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# Development of Fe-Mn-Si based shape memory alloys with no necessity of "training"

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**Abstract.** In ar. ttempt to modify the current Fe-Mn-Si based shape memory alloys so that so-called the "training" treatment may be no more necessary, a small amount of Nb and C were added to Fe-Mn-Si based alloys to form NbC precipitates by aging. The existence of small coherent NbC precipitates in austenite greatly increases the shape recovery and the recovery force without the "training". For Fe-28Mn-6Si-5Cr-0.5NbC (mass %), 100-80 % shape recovery are obtained for tensile strains of 1-4 % and, for Fe-14Mn-6Si-9Cr-5Ni-0.5NbC, 100-80 % shape recovery are attained for tensile strains of 1-3 %. The maximum recovery force is 155 MPa for the former alloy and 130 MPa for the latter. The increase in recovery force of the former alloy compared with the corresponding NbC free alloy is 45 MPa. Our preliminary experiments with transmission electron microscope and atomic force microscope indicate that the stress-induced martensite structures formed in the NbC containing alloys are nearly the same as those in the "trained" sample of the NbC free alloys in accordance with the prediction recently made by Kajiwara.

## 1. INTRODUCTION

Since the discovery of shape memory effect (abbreviated as SME) in Fe-Mn-Si alloys in 1982 by Sato et al.[1], no major practical applications of this shape memory alloy and its modifications have been made so far despite of their low cost, good workability, good machinability and good weldability. The reason for this is that the SME in these alloys is not so good as that of Ti-Ni based shape memory alloys. In order to obtain nearly perfect shape recovery in Fe-Mn-Si base alloys, a special thermomechanical treatment, so-called "training", must be performed. The "training" treatment consists of several thermal cycles of deformation by stress induced martensitic transformation and subsequent heating for the reversion to austenite. It is obvious that this treatment will raise the production cost of this shape memory material and, for somewhat complicated shapes, it would be impossible to make the "training" treatment. Therefore, in order to promote industry applications in various fields, it is absolutely necessary to modify those Fe-Mn-Si based alloys so that the "training" treatment may not be necessary.

Bearing in mind that the mechanism of the "training" effect on SME in this alloy must be first clarified for developing "training-free" new alloys, we have been studying microstructures in the "trained" sample with various magnifications ranging from μm to sub-nm [2-7] and found that the most important condition for exhibiting good SME is as follows. The stress-induced martensite plates produced by deformation at room temperature must be very thin [2,4,5](as thin as about 1 nm in width), and have the same variant and uniformly distributed in austenite [6,7]. It is presumed that, to realize such microstructures in the deformed specimen, stacking faults acting as martensite nuclei must be uniformly distributed in austenite before deformation [4,5,7]. In other words, we can say that the existence of uniformly distributed martensite nuclei in austenite is the prerequisite for exhibiting good SME in Fe-Mn-Si based alloys. As was recently suggested by Kajiwara [4], coherent fine precipitates in austenite could

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be potential nuclei because the martensite would be easily nucleated at these precipitates when external stress is applied. In the present work, in an attempt to modify Fe-Mn-Si based shape memory alloys so that the "training" treatment is no more necessary, we have introduced NbC precipitates in austenite to serve as martensite nuclei. It seems that the NbC precipitate (NaCl type structure) is ideal for such purpose because it has a large elastic strain field as was shown for an Fe-Mn binary alloys [8] and the binding force between Nb and C atoms in the NbC compound is so large that the addition of these elements do not give any effect on chemical free energies of the fcc and hcp phases, which keeps the transformation temperatures unchanged. It was actually found that the NbC addition to the conventional Fe-Mn-Si based alloys produces remarkable effect to improve SME. The present paper reports the essential part of these results.

