

Available online at www.sciencedirect.com



micron

Micron 40 (2009) 151-156

www.elsevier.com/locate/micron

Identification of ε martensite in a Fe-based shape memory alloy by means of EBSD

K. Verbeken^{a,b,1,*}, N. Van Caenegem^a, D. Raabe^b

^a Department of Metallurgy and Materials Science, Ghent University (UGent), Technologiepark 903, B-9052 Ghent (Zwijnaarde), Belgium ^b Microstructure Physics, Max-Planck-Institut für Eisenforschung, Max-Planck-Strasse 1, 40237 Düsseldorf, Germany

Received 14 November 2007; received in revised form 17 December 2007; accepted 30 December 2007

Abstract

Ferrous shape memory alloys (SMAs) are often thought to become a new, important group of SMAs. The shape memory effect in these alloys is based on the reversible, stress-induced martensitic transformation of austenite to ε martensite. The identification and quantification of ε martensite is crucial when evaluating the shape memory behaviour of this material.

Previous work displayed that promising results were obtained when studying the evolution of the amount of ε martensite after different processing steps with Electron BackScatter Diffraction (EBSD). The present work will discuss in detail, on the one hand, the challenges and opportunities arising during the identification of ε martensite by means of EBSD and, on the other hand, the possible interpretations that might be given to these findings. It will be illustrated that although the specific nature of the austenite to ε martensite transformation can still cause some points of discussion, EBSD has a high potential for identifying ε martensite.

© 2008 Elsevier Ltd. All rights reserved.

Keywords: Electron backscatter diffraction (EBSD); ε Martensite; Austenite; Iron based shape memory alloy; Identification; Transmission Electron Microscopy (TEM); Scanning Electron Microscopy (SEM); Confidence index (CI); Image quality (IQ)

1. Introduction

The shape memory effect of iron based shape memory alloys (SMAs) is based on the reversible, stress-induced martensitic transformation of the austenitic phase (fcc) to ε martensite (hcp). During this transformation, the ABCABC stacking sequence of the {1 1 1} planes, typical for a fcc crystal lattice, changes into an ABAB stacking, which is typical for a hcp lattice. The thin ε martensite plates that result from this transformation reveal specific crystallographic relationships relative to each other. This is due to the fact that during the transformation isolated *a*/6 (1 1 2) Shockley partial dislocations glide on every second {1 1 1}_y plane. There are three possible (1 1 2) shear directions on each {1 1 1}_y plane and

four equivalent $\{1\ 1\ 1\}_{\gamma}$ planes. Consequently, the austenite can result in four different ε martensite variants.

Ferrous SMAs based on the Fe–Mn alloy system are often considered to become a new class of SMAs of great technical importance, but the large hysteresis and a poor shape recovery in the Fe–Mn binary system still remain a drawback. Specific alloying additions of Si, Cr, Co, Ni and C were aimed to solve these problems. The shape memory effect in a single crystal of a Fe–30%Mn–1%Si alloy was first reported by Sato et al. (1982). Sato et al. (1986) and Murakami et al. (1986) also succeeded in developing polycrystalline FeMnSi SMAs. Moriya et al. (1991) and Otsuka et al. (1990) developed FeCrNiMnSi and FeCrNiMnSiCo SMAs. More recently, the effect of carbon on the shape memory mechanism in FeMnSiCrNi SMAs was studied by several authors (Van Caenegem et al., 2007; Wen et al., 2004; Bliznuk et al., 2004).

The identification and quantification of ε martensite is of crucial importance in order to evaluate the shape memory behaviour of an iron based SMA. So far, several attempts have been made in order to identify the ε martensite or to obtain a reliable measurement of the fraction of ε martensite, but the results of these attempts were often not satisfactory.

^{*} Corresponding author at: Department of Metallurgy and Materials Science, Ghent University (UGent), Technologiepark 903, B-9052 Gent (Zwijnaarde), Belgium. Tel.: +32 9 2645783; fax: +32 9 2645833.

E-mail address: kim.verbeken@UGent.be (K. Verbeken).

¹ Postdoctoral Fellow with the Fund for Scientific Research—Flanders (Belgium) (FWO-Vlaanderen).

