HREM Study of Stress-Induced Transformation Structures in an Fe–Mn–Si–Cr–Ni Shape Memory Alloy

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Transformation structures produced by extension of an Fe–14Mn–6Si–9Cr–5Ni (mass%) shape memory alloy have been studied by high resolution electron microscope, in order to know the origin of the improved shape recovery of a thermomechanically treated specimen. Nanometric substructures in the "deformation band" which is produced by stress-induced transformation are clarified by taking (00.1) and (10.0) lattice images of the h.c.p. structure of martensite and (111) lattice images of the f.c.c. structure of parent phase. It is found that a distinct difference exists between the deformation bands of the thermomechanically treated specimen and the non-thermomechanically treated specimen, namely, the minimum unit of deformation band with about 0.2 μm thickness consists of lamella structures having a mixture of f.c.c. phase and h.c.p. phase with 1–10 nm widths for the former case, but, for the latter case, it mostly consists of h.c.p. phase only. This difference is discussed in relation to the difference in shape memory effect. Stacking faults in martensite are also studied by electron diffraction.

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I. Introduction

Recently, studies of shape memory effects have begun to concentrate on Fe-based shape memory alloys to find an alloy comparable to the famous NiTi alloy, because the latter alloy is very expensive and a much cheaper shape memory alloy is being sought. The most promising alloy will be among Fe–Mn–Si alloys\(^ {10–13}\) and their modification, i.e., Fe–Mn–Si–Cr–Ni alloys\(^ {10–13}\) which have a property of corrosion-resistance. The martensitic transformation involved in the shape memory effect of these alloys is f.c.c. → h.c.p. and so, the martensite plate (h.c.p.) is usually very thin, which comes from the mode of lattice deformation of this alloy system; that is, the transformation from the austenite (f.c.c.) to the martensite is macroscopically accomplished by a simple shear of 0.35 on the habit plane, \((111)_{h.c.p.}\), and microscopically, by introduction of stacking faults on every second layer. In our preliminary study, using a high resolution differential interference optical microscope, we found that a martensite plate in an Fe–Mn–Si–Cr–Ni alloy, which was induced by extension and seemed to be a single plate by a conventional optical microscope, consisted of much smaller plates with the width of about 0.2 μm. Conventional electron microscopy suggests that this thin plate of about 0.2 μm thickness has further lamella substructures.

In the present work, in order to understand the mechanism of the shape recovery of these alloys, transformation structures induced by extension after different heat treatments which give rise to different degrees of shape recoveries have been studied by high resolution electron microscope from the viewpoint of nanometric scales. Analysis of stacking faults in martensite has also been made by electron diffraction.

II. Experimental Method

The alloy used is an Fe–14Mn–6Si–9Cr–5Ni (mass%) alloy. The result of chemical analysis of this alloy is shown in Table 1. One kind of the specimens has been subjected to such a thermomechanical treatment that a specimen which had been solution-treated at 1320 K for 30 min was first cold rolled by 10% at room temperature and then heated to 970 K for 10 min. This heat treatment produces a better shape memory effect than that of specimens which were merely subjected to the solution-treatment; that is, the shape recovery of the former is about 80%, while that of the latter is about 50% when the amount of shape change is 4% elongation. The Ms temperatures of the thermomechanically treated and the non-thermomechanically treated specimens are 250 K and 300 K, respectively. The specimens 4 mm in width, 40 mm in gauge length and 0.4 mm in thickness were extended by 4% at room temperature after both types of the heat-treatments. Specimens for electron microscope observation were prepared by electropolishing, using a twin-jet polisher. For high resolution transmission electron microscopy and electron diffraction, JEM-4000EX type electron microscope with a top entry specimen holder coupled with a gonio-stage was employed. The accelerated voltage was 400 kV.

