Mechanism of the Improvement of the Shape Memory Effect by “Training” and Ausforming in Fe–Mn–Si Based Shape Memory Alloys^{*1}

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The effects of “training” and ausforming on the morphology of stress-induced martensite and its reversion behavior to austenite in Fe–14Mn–6Si–9Cr–5Ni and Fe–28Mn–6Si–5Cr (mass%) alloys have been studied using atomic force microscopy (AFM), with the aim of clarifying the mechanism of the improvement of the shape memory effect. It is found that uniformly distributed thin martensite plates with a single variant nature are formed in a grain for both of the trained and ausformed samples. Those martensite plates can almost completely revert to the parent phase by shearing process, which is opposite to that of the forward transformation. This complete reverse transformation produces a perfect shape memory effect.

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1. Introduction

Nearly two decades ago it was first shown that Fe–Mn–Si based alloys show good shape memory effect,^{1–3)} but since then, no major industrial applications have been made except a few experimental examples^{4–6)} despite of their low cost, good workability, good machinability and good weldability. The main reason for this is that these alloys exhibit only incomplete shape memory effect in the as-solution treated condition except for some special cases, such as deformation of single crystals^{1–3)} and very small strain of polycrystalline.⁷⁾ For example, the shape recovery ratio is about 50 for 4% strain in Fe–28Mn–6.5Si (mass%)⁸⁾ and Fe–14Mn–6Si–9Cr–5Ni (mass%).^{9,10)} In order to obtain nearly perfect shape memory effect, we must perform a special thermomechanical treatment, so-called the “training”, which consists of several cycles of deformation for stress-induced martensitic transformation at room temperature and the subsequent heating to an intermediate temperature for reversion of the martensite to austenite.¹¹⁾ The ausforming at an appropriate temperature is also effective to improve the shape memory effect.^{12,13)}

Otsuka *et al.*¹¹⁾ pointed out that the training increases the austenite yield stress and reduces the critical stress for the fcc/hcp martensitic transformation for these alloys, and considered that this fact is the key for improvement of the shape memory effect by this treatment. On the other hand, Kajiwar¹⁴⁾ one of the present authors, recently concluded from the microscopic observations^{15–18)} that the formation of very thin martensite plates with uniform distribution is the most important factor to obtain good shape memory effects. The present work by atomic force microscope (AFM) provides clear evidence for this supposition by Kajiwar. One of the great benefits of usage of AFM for studying the fcc/hcp martensitic transformation is that we can identify each martensite variant among three possible variants formed on a

{111} habit plane if the fcc matrix orientation is known.¹⁹⁾ Even in the case of unknown orientations, we can easily find different variants on the same habit plane by AFM images as will be described later. It is impossible to know that by electron microscope, because three different variants on the same habit plane have the exactly same orientation, although they have different shear directions in the fcc to hcp transformation. The direction and amount of shear involved in the transformation are closely associated with the shape memory effect of this alloy system.

2. Experiment Procedure

The alloys used for training and ausforming were Fe–14Mn–6Si–9Cr–5Ni and Fe–28Mn–6Si–5Cr (mass%) respectively. The starting specimens for two kinds of alloys were subjected to solution heat treatment at 1320 K for 30 min. The Ms and Af temperatures were 250 and 630 K for Fe–14Mn–6Si–9Cr–5Ni alloy, and 280 K and 570 K for Fe–28Mn–6Si–5Cr alloy. For the Fe–14Mn–6Si–9Cr–5Ni alloy, the “training” means the processes of stress-induced martensitic transformation by 4% extension at room temperature and subsequent reversion treatment at 870 K for 10 min in an evacuated silica capsule. After each of the first and the fourth training cycles, the specimen surface (~20 μm) was slightly polished using electrolytic method to remove the retained surface relief. This process was necessary for the observation of newly introduced martensite in the subsequent training cycle. Several areas of the specimen surface were continuously observed by AFM after each stepwise deformation and stepwise heating on the training cycles. AFM observation was performed in air under a tapping mode using Nanoscope Dimension 3000 of Digital Instruments Inc.

3. Results and Discussion

AFM images shown in the present paper are a gray-scale representation of the derivative of the height of the specimen surface with respect to the scanning distance. When

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martensitic transformation occurs, the specimen surface of the martensite is tilted and a martensite plate appears in a color depending on the value of the surface tilt created by the transformation shear; that is, one color is associated with one shear value. Therefore, different martensite variants on the same $\{111\}_\gamma$ habit plane appear with different colors. This is a characteristic feature of AFM images which is very useful for identifying the deformation mode in this kind of shape memory alloys.

Figures 1(a), (b) and (c) show AFM micrographs of a same area in a grain taken at each stage on training cycles. Micrographs (a), (b), (c) are of the specimen deformed by about 4% strain on the 1st, 2nd and 5th cycle respectively, and their shape recovery ratios were 56, 79 and 96%, respectively. It is clearly seen in this series of micrographs that the number of martensite plates is increased and their width becomes smaller with the training cycles. The distribution of martensite plates becomes more uniform with increasing training cycles and, moreover, the color of martensite plates in the original AFM color pictures becomes the same for those in the 5th cycle. This fact means that all of those thin martensite plates in the

5th cycle have the same variant.