^{0968-4328/\$ –} see front matter \odot 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.micron.2007.12.012

Most work was done by XRD (Ariapour et al., 1999; Jiang et al., 1996; Nakatsu et al., 1993; Tatar, 2006; Sawaguchi et al., 2006; Huang et al., 2008; Wen et al., 2007; Lin et al., 2006), but also Mössbauer spectroscopy (Jee et al., 2004), AFM (Sawaguchi et al., 2006) and dilatometry (Tomota, 1991) were used.

Previous work (Verbeken et al., 2008) showed an evaluation of the different amounts of ε martensite in a Fe-based SMA after different processing steps. This evaluation was performed by means of Electron BackScatter Diffraction (EBSD), making use of the automated version, known as orientation imaging microscopy (TSL-OIM[®]). Comparison was made between the obtained results and volume fractions measured by XRD. Although the results were considered to be very promising, the present work discusses in detail the challenges and opportunities that arise during the identification of ε martensite by means of EBSD and which are the possible interpretations that might be given to these findings.

2. Materials and methods

A FeMnSiCrNi SMA (0.05 m% C, 16.2 m% Mn, 6.4 m% Si, 9.5 m% Cr, 5.4 m% Ni) was cast in an air furnace, air cooled, reheated to $1200 \text{ }^{\circ}\text{C}$ and hot rolled on a laboratory mill from 20 mm to 2 mm and air cooled. After hot rolling, the alloy was isothermally annealed at $1100 \text{ }^{\circ}\text{C}$ for 15 min and water quenched to room temperature.

Samples for light optical microscopy (LOM) were first mechanically polished and then electropolished by means of a LectroPol-5 set-up. The electrolyte was a solution of 20% perchloric acid and 80% butylcellosolve. The electrolytical polishing is necessary to eliminate the ε martensite possibly formed on the surface during the mechanical polishing.

Thin foil TEM analysis was carried out on a Philips EM420, operated at 120 kV. Samples were prepared by electrolytical polishing with a solution of 95% CH₃COOH + 5% HClO₄ at a temperature of 12.5 °C and a voltage of 50 V.

X-ray diffraction (XRD) was also used to determine the different phases and their volume fraction. The measurements were done using a Siemens D5000 diffractometer with Mo radiation ($\lambda_{Mo} = 0.071$ nm). Volume fractions were determined using the formulas proposed by Cullity (1978) and by fitting the peaks in the $2\theta_{Mo}$ range of $18-29^{\circ}$, which mainly consists of the $\{1\ 1\ 1\}_{\gamma}$, $\{2\ 0\ 0\}_{\alpha}$ and $\{1\ 0\ 1\}_{\epsilon}$ peaks.

EBSD-scans were performed with a FEI XL30 ESEM microscope equipped with a LaB₆ filament. The samples were prepared by standard metallographic procedures. A statistically relevant area was scanned using a step size of 0.75 μ m. The raw data were post-processed in detail by making use of the TSL-OIM Analysis Software (2005). Each measurement point is characterized by its crystallographic orientation, a confidence index (CI) and an image quality (IQ).

The IQ describes the quality of the electron backscatter diffraction pattern. For the indexing of this pattern, a Hough transform (TSL Data Collection, 2005) is applied. This method has resulted in the definition of the IQ parameter as the sum of the detected peaks in the Hough transform (Kunze et al., 1993) and consequently, the Image Quality provides information on the pattern sharpness.

The CI is a measure for the reliability of the indexing of the diffraction pattern. For a given diffraction pattern several possible orientations may be found which satisfy the diffraction bands detected by the image analysis routines. The software ranks these orientations (or solutions) using a voting scheme. The confidence index is based on the voting scheme and is given as $CI = (V_1 - V_2)/V_{IDEAL}$ where V_1 and V_2 are the number of votes for the first and second solutions and V_{IDEAL} is the total number of number of Kikuchi bands triplets available (Field, 1997). A CI = 0 indicates a reliability of nearly 50% for correct indexing (Field, 1997). Points with a confidence index of less than 0.1 were not included when studying the obtained results.