## 2. EXPERIMENTAL

The composition of newly designed alloys is listed in Table 1. Two typical alloys, Fe-28Mn-6Si-9Cr and Fe-14Mn-6Si-9Cr-5Ni (mass%), were selected as reference alloys. The alloys were prepared by vacuum induction melting, with introduction of argon at the time of Mn melting. The ingots of 45×64×100 mm were forged and hot-rolled to 20 mm thickness, and then square-pillar shaped specimens with the size of 18×20×70 mm were cut out and solution treated at 1470 K for 10 h in argon. To prevent evaporation of Mn during this heat treatment, the surface of the specimens was coated with a mixture of $Si_2O$, $Na_2O$ and $Al_2O_3$. The plate specimens were spark-cut from the as-solution treated sample and subjected to aging treatments in vacuum capsules at various temperatures ranging from 670 K to 1370K, followed by quenching into water. Shape memory effect was measured by bending and extension test. For bending test, the specimen with the dimension of 0.6×4×20 mm was bent at room temperature by about 4 % using a rod as bending guide and then heated to 870 K for reverse transformation. For extension test, specimens of 0.6×4×15 mm with the standard grip shoulders were extended by various amounts (up to 8 %) at room temperature, and the elongation by tensile deformation and its length recovery after heating to 870 K were measured using a measuring microscope. Recovery force was evaluated with those specimens used for extension SME test. Stress-induced martensite was observed using atomic force microscopy (AFM) from Digital Instrument 3000 at tapping mode in air.

Table 1: Alloy composition of the new alloys and conventional ones (mass%)

| Alloy No. | Mn | Si | Cr | Ni | Nb | C | Fe | NbC |
|---|---|---|---|---|---|---|---|---|
| 1 | 28 | 6 | 5 | | | | bal. | |
| 2 | 28 | 6 | 5 | | 0.47 | 0.06 | bal. | 0.5(vol.) |
| 3 | 28 | 6 | 5 | | 0.93 | 0.12 | bal. | 1.0(vol.) |
| 4 | 28 | 6 | 5 | | 1.40 | 0.18 | bal. | 1.5(vol.) |
| 5 | 14 | 6 | 9 | 5 | | | | |
| 6 | 14 | 6 | 9 | 5 | 0.47 | 0.06 | bal. | 0.5(vol.) |
| 7 | 14 | 6 | 9 | 5 | 0.93 | 0.12 | bal. | 1.0(vol.) |
| 8 | 14 | 6 | 9 | 5 | 1.40 | 0.18 | bal. | 1.5(vol.) |

## 3. RESULTS

### 3.1 Shape memory effect

Fig. 1 shows the dependence of shape recovery on aging temperature for Fe-28Mn-6Si-5Cr alloys containing 0.5 - 1.5% NbC. The shape recovery was measured by bending test, employing the specimen bent by about 4% strain. The shape recoveries of the as-solution treated samples of these new alloys and the NbC free Fe-28Mn-6Si-5Cr alloy are also shown for comparison in the figure. The shape recoveries of the NbC containing alloys are nearly the same (around 50%) as that of the NbC free alloy in the case of the as-solution state. However, for the NbC containing alloys, the shape recovery is increased by aging treatment; especially, the improvement of the shape recovery is remarkable by aging at higher temperatures. For example, with aging treatment at 1070K for 2h, the shape recoveries of the three NbC containing alloys are all increased to about 90% from about 50%. For the alloy with 1.0% NbC, the aging treatment at lower temperatures such as 770K or 870K is also effective to improve the shape recovery. Fig. 2 shows the shape recoveries for Fe-14Mn-6Si-9Cr-5Ni containing 0.5-1.5 NbC and its reference alloy (NbC free). As seen in this figure, the shape recoveries of the three NbC containing alloys are also much improved by aging treatment, especially at higher temperatures. It should be noted in Figs. 1 and 2 that aging treatment at too high temperature becomes less effective to improve SME; the shape recovery is decreased with further increasing aging temperature over 1170K.