Figures 2(a), (c) and (e) are the enlarged micrographs of the small white-framed areas in Figs. 1(a), (b) and (c), respectively. Micrographs (b), (d) and (f) in this figure show the same areas as those of (a), (c) and (e) after being heated to 670 K. We can notice by detail inspection of micrograph (a) that thin martensite plates with darker contrast are mixed with those of the lower contrast in the case of the 1st cycle. In the original color picture, the color of the former ones is dark brown while that of the latter ones is light brown, which indicates these martensite plates are of different variants although they have been formed on the same habit plane. In micrograph (e), there are seen martensite plates on the two different habit planes, but all the martensite plates on each habit plane have the same color in the original picture, which means that the martensite plates with the same variant have been formed on the respective habit plane. It seems that there is a grain boundary at the location indicated by a pair of short lines in (e). This boundary has probably appeared in sight by removal of the surface layers after the 1st and 2nd training cycles. It should be noted in this micrograph that thin martensite plates with a same variant have been formed in the respective grains, suggesting that one kind of martensite variant is likely to be formed for each grain after several training cycles. This has been found to be generally true in the trained sample. By comparing the corresponding micrographs before and after heating to 670 K, it is clear that considerable number of martensite plates have not reverted to the original austenite for the non-trained sample, (b), especially most of the intersected martensite plates on the different habit planes do not undergo the reversion. On the other hand, thin martensite plates in the trained sample have almost completely disappeared by heating, (f).

Figures 3(a) and (b) show the deformed state by 4% tensile elongation at room temperature and the same area after heating to 670 K for an ausformed sample of Fe–28Mn–6Si–5Cr alloy. This sample was subjected to pre-straining by 9% of elongation at 970 K. This treatment gives shape recovery of 90%. Thin martensite plates in (a) have completely disappeared by heating in (b). The martensite plates have the same color in the original AFM picture, indicating that they are the same variant. In fact, this can be verified by the cross-sectional roughness of the sample surface shown in Fig. 3(c). This roughness curve represents the height change of the surface along a white line x - y in (a) and the regions with the negative slope correspond to the martensite plates. It is seen in this curve that the slopes of those regions are nearly the same, which clearly show that they are the same variant. The corresponding curve after heating is shown in Fig. 3(d). As a matter of course, the roughness is virtually flat. A similar AFM observation was made for the samples subjected to ausforming at other temperatures, but, the same deformation structures such as shown in Fig. 3(a) were not observed and the behavior of shape recovery for those samples was not so good as shown in Table 1. Therefore, we can conclude that the formation of thin martensite plates with the same variant is essential to exhibit good shape memory effect also for the ausformed sample.

The results of the present work strongly support the proposition made by Kajiwar¹⁴ that the formation of thin martensite plates with the same variant is the key factor to obtain good shape memory effect in Fe–Mn–Si based shape memory alloys. Kajiwar also discussed the origin of the formation of such martensite structures and assumed that uniformly

Fig. 1 Series of AFM micrographs of a same area in the training cycles. (a) 1st cycle, (b) 2nd cycle and (c) 5th cycle. All the micrographs show the deformed state by about 4% extension.

Fig. 2 (a), (c) and (e) are enlarged micrographs of small white-framed areas of Figs. 1(a), (b) and (c), respectively. Micrographs (b), (d) and (f) show the corresponding surface of those of (a), (c) and (e) after being heated to 670 K. Micrograph (f) is somewhat shifted to the right with respect to (e) and an identical point is indicated by arrow. A pair of lines in (e) and (f) indicates the location of a grain boundary which has been in sight by removal of the surface layers after 1st and 2nd training cycles.

distributed stacking faults in austenite, which are introduced by the training, are the primary factor for producing such structures. Very recently, Wang *et al.*¹³⁾ reported that uniformly distributed stacking faults are produced by ausforming at 970 K for Fe–28Ni–6Si–5Cr alloy, which is the most appropriate ausforming temperature to obtain good shape memory effect as shown in Table 1. This is further evidence for the validity of the assumption made by Kajiwara.

4. Concluding Remarks

The effects of “training” and ausforming on formation of stress-induced martensite and its reversion behavior to austenite in Fe–14Mn–6Si–9Cr–5Ni and Fe–28Mn–6Si–5Cr (mass%) alloys have been studied using atomic force microscopy (AFM) aimed for clarifying the mechanism of the improvement of the shape memory effect. It is found that uniformly distributed thin martensite plates with a single variant are formed in a grain for both of the trained and ausformed samples. Those martensite plates can almost completely re-

vert to the parent phase by shearing process, which is opposite to that of the forward transformation. This complete reverse transformation produces a perfect shape memory effect. It is suggested that the existence of uniformly distributed stacking faults in austenite is the most indispensable condition for formation of uniformly distributed thin martensite plates with a single variant. In order to obtain such internal structures of austenite, some kinds of thermomechanical treatments, such as the “training” and ausforming are unavoidable, however, this would substantially raise the production cost of the shape memory materials. Alternative method would be to produce very small coherent precipitates in austenite, which can serve as nucleation sites for hcp martensite. Then, uniformly distributed thin martensite plates would be formed by applied stress and, consequently, good shape memory effect could be obtained without any complicated thermomechanical treatments. Intensive research along this line is now being made in our laboratory, and some primary results will be reported recently.^{20–22)}

Fig. 3 (a) and (b): AFM micrographs of deformed state by 4% extension and the corresponding area after being heated to 670 K. Both micrographs are taken from the same areas before and after reverse transformation. Same spots are indicated by arrows. (c) and (d): Curves showing change in the surface height along while lines in (a) and (b), representing the cross-section of the respective surfaces.