3. Results and discussion

The light optical microstructural analysis of the material studied revealed the presence of large austenite grains and large coherent twins (TB) as sharp parallel lines with dark contrast within the austenite, as illustrated in Fig. 1. Thin lines are visible in different directions in most of the austenite grains. These lines can possibly be identified as stacking faults or as ε martensite plates. Other measurement techniques are needed to exclude one of them, which indicates immediately the limitations of optical microscopy for the identification of ϵ martensite. Moreover, as previous work for TWIP (Twinning Induced Plasticity) steels (Bracke et al., submitted for publication) illustrated nicely, it was also impossible to accurately identify micro-twins in TWIP steels with LOM, because it appeared to be unfeasible to distinguish between areas containing micro-twins and those that did not. In TWIP steels, different grains, observed with LOM, looked as if they had deformed by twinning, but local studies by EBSD of the misorientations in these areas later on showed that this was not the case.



Fig. 1. LOM microstructure of the SMA studied, hot rolled, air cooled, annealed at 1100 °C during 15 min and water quenched to room temperature, showing coherent twins with indicated twin boundaries (TB) and thin plates (TP) with different ε variants identified.



Fig. 2. (a) Bright field TEM image of a zone with ε martensite; (b) same area in dark field.

The present material was also studied by X-ray Bragg diffraction measurements, which revealed, after fitting, the presence of 3% of ε martensite. However, the use of such a fitting procedure for quantification raises some questions. At first, in literature, the inaccuracy of the XRD technique for small volume fractions of ε martensite is mentioned and it is stated that at least 5% of ε martensite is necessary to reveal this phase with XRD (Ariapour et al., 1999), while other sources (Stanford et al., 2007) mention the lack of ε peaks in a XRD diffractogram of a sample that is estimated to contain 3% of ε martensite. Secondly, a pronounced crystallographic texture will influence the height of the peaks. This disadvantage is believed to have an impact when studying samples with stress-induced ε martensite rather than for thermal ε martensite. This is because of the fact that there are three possible $\langle 1 \ 1 \ 2 \rangle$ shear directions on every $\{1 \ 1 \ 1 \}_{\gamma}$ plane. The thermally induced ε martensite consists of three laminated variants with different shear directions in order to minimize the total shape strain of the transformed region. The stress-induced ε transformation is accomplished by the selective motion of a single type of Shockley partial dislocation being most favourable to the direction of the applied stress. Therefore, the stressinduced ε band consists of a single variant. This results in a textured stress-induced martensite. Consequently, it can be stated that XRD rather gives a qualitative idea on the amount of ε martensite.

Another complicating factor when studying the presence of ε martensite in Fe-based alloys is the specific nature of the ε martensite. In a material, the ε containing areas appear as a lamellar structure consisting of a mixture of ε and γ phases. Concerning the growth mechanism of stress-induced ε martensite, Kikuchi et al. (1995) proposed that thin martensite plates are first formed rather uniformly through the grain and, in the further stage of transformation; some other thin plates nucleate and grow close to the first ones. This mechanism leads to a band structure containing some residual austenite between individual thin martensite plates. The thickness increase of the band does not result from a lateral growth of the martensite plates but from nucleation of some new plates close to the existing ones.

In order to illustrate the features of ε martensite, TEM was performed on a slightly deformed sample of the alloy studied in this work. The deformation increased the amount of ε martensite present and consequently made it easier to retrieve the ε martensite from the sample. In order to identify the ε martensite reflections, dark field TEM micrographs were taken, by setting these reflections at the exact Bragg-condition. Fig. 2 shows on the right the dark field image. The thin plate ε martensite plates light up in the dark field image and correspond

<1120>&



Fig. 3. Combined phase and IQ map for the material studied. The different phases each have their own color (γ : yellow, α : red, ϵ : green). The grey values give an indication of the IQ-factor; darker grey corresponds with a lower IQ.

to the black thin lines in the bright field image, nicely illustrating the appearance of a mixture of ε and γ phases. Fig. 2 shows that an identification of ε martensite by TEM is perfectly possible, but this technique does not allow to study a larger amount of material in an efficient manner and is therefore not suitable for quantification.

In previous work (Verbeken et al., 2008), the possibilities of EBSD to identify ε martensite in a Fe-based SMA were indicated. Fig. 3 shows a combined phase + IQ map of the present alloy. In this figure, the three phases have a specific colour, while the grey values give an indication for the IQ. Numerous small grains were identified as ferrite (red). The larger grains are austenitic (yellow) with clear twin boundaries present in several grains. Inside quite a few austenitic grains, different areas were identified as ε martensite (green). It should also be noticed that within the

austenite grains regions with a considerably lower IQ-factor are present, although these zones are identified as austenite.