| Table 1 Chemical composition (mass%) of the alloy used. |
|----------------|---------|---------|---------|---|-------|---|---|
| Mn  | Si  | Cr  | Ni  | C  | P  | S  | Fe |
| 14.09 | 6.17 | 8.97 | 5.29 | 0.004 | 0.003 | 0.0004 | bal. |
III. Experimental Results

1. Electron microscopic observations

It is important to know what kinds of lattice defects are present in the thermomechanically treated specimens. Figures 1 and 2 are typical examples of electron micrographs obtained from the thermomechanically treated specimens before extension. Many stacking faults are observed; Figure 1 shows wide stacking faults and, in Fig. 2, we notice fragmental stacking faults and some dislocations. These dislocations, however, seem to be very easily extended and become partial dislocations as seen from the fact that a part of a dislocation line often accompanies the stacking fault fringe. Ordinary perfect dislocations were scarcely observed. In the case of the specimens solution-treated only, there were no such stacking faults as shown in Figs. 1 and 2.

For convenience sake, we denote hereafter in this paper the specimens thermomechanically treated as specimen A and those solution-treated only as specimen B.

Figure 3 shows an example of rather low magnification micrograph of a specimen which was extended by 4% at room temperature. Bands with black contrast are h.c.p. martensite induced by extension and its basal plane is perpendicular to the specimen foil. Figure 4 shows an electron micrograph with a relatively high magnification, showing that each of the black bands in Fig. 3 actually consists of further lamella structures with an approximately 200 nm width. In this figure the basal plane of h.c.p. (martensite) is also perpendicular to the specimen.

Fig. 1 Electron micrograph showing wide stacking faults in austenite of thermomechanically treated specimens (specimen A).

Fig. 2 Electron micrograph showing fragmental stacking faults and dislocations in austenite in specimen A.

Fig. 3 Bands of martensite (h.c.p.) in low magnification electron micrograph. The habit plane, (111), is approximately normal to the foil plane (specimen A).
foil and so we can see finer striated structures in each lamella. Figures 3 and 4 were taken from specimen A, but up to this magnification there is no difference between specimens A and B. A distinct difference has appeared when we compare lattice images of these differently heat-treated specimens.

Figure 5 shows an electron diffraction pattern which consists of \([0\bar{1}1]_\text{f.c.c.}\) zone axis and \([01.0]_\text{h.c.p.}\) zone axis and most of lattice images shown hereafter were taken with all the diffraction spots in this figure which pass through an objective lens aperture. Lattice images of \((00.1)_{\text{h.c.p.}}\) are seen parallel along arrow with \(\mathbf{h}\) in large parts of the area in Fig. 6 and almost all over the place in Fig. 7. The former were taken from specimen A and the latter from specimen B. The rest of the area indicated by upward arrows in Figs. 6 and 7 is the f.c.c. parent phase, though the lattice images of \([111]_\text{f.c.c.}\) can be clearly identified only in a more magnified micrograph such as Fig. 8. It should be noted that the area of f.c.c. is very small in Fig. 7. It is considered that different contrasts in the \((00.1)_{\text{h.c.p.}}\) lattice images in Figs. 6 and 7 indicate that stacking faults exist at such places. Figures 8 and 9 show further enlargements of these micrographs. In these extremely high magnification micrographs, \((10.0)\) lattice images in the h.c.p. structure are resolved as well as \((00.1)_{\text{h.c.p.}}\) lattice images and \([111]_\text{f.c.c.}\) lattice images. The spacings of these lattice images are 0.22 nm, 0.42 nm and 0.21 nm, respectively. We can see in these high magnification micrographs that f.c.c. phase with the thickness of down to 3–5 layers of the \((111)\) lattice spacing are mixed (indicated by arrows in Fig. 8) with the h.c.p. phase in specimen A, but no such mixture is seen in the case of specimen B (Fig. 9). Lattice images with the spacing of 0.63 nm are seen besides those of \((00.1)_{\text{h.c.p.}}\) in Fig. 9 and these are considered to correspond to stacking faults with a stacking order similar to 9R structure, namely, ABC/BCA/CAB, because the spacing of the lattice

**Fig. 4** High magnification electron micrograph showing that the band consists of fine lamella structures (specimen A).