From the results of the dependence of shape recovery on aging treatment temperature, we have known that the aging treatment around 1070K for 2h is the best to improve SME for all the alloys containing NbC. Therefore, in order to know the effect of the amount of deformation on SME, we have examined only those samples that were subjected to the aging treatment at 1070 K for 2 h. To evaluate this effect more accurately, the extension SME test was performed instead of the bending test. The results are shown in Fig. 3. It is emphasized that the shape recoveries of 100-80 % are obtained for 1-4 % strains in Fe-28Mn-6Si-5Cr-0.5NbC and for 1-3 % strains in Fe-14Mn-6Si-9Cr-5Ni-0.5NbC without the "training". By comparison at 4 % strain, the shape recovery is increased from 50 % to 80 % by addition of 0.5 % NbC to the current Fe-28Ni-6Si-5Cr alloy. As a matter of course, the shape recovery is decreased with increasing amount of deformation strain of the test sample. Besides this general dependence, however, we can see a clear indication in Fig. 3 that the decrease in shape recovery with strain for the new alloys with 28 Mn (alloys No. 2, 3) is not so rapid compared with the corresponding conventional Fe-28Mn-6Si-5Cr containing no NbC. The other prominent features seen in this figure are that the shape recoveries of the new alloys with 28 Mn are much better than those of 14 Mn (alloys No. 6, 8), and those with 0.5 NbC are greater than those with 1.0-1.5 NbC. It is also noted that the shape recoveries at 4 % strain in the case of extension SME test are much smaller for all the alloys if compared with those obtained by bending SME test in Figs. 1 and 2. This may be partly due to that the 4 % strain by bending, which was estimated by a simple formal equation using the bent radius and the specimen thickness, involves much more complicated deformation and then it cannot be equivalent to the 4 % strain by tensile deformation. Nevertheless, this fact may indicate that the recoverable strain in SME may be strongly dependent on the pattern of deformation, more specifically, the formation pattern of stress-induced martensite plates.

### 3.2 Recovery force

In most of the applications of shape memory alloys, the recovery force is also important. For example, when a shape memory alloy is used for pipe coupling, the fastening force is decided by recovery force, and a larger recovery force increases the proof stress of the connected pipe system. In the present study, we have examined the recovery forces of NbC free and NbC containing alloys as a function of recovery strain with the tensile-deformed samples. In our experiments, we firstly measured the curve of the shape recovery strain vs. heating temperature by stepwise heating. From this curve, we know the appropriate heating temperature to obtain a certain amount of the recovery strain. In order to measure the recovery force corresponding to this recovery strain, the deformed sample is firstly heated to a pre-determined temperature to produce the expected recovery strain, and then two ends of the same specimen is fixed on the micro-tensile machine at room temperature. After this, the specimen is heated again all the way to above Af temperature and the maximum stress appeared in this heating process is regarded as a recovery force for an intended shape recovery strain. The recovery force measured in this way is plotted as a function of shape recovery strain in Fig. 4. Besides the new alloys with 0.5 NbC, the recovery forces for the as-solution treated and 5 cycle-"trained" Fe-28Mn-6Si-5Cr are also shown for comparison in this figure. The amounts of tensile deformation of the samples before the test were 3.1, 4.1, 4.1 and 5.0 % for the as-solution treated, "trained" Fe-28Mn-6Si-5Cr, Fe-28Mn-6Si-5Cr-0.5NbC and Fe-14Mn-6Si-9Cr-5Ni-0.5NbC, respectively. The recovery force is remarkably increased for the new alloys with NbC, the amount of the increase being 50-70 MPa for various shape recovery strains. However, regrettably, the recovery forces of the new alloys do not reach that of the "trained" Fe-28Mn-6Si-5Cr as seen in this figure.

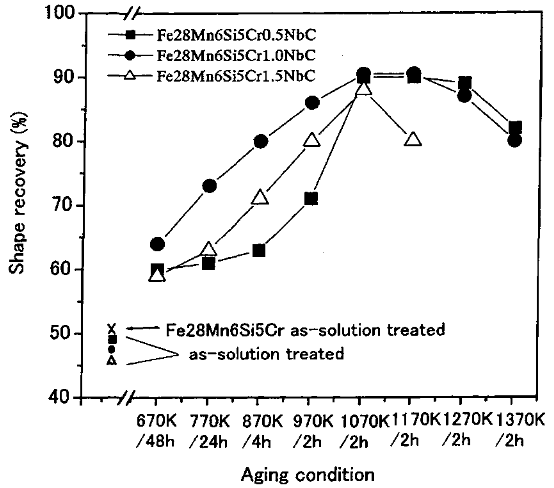


**Figure 1**: Effect of aging temperature on shape recovery in three kinds of Fe-28Mn-6Si-5Cr alloys containing 0.5, 1.0 and 1.5 % NbC. Aging time is also indicated for each aging temperature.