Taking into account the features of the ε martensite formation, the spatial resolution of the electron microscope used was insufficient to reveal separate ε laths. This resolution is estimated to be about 0.1–0.2 µm and it was tried to optimize this resolution by decreasing the spot size during the measurements performed. Although because of the specific nature of the $\gamma \rightarrow \varepsilon$ transformation it remains impossible to resolve the different ε lamellae, it was shown that a correct indexing of the ε martensite is perfectly possible, as illustrated in Fig. 4(a). This figure shows an indexed ε martensite pattern (CI = 0.804) for which neither γ (CI = 0.004) nor α (CI = 0.018) appeared to be an alternative. Previous work (Verbeken et al., 2008) also showed that the four ε variants



Fig. 4. (a) Example of a diffraction pattern of ε martensite, illustrating the possibility to obtain an indexing with a high CI; (b) example of a diffraction pattern with clear band contrast which was indexed with CI = 0 because of 'dual' identification; (c) indexing of the diffraction pattern as ε martensite; (d) indexing of the diffraction pattern as austenite.

could be identified in a single austenite grain. However, the presence of a diffraction pattern with a good band contrast (cf. Fig. 4(b)) not always guaranteed a good indexing. As is illustrated in this figure, two 'reliable' indexings were possible for this diffraction pattern, both with the same CI: i.e. an indexing as ε martensite (cf. Fig. 4(c), CI = 0.167) and one as austenite (cf. Fig. 4(d), CI = 0.167). During an automatic OIM measurement, such a point results in a point with CI = 0 in the raw data file, since the reliability of the indexing will be 50%. This point is then omitted from further analysis of the data despite the clear diffraction pattern.

It could be aimed for to upgrade this data point in order to be able to include it into further analysis. As was pointed out by Nowell and Wright (2005), one of the variables in indexing EBSD patterns is the number of bands to be detected. In case of a too small amount of bands, it may become more difficult to determine a unique solution; a too high amount of bands can increase the difficulties for band detection algorithms to find bands in the diffraction pattern. Since both solutions of the diffraction pattern shown have some bands in common, due to the well-known orientation relationship between austenite and ϵ martensite, a thorough investigation of the collected pattern will be necessary in order to find an efficient indexing routine to determine the unique solution. Another way to be sure of a correct indexing of the pattern shown might be to apply a postprocessing algorithm as the one defined by Nowell and Wright (2005). If the orientation difference between a low CI point and one of its high CI neighbours is within a certain tolerance angle, the indexing solution for the low CI point can be considered to be the correct one. Although this procedure will certainly improve the statistics of the measurement, it could not be applied on the specific pattern shown in Fig. 4 because this pattern was collected during the start-up stage of the actual measurement.

The present results could be related to the specific appearance of ε martensite in the material (cf. Fig. 2). Every point that is measured during an EBSD measurement generates a diffraction pattern that contains information that arises from the diffracting volume. It might be reasonable to think that this volume consists for quite a few data points of a mixture of ε martensite and austenite. Consequently, it can be suggested that the high quality indexing in Fig. 4(a) is related with a high amount of ε martensite in the corresponding diffracting volume, whereas in the case of Fig. 4(b–d) the diffracting volume would contain similar amounts of both phases.

Another feature that is observed during EBSD measurements of Fe-based SMAs is the significantly lower IO-factor of the regions that are identified as ε martensite. This feature can be attributed to the presence of residual austenite in between the ε laths, which will influence the quality of the diffraction pattern negatively, but will nevertheless not make a correct indexing impossible (cf. Fig. 4(a)). Besides that several regions that are identified as austenite also have a lower IQ, as was demonstrated in Fig. 3. So far, it remains unclear what the exact explanation of this finding might be. One possible reason might be the presence of stacking faults in the austenite, which are considered in literature as embryos for ε martensite. Since they cause a distortion in the crystal lattice and consequently in the diffraction pattern, they lower the IQ-factor. Another reason might be that volume changes, caused by the $\gamma \rightarrow \epsilon$ transformation locally influence the IQ-factor. Future work, including high resolution SEM and TEM should provide more information on a possible interpretation.



