Effect of Pre-Deformation of Austenite on Shape Memory Properties in Fe–Mn–Si-based Alloys Containing Nb and C

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The shape memory properties of Fe–Mn–Si-based alloys containing Nb and C are further improved by pre-rolling of the solution-treated austenite and the subsequent ageing treatment. For an Fe–28Mn–6Si–5Cr–0.53Nb–0.06C (mass%) alloy, 90% of an initial 4% strain is recovered on heating without any previous training treatment, if the alloy in austenitic state is rolled by 6–14% at 870 K and aged at 1070 K for 10 min to produce NbC precipitates. In the same condition, the alloy develops shape recovery stresses of 255 MPa and 295 MPa for 6% and 14% pre-rolling, respectively, when initially deformed by 4.5%. TEM observations indicate that these improved shape memory characteristics are related to a fine distribution of NbC precipitates in the fcc matrix and their interaction with stacking faults.

(Received January 7, 2002; Accepted February 8, 2002)

Keywords: iron based shape memory alloy, shape recovery, shape recovery stress, training process, niobium carbide

1. Introduction

It was recently found that the shape memory effect (SME) in Fe–Mn–Si-based alloys can be greatly improved by addition of small amounts of Nb and C.1–3) Good shape recoveries were attained in these alloys by producing NbC precipitates by ageing without any previous “training” treatment. For example, 80% shape recovery was reported for an Fe–28Mn–6Si–5Cr–0.5NbC alloy initially strained by 4%,1,11 in comparison to 50% shape recovery for a non-trained similar alloy without NbC. The training treatment in Fe–Mn–Si based shape memory alloys consists of several thermal cycles, each of which includes a small amount of deformation by stress-induced martensitic transformation at room temperature and the subsequent heating above the reverse transformation temperature.4) Previous research5–7) showed that the key to obtain high shape recoveries by training in Fe–Mn–Si-based alloys is to produce very thin martensite plates of the same variant in each grain. In order to further improve both the shape recovery and the shape recovery stress in the newly developed Fe–Mn–Si-based alloys containing NbC, we investigate the effects of pre-deformation of the austenite and time of the subsequent ageing on SME.

2. Experimental

An Fe–28Mn–6Si–5Cr–0.53Nb–0.06C (mass%) alloy was prepared by induction melting. The details of the alloy preparation are given elsewhere2,3) For a reference, an Fe–28Mn–6Si–5Cr alloy was also re-tested with more accuracy than in the previous work.1–3) In the present work, the SME was evaluated by measuring length change. Both alloys were first solution treated at 1470 K for 10 h. Extension test pieces of 0.7 mm thickness and 1–4 mm width with the gauge length of 15 mm were spark cut from those solution-treated samples. These are labelled “As-annealed” samples. Some of the tensile samples of the reference alloy were trained 5 times by extending 4% at room temperature and heating to 870 K. To know the effect of pre-deformation of the austenite, some solution-treated samples of the alloy containing Nb and C were rolled at 870 K by 6% and 14%. At this temperature, no martensite was induced by rolling. These pre-rolled samples as well as the non pre-rolled ones were subjected to ageing at 1070 K in order to produce NbC precipitates. Straining of the samples was performed by extension at room temperature. The shape recovery was measured after heating the strained samples up to 870 K. For measuring the shape recovery stress, the tensile samples were initially strained about 4% and then heated up to 670 K while keeping their ends fixed in a mechanical testing device. The rolled and aged samples before extension were observed by transmission electron microscopy (TEM).

3. Results

3.1 Shape recovery and shape recovery stress

Figure 1 shows the shape recovery of the alloy containing Nb and C in different pre-rolling conditions. The results of the reference alloy for the as-annealed and trained states are also included in the figure (open symbols). The improvement

![Fig. 1. Shape recovery as a function of the initial strain for the Fe–28Mn–6Si–5Cr–0.5NbC alloy in different pre-rolling conditions. The non pre-rolled sample was aged 2 h at 1070 K. The pre-rolled samples were aged 10 min at 1070 K. Results from the Fe–28Mn–6Si–5Cr reference alloy in the as-annealed and trained states are also shown for comparison.]
of the shape recovery due to the presence of NbC precipitates can be evaluated by comparing the curves corresponding to the Fe–28Mn–6Si–5Cr samples without training and Fe–28Mn–6Si–5Cr–0.5NbC in the non pre-rolled state. For example, the former alloy shows only 50% shape recovery for a 4% initial strain, while the new alloy containing NbC exhibits about 70% recovery in the same condition. The shape recovery is further improved by the pre-rolling treatment as clearly seen in this figure. For the alloy containing Nb and C, the samples that were pre-rolled 6% and 14% and then aged at 1070 K for 10 min recover 90% of a 4% initial strain. This large shape recovery is comparable to that of reference alloy sample subjected to 5 cycles of training. In this sense, the effect of pre-rolling of the alloy containing Nb and C is similar to the so-called “training” treatment. The effect of varying the ageing time at 1070 K for the pre-rolled samples was also investigated. No recognisable effect on the shape recovery was found in the range from 5 min to 2 h. This result indicates that the precipitation of NbC occurs rather rapidly. No significant effect of the ageing time was observed for the non pre-rolled samples either. From the viewpoint of industrial applications, this is quite beneficial because long ageing times are not necessary.