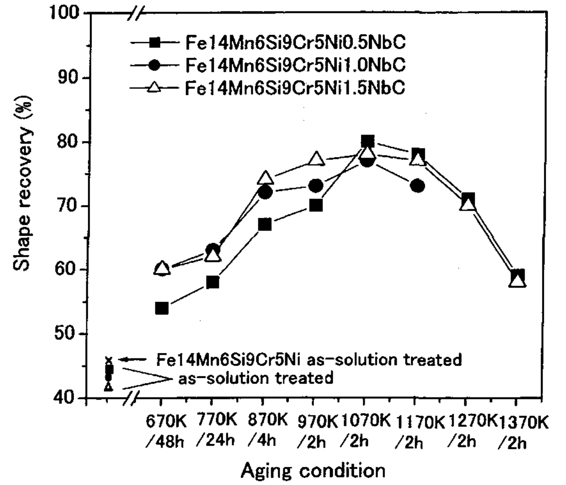


**Figure 2**: Effect of aging temperature on shape recovery in three kinds of Fe-14Mn-6Si-9Cr-5Cr alloys containing 0.5, 1.0 and 1.5 % NbC. Aging time is also indicated for each aging temperature.

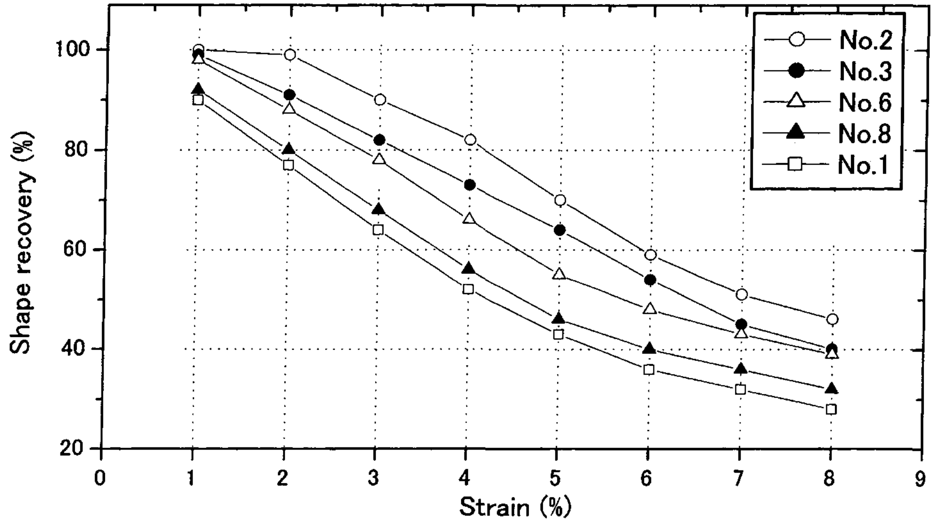


**Figure 3**: Effect of strain on shape recovery for tensile deformation. Alloys No. 2 and 3 with 28 % Mn show better shape recoveries than those with 14 % Mn (No. 6 and 8). Alloys with 0.5 NbC exhibit better shape recoveries than those with 1.0 or 1.5 NbC. The shape recovery for Fe-28Mn-6Si-5Cr (No. 1) is also shown for comparison.