**Fig. 5** Electron diffraction spots with which lattice images of \((00.1)_{\text{h.c.p.}}, (10.0)_{\text{h.c.p.}}\) and \([111]_\text{f.c.c.}\) were taken.
image is about 1.5 times larger than that of (00.1)_{h.c.p.} lattice image.

In order to know more quantitatively the distribution of the mixture of f.c.c. and h.c.p. phases, lattice images of each phase have been examined along a given line perpendicular to the (00.1)_{h.c.p.} lattice image. (In some area atom rows of [011]_{f.c.c.} are clearly resolved in the structure image.) The observed distributions of the f.c.c. and h.c.p. phases and stacking faults in h.c.p. phase are shown in Figs. 10 and 11 for specimens A and B, respectively. The width of the observed deformation bands was in the range of 100–200 nm. More than ten of such bands in each specimen were examined in detail and Figs. 10 and 11 show three examples of them for each specimen.

In these figures the lengths of horizontal lines represent the thickness of each phase, and stacking faults are mostly expressed by dots or in some case by a continuous line which means that stacking faults occur continuously. A set of notations, s.f. (which denotes "stacking fault"), h.c.p. and f.c.c. are labelled at the left side for each group of the measurements and the horizontal axis indicates the distance from the end of the band along a line perpendicular to the (00.1)_{h.c.p.} lattice image. As shown in these figures, there is a clear difference in the distribution between specimens A and B; that is, for specimen A, the band usually consists of a mixture of f.c.c. and h.c.p. phase with the thickness of 1–10 nm, while for specimen B, there are very few cases where the f.c.c. phase is mixed...
with h.c.p. phase in the band, i.e., in most cases there exists no f.c.c. phase in the band as seen in the bottom two examples of Fig. 11.

2. Electron diffraction analysis

As described in the preceding section, there are many stacking faults in the h.c.p. phase. It is considered that electron diffraction spots are diffused and shifted due to these stacking faults. Figure 12 (a) and (b) show parts of diffraction patterns of h.c.p. phase, which also contain spots from f.c.c. phase; (a) was taken from a region of 5 μm in diameter and (b) from a region of 0.2 μm in diameter. The both patterns were taken from specimen A. In (b), spots with weak intensities and small separations are observed between the main spots, which indicates the existence of rather regular faulting with long periods. In the case of (a), the diffraction pattern was taken from a large area, 25 times larger than in (b), these small spots are then averaged out and appear as streak. In the present work, however, only main spots are analyzed to examine stacking faults in the h.c.p. martensite. In Fig. 12 the distance between 10.1 and 10.2 spots of h.c.p phase is smaller than that between 10.0 and 10.1 spots, which indicates that spots 10.0 and 10.2 have shifted toward the right and the spot 10.1 toward the left, namely, these spots approach f.c.c. spots such as 200 and 111.
The extent of the shifts is such that the distance between 10.1 and 10.2 spots (and its equivalent distance between 10.0 and 10.1 spots) is in the range of 165°–175° when the unshifted value is taken as 180°, i.e., one period along c*-axis is expressed as 360°. From the amounts of the shifts of these diffraction spots, the fault parameter \( \alpha \) has been estimated to be 0.1–0.3 after the method employed by Kajiwara\(^{88} \) for Co and its alloys. The meaning of the fault parameter is such that \( \alpha = 1 \) represents the normal unfaulted stacking sequence of f.c.c. crystal, i.e., ABCABC—. The value of \( \alpha \) was different from band to band mentioned in the preceding section. However, there was no systematic difference in obtained value of \( \alpha \) between specimens A and B. Although we do not describe the detail of analysis in this paper, the fact that the observed h.c.p. spots are shifted toward the matrix f.c.c. spot indicates that the stacking faults in the h.c.p. martensite occur in such a way that the stacking order may approach that of the parent f.c.c. crystal. It should be noted that the stacking order do not approach that of the twin of the matrix f.c.c. phase. That is, the ABAB— stacking sequence in the martensite is likely to be faulted.
toward the ABCABC—stacking sequence, not toward the CBACBA—stacking sequence. Such result of the analysis of the faulting in the martensite may suggest a mechanism of the martensite formation as will be discussed later.