Fig. 5. Results of the recalculation of the results shown in Fig. 3 allowing only one phase to be possible. Black points have a CI < 0.2. (a) Austenite; (b) ferrite; (c) ϵ martensite.

In order to try to clarify the lower IQ-factor and to study the effect of the dual indexing (cf. Fig. 4), the data of the measurement presented in Fig. 3 were used for recalculations. This was done by loading the corresponding data file, which included the Hough peaks (TSL Data Collection, 2005), into the data collection software and to analyse them again under the assumption that only one phase was present, namely either austenite or ferrite or ε martensite. In the present case, this resulted in three files from which the Inverse Pole Figure maps are shown for austenite (Fig. 5(a)), ferrite (Fig. 5(b)) and ε martensite (Fig. 5(c)), respectively. In this figure, data points with a CI < 0.2 are shown in black. It can be seen clearly from these figures that the sum of the three parts is more than 100% and that there are some austenitic grains which appear to be indexed completely as austenite in Fig. 5(a), also contain several data points that can reliably be indexed as ε martensite as shown in Fig. 5(c). When comparing these results with those in Fig. 3, it is seen that in the global picture in Fig. 3, these grains are identified as austenite, mostly even without a trace of ε martensite. The results shown in Fig. 5(c), however, clearly indicate the presence of ε martensite in these grains. Moreover, these grains also appeared to have a high IQ-factor. Furthermore, when looking at the austenitic grains with a low IQ-factor (cf. Fig. 3); this lower IQ-factor did not result in the appearance of a significant amount of ε martensite in these regions in Fig. 5(c). This observation favours the suggestion that the lower IQ-factor is due to the volume changes accompanied with the ε formation.

Although the present results show that EBSD has a high potential in analysing a reasonably large area for the presence of ε martensite, the specific nature of the ε martensite causes different difficulties to the analysing software and consequently in the interpretation of the results. Further research of the results shown in the present work is necessary in order to understand how the 'dual' identification will affect the correctness of the quantification of the ε martensite by means of EBSD and will give a clue on the overall correctness of previously obtained results (Verbeken et al., 2008) and on what interpretation can be given at the locally lower IQ-factor.

4. Conclusions

The identification of ε martensite is of crucial importance during the investigation of the shape memory behaviour of an iron based SMA. In the present work, the presence of ε martensite in a FeMnSiCrNi shape memory alloy was studied by means of Electron BackScatter Diffraction. Despite the specific nature of the $\gamma \rightarrow \varepsilon$ transformation, EBSD has a high potential for identifying ε martensite, although this specific nature also causes some points of discussion to remain unanswered for the moment.

References

- Ariapour, A., Yakubtsov, I., Perovic, D.D., 1999. Effect of nitrogen on shape memory effect of a Fe–Mn-based alloy. Mater. Sci. Eng. A262, 39–49.
- Bracke, L., Verbeken, K., Kestens, L., Penning, J. Study of the cold rolled microstructure and texture of a high Mn TWIP steel. Acta Mater., submitted for publication.

