensitic strain is as large as 19 % in this orientation, as shown in figure 4c, meaning that a significant elongation would be obtained by tensile deformation of the sample.
Figure 3. Image showing the microstructure of the tensile sample. a) Orientation image obtained by EBSD. b) Image of the area marked by a rectangle in figure 3a obtained by white X-ray diffraction. Crosses (+) in (b) denote stress measurement points.

Figure 4. a) EBSD inverse pole figures showing the orientation of the grain in the tensile direction. Stereo-triangles showing b) the Schmid factor, and c) the transformation strain of grain orientation in the tensile direction.

3. Results and discussion

Figure 5 shows the variation of the Laue patterns during a shape-memory cycle obtained at the position marked with P1 in figure 2. Laue spots at 23% strain show pronounced streaking. Laue spots often display streaked peaks because of the existence of geometrically necessary dislocations and deviation of the crystal orientation [16, 17]. The streaking of Laue spots in this alloy could be mainly attributed to the formation of stress-induced ε martensite. After recovery heating, the Laue spots nearly recovered their initial shape, although the incomplete restoration of their original shape may be due to residual martensite and slip deformation. In shape-memory alloys, the reversible change of the Laue patterns is most likely to be associated with a reversible martensitic transformation during the shape-memory process.

Laue spots were indexed based on their measured lattice spacing values using a stress calculation programme [18]. All of the Laue spots at 0% strain were indexed to lattice planes of the γ phase, as shown in figure 5a, which is in good accordance with the EBSD phase analysis of the sample. At 23% strain, Laue spots are mostly indexed to the lattice planes of ε martensite, although some are indexed as γ phase, suggesting that γ phase is almost transformed to ε martensite at this strain. Laue spots indexed as ε martensite were not observed after recovery heating, indicating that the ε martensite on the deformed microstructure reverse-transformed to γ phase after recovery heating. Although some residual martensite can remain in the microstructure after recovery heating, its detection is considered to be difficult due to its low quantity.
Figure 5. Laue patterns obtained from a point marked by P1 in figure 3b. a) Before deformation; b) at 23 % strain; and c) after recovery heating. Laue spots were indexed based on their lattice spacing values.

The recovery strain of the sample that was subjected to a 23 % strain deformation and subsequent recovery heating is shown in figure 6. For comparison, the recovery strain of a conventional polycrystalline Fe–Mn–Si shape-memory alloy is also presented [2]. It shows that a recovery strain of about 2 % is achievable in a conventional polycrystalline Fe-based shape-memory alloy. Note that a significantly higher recovery strain of 17 % was obtained in this sample. The outstanding shape-recovery properties are attributed to its coarse grain structure with a characteristic orientation of <144>, where a martensitic transformation is favoured and a large elongation is obtained.

According to Otsuka et al. [19], the amount of martensite is related to the recovery strain as expressed by equation (1):

\[
\text{Recovery strain} \% = TS \times (V_\varepsilon/100)f
\]

where \(TS\) is the transformation strain, \(V_\varepsilon\) is the volume fraction of stress-induced martensite, and \(f\) is a factor \((0 < f \leq 1)\) that depends on the polycrystalline condition determined by thermal or mechanical treatment. According to eq. (1), the recovery strain is proportional to the volume fraction of
stress-induced martensite. In particular, the maximum recovery strain can be obtained when the reverse transformation of martensite is complete, i.e., when $f$ is equal to 1. A maximum recovery strain of 19% can be obtained under the conditions, $f = 1$ and $x = 100$, according to eq. (1). The strain level of 17% obtained in this sample is fairly large considering a maximum achievable recovery strain of 19%. This means that the martensite in this sample has a good reverse-transformation ability.