IV. Discussion

HREM has revealed that in specimen A the band of about 200 nm thickness, which is the minimum unit of deformation structures, consists of a mixture of h.c.p. phase (martensite) and f.c.c. phase (parent phase) with very small thickness of 1–10 nm, while in specimen B this band is scarcely mixed with the f.c.c. phase. This fact may be related to the difference in shape recovery between specimens A and B. That is, it is quite conceivable that the reverse transformation to the parent phase is much easier for specimen A than for specimen B, because it is not necessary to nucleate the f.c.c. phase in specimen A. But in specimen B it will be necessary to nucleate the f.c.c. phase in the band in order to initiate the reverse transformation in nanometric scales. To minimize the shape deformation of each martensite plate for the shape recovery, it will be important to make the reverse transformation proceed in a scale as small as possible. If the reverse transformation occur in a large scale in the sense that the h.c.p. band transforms as a whole, then the resistance accompanying the shape deformation may be greater because the accommodation deformation must be large in that case.

There is a similar thermomechanical treatment of so-called the “training” for Fe-Mn-Si\(^{10}\) and Fe-Mn-Si-Cr-Ni\(^{12}\) alloys, in which deformation by 2.5% at room temperature and annealing at 870 K for 10 min are repeated several times. By this heat-treatment the shape recovery is increased from 60% to 100%. Otsuka et al.\(^{12}\) concluded that such improvement of the shape memory effect is attributed to (1) the increase in yield stress of austenite and (2) the decrease in the critical stress for the martensite formation. They claim that the former is brought about by work hardening during the “training” and useful for suppressing slip in austenite, and that the latter is caused by introduction of stacking faults which may serve nucleation sites for the f.c.c. to h.c.p. transformation. These two factors are certainly effective for the improvement of shape memory effect (SME). However, it should be emphasized that there is another effect of the “training” on SME, that is, the “training” will make the reverse transformation easier by producing the band structure with a mixture of f.c.c. and h.c.p. phase in nanometric scales as in the present thermomechanical treatment.

Finally we discuss the result of electron diffraction analysis of the stacking faults in h.c.p. martensite. The fact that the stacking order in the martensite is faulted in such a way that the stacking sequence approaches that of the parent f.c.c. phase means that the transformation from f.c.c. to h.c.p. by deformation is not accomplished by the regular introduction of stacking faults every two layers, but some extent of skipping of such faulting have frequently occurred. This is probably caused by the resistance to the shape deformation accompanying the f.c.c. to h.c.p. transformation. On the other hand, the existence of such stacking faults will provide the nucleation sites for the reverse transformation on heating.

V. Concluding Remarks

A mixture of f.c.c. and h.c.p. phases in nanometric scales in specimen A is considered to have resulted from the existence of stacking faults in austenite before the extension as shown in Figs. 1 and 2. That is, these stack-
ing faults provide nucleation sites for the f.c.c. to h.c.p.
transformation. In specimen B, since there are no such
stacking faults, the transformation by extension will pro-
ceed by thickening a band once the h.c.p. phase has
nucleated at a certain place. Therefore, it is necessary
that, to obtain good shape memory effect, many stacking
faults in austenite are scattered as uniformly as possible
so that the resulting deformation band consists of a
uniform mixture of f.c.c. and h.c.p. phase in nanometric
scales. So-called “the training effect” in this kind of
alloys may play an important role to increase the number
of stacking faults, besides the increase in yield stress of
the parent phase.

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