Table 1 Shape memory recovery ratio dependence on ausforming temperature for the same pre-straining of 9%.

Ausforming temperature	As-solution treated	570 K	770 K	970 K	1170 K
Recovery ratio	55%	61%	71%	77%	64%

REFERENCES

- 1) A. Sato, E. Chishima, K. Soma and T. Mori: *Acta Met.*, **30** (1982), 1177–1183.
- 2) A. Sato, E. Chishima, Y. Yamaji and T. Mori: *Acta Met.*, **32** (1984), 539–547.
- 3) A. Sato, Y. Yamaji and T. Mori: *Acta Met.*, **34** (1986): 287–294.
- 4) H. Takahashi, T. Maruyama and H. Kubo: *Proc. 3rd IUMRS Int. Conf. on Advanced Materials*, Ikebukuro, Tokyo, (1993)/B: Shape Memory Materials and Hydrides; *Trans. Mat. Res. Soc. Japan*, **18B** (1994), 1149–1154.
- 5) D. Z. Liu, W. X. Liu and F. Y. Gong: *Proc. Int. Conf. on Martensite Transformation*, Lausanne, (1995), *J. Physique IV*, C8 (1995), 1241–1246.
- 6) D. Z. Liu, D. F. Wang, W. Y. Ji and W. X. Liu: *Proc. 2nd Int. Conf. on Shape Memory and Superelastic Technologies*, California, 1997, published by SMST, (1997), pp. 329–334.
- 7) M. Murakami, H. Otsuka, H. G. Suzuki and S. Matsuda: *Proc. Int. Conf. on Martensitic Transformations*, Nara, 1986, Japan Inst. Met., (1987), pp. 985–990.
- 8) J. S. Robinson and P. G. McCormick: *Scripta Metall.*, **23** (1989), 1975–1978.
- 9) H. Inagaki: *Z. Metallkd.*, **83** (1992), 304–309.
- 10) M. M. Reyhani and P. G. McCormick: *Mater. Sci. and Eng., A* **160** (1993), 57–61.
- 11) H. Otsuka, M. Murakami and S. Matsuda: *Proc. of MRS Int. Meeting on Adv. Mater.*, Materials Research Society, Tokyo, (1989), pp. 451–456.
- 12) M. Murakami, H. Otsuka and S. Matsuda: *Trans. ISIJ*, **27** (1987), B-89.
- 13) D. Wang, W. Ji, M. Han, D. Jia and W. Liu: *Proc. Int. Symp. on Shape Memory Materials*, Kanazawa, Japan, 1999, Materials Science Forum, **327–328** (2000), 263–266.
- 14) S. Kajiwaru: *Proc. Int. Conf. on Martensitic Transformation*, 1998, Bariloche, Argentina, *Mat. Sci. & Eng., A* **273–275** (1999), 67–88.
- 15) K. Ogawa and S. Kajiwaru: *Mater. Trans. Japan Inst. Met.*, **34** (1993), 1169–1176.
- 16) T. Kikuchi, S. Kajiwaru and Y. Tomota: *Mater. Trans. JIM*, **36** (1995), 719–728.
- 17) T. Kikuchi, S. Kajiwaru and Y. Tomota: *Proc. Int. Conf. on Martensitic Transformation*, 1995, Lausanne, Switzerland, *J. Physique IV*, C8 (1995), 445–450.
- 18) S. Kajiwaru and K. Ogawa: *Proc. Int. Symp. on Shape Memory Materials*, Kanazawa, Japan, Materials Science Forum, **327–328** (2000), 211–214.
- 19) D. Z. Liu, T. Kikuchi, S. Kajiwaru and N. Shinya: *J. Intelligent Mater. Systems and Structures*, (2000), in press.
- 20) D. Z. Liu, S. Kajiwaru, T. Kikuchi and N. Shinya: *Collected Abstracts of the 2000 Spring Meeting of Japan Inst Metals*, p. 250.
- 21) D. Z. Liu, S. Kajiwaru, T. Kikuchi and N. Shinya: *Proc. of the 3rd International Conference on Shape Memory and Superelastic Technologies*, April 30 to May 4, 2000, CA, USA, published by International Organization on Shape Memory and Superelastic Technologies, in press.
- 22) S. Kajiwaru, D. Liu, T. Kikuchi and N. Shinya: *Proc. 5th European Symposium on Martensite Transformations and Shape Memory Alloys*, Villa Olmo, Como, Italy, 4–8 September (2000), *J. de Physique IV*, in press.