Laue patterns of deformed shape-memory alloys would be composed of many spots that are generated from both the $\gamma$ phase and stress-induced $\varepsilon$ martensite. The presence of $\varepsilon$ martensite can be verified by measuring the lattice spacing of the Laue spots. Lattice planes were manually indexed based on the measured lattice spacing and the results of the examples are shown in figure 7. The lattice spacing was calculated from the obtained energy profile of the respective Laue spots according to Bragg’s law [14]. Obviously, the lattice spacing profile of figure 7b obtained from the energy profile of figure 7a shows a peak corresponding to the (101) plane of $\varepsilon$ martensite. The energy profile sometimes presents two distinct energy peaks, as exemplified in figure 7c. In that case, the measured lattice spacing needs to be compared with the anticipated lattice spacings for $\gamma$ phase and $\varepsilon$ martensite for accurate indexing. Otherwise, accurate measurements of lattice strains/stresses cannot be made due to mis-indexing. As shown in figure 7d, the two peaks are referenced to the (111) plane of $\gamma$ phase and (100) plane of $\varepsilon$ martensite based on the measured lattice spacing, indicating the co-existence of the two phases at 23% strain. It also means that the overlap of Laue spots occurs during diffraction, making automatic indexing using the calculation programme very difficult. For this reason, clearly distinguishable non-overlapped Laue spots of high intensity were used for strain/stress measurements in this study. The strain/stress was measured only for the $\gamma$ phase because the calculation programme used is only capable of measurements for $\gamma$ phase with an fcc structure at present. Development of the calculation programme for strain/stress measurements of hcp martensite is in progress.

Figure 8 shows the evolution of the principal stresses of the $\gamma$ phase at three points within a grain during the shape-memory cycle. The red and blue arrows indicate the tensile stress and compressive stress, respectively. The stress data contained a measurement error of about ± 40 MPa, based on an experimental strain resolution of about ± 0.04% [15]. At 0% strain (before deformation), there were some small stresses, which might be induced during the production process of the alloy or the preparation of the tensile sample. Stresses in the $\gamma$ phase were not measured at 23% strain because there were a limited number of measurable lattice planes for the $\gamma$ phase, most likely due to the

![Figure 7. Energy profiles of Laue spots at 23% strain and the corresponding lattice spacing profiles.](image-url)
transformation of most of the $\gamma$ phase to $\varepsilon$ martensite. However, large stresses probably exist at deformed states considering the significant Laue spot streaking. In a previous study on microscopic stress analysis in several grains of shape-memory alloys, it was found that large compressive residual stresses were developed in grains with a high Schmid factor for a martensitic transformation at 4% strain [15]. Furthermore, the magnitudes of the compressive residual stresses in the grains differed due to the different martensitic transformation behaviours in the grains. Considering this fact, large compressive stresses could be formed in the $\gamma$ phase at 23% strain. Meanwhile, because martensite newly forms during deformation, there would be a stress redistribution between the parent phase and the martensite. It would also be of interest to study the stress evolution in the martensite phase; this will be explored in our future studies.

![Figure 8](image)

Figure 8. Principal stresses of the $\gamma$ phase measured at three points at a) 0% strain, and b) after recovery heating.

Figure 8b shows that the residual stresses after recovery heating in all positions are very small, despite the applied high strain of 23%. It is considered that stresses developed by deformation are released due to shape recovery. In fact, this sample exhibited a very large recovery strain of 17% at the applied strain of 23%. Therefore, one may conclude that the stresses developed by deformation in this sample were mostly released by a pronounced shape recovery, resulting in very small residual stresses, which are comparable with those at 0% strain.

The reason for the good shape recovery can be revealed by observation of the martensitic transformation behaviour during the shape-memory process. The microstructural evolution during tensile deformation and after recovery heating was observed using EBSD. The results shown in figure 9 reveal that martensite gradually forms with tensile strain and almost disappears after recovery heating due to the reverse transformation of martensite to $\gamma$ phase. To obtain a shape-memory effect, martensite must be transformed back to the parent phase by a backward movement of the Shockley partial dislocations, these dislocations having operated in the forward transformation process [20]. In the case of the sample with the $<144>/<LD$ orientation, only one shear system with the highest Schmid factor of 0.5 operates during both forward and reverse transformations, thereby leading to good transformation reversibility of martensite. The formation of one martensite variant is verified in the EBSD phase map of figure 9 and is indicated by a dashed line. From a crystallographic analysis, the most plausible active shear system among 12 possible shear systems of $\{111\}<112>$ was found to be $<110>[1\bar{1}2]$, as shown in figure 10c. Therefore, the outstanding shape recovery of this sample is attributed to the good reversibility of the martensitic transformation. Furthermore, the highly reversible martensitic transformation accounts for the observed reversible Laue pattern change and the low residual stresses after recovery heating.
Figure 9. EBSD phase maps showing the evolution of $\varepsilon$ martensite with the increase of accumulated tensile strain and after recovery heating. Martensite is coloured in blue.