Figure 2 shows the effect of pre-rolling on the shape recovery stress for the alloy containing Nb and C. The samples pre-rolled 6% and 14% are compared with the non pre-rolled one. The former samples were aged for 10 min at 1070 K, while the latter one for 2 h at the same temperature. During heating to 670 K, the stress increase due to shape recovery is similar for the 6% pre-rolled and non pre-rolled samples, but it is much greater for the 14% pre-rolled one. On cooling, for the pre-rolled samples, the stress is further increased due to thermal contraction up to a point where the fcc to hcp martensitic transformation takes place and a part of the stress is relieved. For the non pre-rolled sample, no significant increase is observed. The final shape recovery stresses at room temperature are 255 MPa, 295 MPa and 145 MPa for the 6%, 14% and non pre-rolled samples, respectively. The difference in the final shape recovery stress seems to be related with two factors. The first one is the different microstructural state of these samples and is reflected to the slopes of the shape recovery stress vs. temperature curves on cooling. The slopes for the pre-rolled samples are steeper than for the non pre-rolled sample probably because some of the plastic deformation introduced by rolling still remained after the ageing treatment and resists the re-transformation. The other important factor is a high recovery stress obtained during the shape recovery process as notably seen in the 14% pre-rolled sample. Thus, a high shape recovery stress on heating can result in a very high final shape recovery stress at room temperature if no large stress relief occurs on cooling.

For certain applications, for example, the tube coupling, the shape memory material will recover a part of the initial strain before making contact with the parts to be coupled when heated. In this process, some of the attainable recovery stress is lost. Figure 3 shows the results of experiments carried out to simulate such a situation where an initial 4% strain was partially recovered before starting to measure the recovery stress in the way described in Section 2. The shape recovery stresses obtained for the 14% pre-rolled samples of the alloy containing NbC are higher than those for the 5 cycles-trained samples of the Fe–28Mn–6Si–5Cr reference alloy in all the conditions studied. Even after recovering 3% strain, this pre-rolled sample developed a stress of 160 MPa.

3.2 TEM observation

The microstructure of the alloy containing NbC precipitates in the 6% pre-rolled condition was observed by TEM. Figure 4(a) is a TEM micrograph of the pre-rolled sample aged for 2 h at 1070 K and Fig. 4(b) shows an electron diffraction pattern from the area shown in (a). Parallel fringes seen in (a) are considered to be due to stacking faults because all of them are parallel to the traces of {111} planes. We confirmed by TEM that a lot of such stacking faults had existed before ageing, which indicates that those stacking faults in Fig. 4(a) have been produced by 6% pre-rolling. Besides the stacking faults, we see many dotted dark contrasts in (a). These dots are due to the presence of NbC precipitates, which are revealed by dark field image shown in Fig. 4(c). This image was taken by a 002 spot of NbC precipitates such as indicated by arrows in Fig. 4(b). There is seen fairly good one to one correspondence between dotted dark contrasts in (a)
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Stacking faults have been produced to relieve the strains due to the formation of the precipitates. The lattice constant of NbC precipitate having the NaCl type structure is larger than that of the fcc matrix by 24%. By analysis of many electron micrographs taken from various incident beam directions, it is concluded that the shape of the NbC precipitate is polyhedral with the facets mostly consisting of \{111\} planes for both the cases of pre-rolled and non pre-rolled samples. Besides the precipitate size, another important difference between the non pre-rolled and pre-rolled samples is that the distribution of the NbC precipitates is more uniform in the pre-rolled case.

4. Discussion

From the results described in the previous section, it is quite clear that the pre-rolling of the austenite greatly improves both the shape recovery and shape recovery stress. In this section, we discuss possible reasons for this improvement. From the TEM observations, it seems that the key factor is the existence of very small NbC precipitates associated with stacking faults.
cipitate. Then, in the reverse transformation on heating, the back stress exerted from the precipitate will assist the reverse movement of Shockley partial dislocations on the martensite plate tip, realising the reversion to the fcc matrix by the same atomic path as that of the forward transformation. This is the essential requisite to produce a good SME. 5, 6) Thus it is presumed that the higher the density of such NbC precipitates is, the better the SME is attained. As mentioned in Section 3.2, the size of NbC precipitates is much smaller in the pre-rolled sample than in the non pre-rolled sample, which means that the density of the precipitates is much greater in the pre-rolled case.

It is self evident that the hardness of the austenite is increased with increasing amount of rolling, which will effectively prevent the re-transformation of the reversed austenite on cooling. Expecting a higher shape recovery stress, we examined the samples which were pre-rolled 70% at 870 K and aged at 1070 K for 20 min. However, it turned out that the shape recovery stress at room temperature was 200 MPa, much lower than for the 14% pre-rolled sample. This is because a shape recovery stress of only 60 MPa was attained on heating although no sign of the re-transformation on cooling was recognised as we expected. The poor shape recovery stress by reversion may be due to too much complicated substructures caused by such a large amount of pre-rolling. Thus we can say that there must be an optimum amount of pre-rolling to give the best SME. Further study is under way to find this condition.

Acknowledgements

One of the authors (A. Baruj) sincerely acknowledges the Science and Technology Agency of the Japanese Government for providing the STA Fellowship.

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