- Bliznuk, V.V., Gavriljuk, V.G., Kopitsa, G.P., Grigoriev, S.V., Runov, V.V., 2004. Fluctuations of chemical composition of austenite and their consequence on shape memory effect in Fe–Mn–(Si, Cr, Ni, C, N) alloys. Acta Mater. 52, 4791–4799.
- Cullity, B.D., 1978. Elements of X-ray Diffraction, second ed. Addison-Wesley Publishing Co Inc., p. 508.
- Field, D.P., 1997. Recent advances in the application of orientation imaging. Ultramicroscopy 67, 1–9.
- Huang, S.K., Wen, Y.H., Li, N., Teng, J., Ding, S., Xu, Y.G., 2008. Application of damping mechanism model and stacking fault probability in Fe–Mn alloy. Mater. Char. 59, 681–687.
- Jee, K.K., Han, J.H., Jang, W.Y., 2004. Measurement of volume fraction of epsilon martensite in Fe–Mn based alloys. Mater. Sci. Eng. A378, 319–322.
- Jiang, B., Xuan, Q., Zhou, W., Xi, L.Z., 1996. The effect of nitrogen on shape memory effect in Fe–Mn–Si alloys. Scripta Mater. 34 (9), 1437–1441.
- Kikuchi, T., Kajiwara, S., Tomota, Y., 1995. Microscopic studies on stressinduced martensite-transformation and its reversion in an Fe–Mn–Si–Cr–Ni shape-memory alloy. Mater. Trans. 36, 719–728.
- Kunze, K., Wright, S.I., Adams, B.L., Dingley, D.J., 1993. Advances in automatic EBSP single orientation measurements. Text. Microstruct. 20, 41–54.
- Lin, H.C., Lin, K.M., Wu, S.K., Wang, T.P., Hsiao, Y.C., 2006. Effects of thermo-mechanical training on a Fe₅₉Mn₃₀Si₆Cr₅ shape memory alloy. Mater. Sci. Eng. A438–440, 791–795.
- Moriya, Y., Suzuki, M., Hashizume, S., Sampei, T., Kozasu, I., 1991. Effect of alloying elements on shape memory effect. In: Proc. ICSS. pp. 527–532.
- Murakami, M., Otsuka, H., Suzuki, H.G., Matsuda, S., 1986. Complete shape memory effect in polycrystalline Fe–Mn–Si alloys. In: Proceedings of the International Conference on Martensitic transformations (ICOMAT-86), Japan Inst. Met., pp. 985–990.
- Nakatsu, H., Takaki, S., Tokunaga, Y., 1993. Effect of austenite grain size on epsilon martensitic transformation in Fe-15 mass percent Mn alloy. J. Jpn. Inst. Met. 57, 858–863.
- Nowell, M.M., Wright, S.I., 2005. Orientation effects on indexing of electron backscatter diffraction patterns. Ultramicroscopy 103, 41–58.
- Otsuka, H., Yamada, H., Maruyama, T., Tanahashi, H., Matsuda, S., Murakami, M., 1990. Effects of alloying additions on Fe–Mn–Si shape memory alloys. Trans. ISIJ 30, 674–679.
- Sawaguchi, T., Sahu, P., Kikuchi, T., Ogawa, K., Kajiwara, S., Kushibe, A., Higashino, M., Ogawa, T., 2006. Vibration mitigation by the reversible fcc/ hcp martensitic transformation during cyclic tension-compression loading of an Fe–Mn–Si-based shape memory alloy. Scripta Mater. 54 (9), 1885– 1890.
- Sato, A., Chishima, E., Soma, K., Mori, T., 1982. Shape memory effect in gamma reversible epsilon transformation in Fe–30Mn–1Si alloy singlecrystal. Acta Metall. 30, 1177–1983.
- Sato, A., Chishima, E., Soma, K., Mori, T., 1986. Physical properties controlling shape memory effect in Fe–Mn–Si alloys. Acta Metall. 34, 287–294.
- Stanford, N., Dunne, D.P., Monaghan, B.J., 2007. Austenite stability in Fe–Mn– Si-based shape memory alloys. J. Alloys Compd. 430, 107–115.
- Tatar, C., 2006. The effect of prior pressure-treatment on the transformation behavior of Fe–32%Mn–6%Si alloy. Mat. Lett. 120–123.
- Tomota, Y., 1991. Phase-transformation, microstructure, and mechanical-behavior in Fe–Mn alloys. Tetsu-to-hagane 77, 315–325.
- TSL[®]OIM Analysis for Windows, 2005.
- TSL [®] OIM data collection for Windows, 2005.
- Van Caenegem, N., Duprez, L., Verbeken, K., De Cooman, B.C., Houbaert, Y., Segers, D., 2007. Effect of carbon on the shape memory effect in FeMn-SiCrNi SMAs. ISIJ 47, 723–732.
- Verbeken, K., Van Caenegem, N., Verhaege, M., 2008. Evolution of the fraction ε-martensite in a FeMnSiCrNi shape memory alloy. Mater. Sci. Eng. A. 481–482, 471–475.
- Wen, Y.H., Yan, M., Li, N., 2004. Effects of carbon addition and aging on the shape memory effect of Fe–Mn–Si–Cr–Ni alloys. Scripta Mater. 50, 441– 444.
- Wen, Y.H., Zhang, W., Li, N., Peng, H.B., Xiong, L.R., 2007. Principle and realization of improving shape memory effect in Fe–Mn–Si–Cr–Ni alloy through aligned precipitations of second-phase particles. Acta Mater. 55, 6526–6534.