Figure 10. EBSD pole figures of a) $\gamma$ phase and b) $\varepsilon$ martensite at 2.3 % strain. c) Stereographic projection showing configuration of the most plausible active shear system of $\{111\}[112]$.

4. Conclusions
In conclusion, the residual stress evolution during a shape-memory cycle of a tensile sample in an austenite grain in an Fe–Mn–Si–Cr shape-memory alloy was investigated using white X-ray microbeam diffraction. The X-ray diffraction experiments were conducted on the coarse grain with an orientation close to the $<144>$ direction with a high Schmid factor for a martensitic transformation. The sample, which was subjected to a tensile strain of 23 % and subsequent recovery heating, showed a large recovery strain of 19 %. Microstructural analysis using EBSD revealed that the outstanding shape recovery resulted from a highly reversible martensitic transformation. The residual stresses after recovery heating were found to be very small and comparable with those before deformation despite the applied high level of tensile deformation (23 % strain). The low residual stresses observed in the sample after recovery heating may be attributed to the good reversibility of the martensitic transformation, resulting in the release of the stresses developed due to tensile deformation.
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References
[1] Sato A, Chishima E, Soma K and Mori T 1982 Acta Metall. 30 1177-1183
[2] Kwon E P, Fujieda S, Shinoda K and Suzuki S 2010 Mater. Sci. Engng. A 527 6524-6532
[3] Nozaki H and Tomota Y 2000 Mater. Trans. 41 727-732
[4] Tomota Y and Maki T 2000 Mater. Sci. Forum 327-328 191-198
[5] Tsuzaki K, Natsume Y, Tomota Y and Maki T 1995 Scripta Mater. 33 1087-1092
[6] Tomota Y, Harjo S, Lukas P, Neov D and Sittner P 2000 JOM 52 32-34
[7] Ice G E, Larson B C, Yang W, Budai J D, Tischler J Z, Pang J W L, Barabash R I and Liu W 2005 J. Synchrotron Rad. 12 155-162
[8] Ice G E, Pang J W L, Barabash R I and Puzyrev Y 2006 Scripta Mater. 55 57-62
[9] Ice G E, Larson B C, Tischler J Z, Liu W and Yang W 2005 Mater. Sci. Engng. A 399 43-48
[10] Kajiwara K, Sato M, Hashimoto T, Hirosawa I, Yamada T, Terachi T, Fukumura T and Arioka K 2009 Phys. Status Solidi A 206 1838-1841
[11] Kwon E P, Sato S, Fujieda S, Shinoda K, Kainuma R, Kajiwara K, Sato M and Suzuki S 2015 Metals 5 1845-1856
[12] Suzuki S, Hotta K, Kwon E P, Fujieda S, Shinoda K, Kumagai M, Kajiwara K, Sato M and Sato S 2015 ISIJ Int. 55 2158-2165
[13] Kubo H, Otsuka H, Farjami S and Maruyama T 2006 Scripta Mater. 55 1059-1062
[14] Pyzalla A 2000 J. Nondestructive Eval. 19 21-31
[15] Kwon E P, Sato S, Fujieda S, Shinoda K, Kajiwara K, Sato M and Suzuki S 2013 Mater. Sci. Engng. 570 43-50
[16] Barabash R I, Ice G E and Walker F J 2003 J. Appl. Phys. 93 1457
[17] Hofmann F, Song X, Abbey B, Jun T S and Korsunsky A M 2012 J. Synchrotron Rad. 19 307-318
[18] Kajiwara K, Sato M, Hashimoto T, Yamada T, Terachi T, Fukumura T and Arioka K 2013 ISIJ Int. 53 165-169
[19] Otsuka H, Yamada H, Maruyama T, Tanahashi H, Matsuda S and Murakami M 1990 ISIJ Int. 30 674-679
[20] Tsuzaki K, Natsume Y and Maki T 1995 J. Physique IV 5 409-414