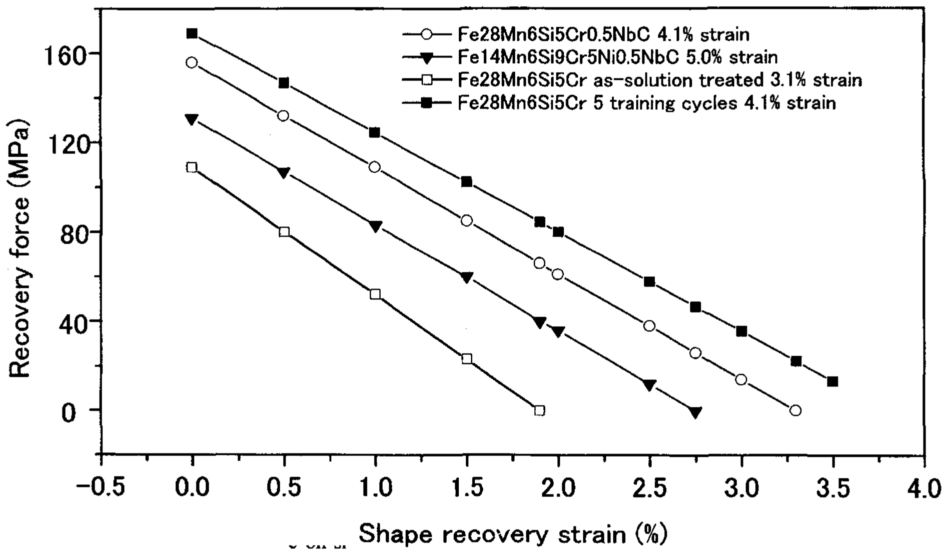


**Figure 4**: Dependence of recovery force on shape recovery strain for Fe-28Mn-6Si-5Cr-0.5NbC and Fe-14Mn-6Si-9Cr-5Ni-0.5NbC. The recovery force for Fe-28Mn-6Si-5Cr containing no NbC is also plotted for the cases of as-solution treated sample and 5-cycled "trained" sample. The specimens were extended by 3-5 % at room temperature before the test to measure the recovery force

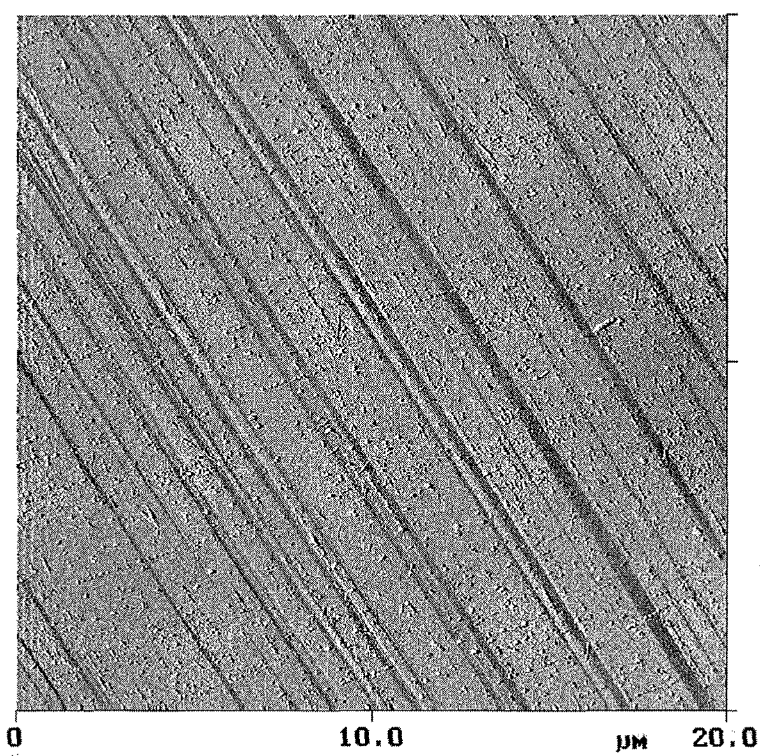


**Figure 5**: AFM image of stress-induced martensite plates for Fe-14Mn-6Si-9Cr-5Ni-0.5NbC aging treated at 1070 K for 2 h. The sample was tensile deformed by 3.6 % at room temperature. All the martensite plates have the same color in the original color picture, indicating that they have the same variant. Note that thin martensite plates are uniformly distributed.

## 4. DISCUSSION

As described in the preceding section, addition of small amounts of Nb and C to the current Fe-Mn-Si based shape memory alloys is quite effective to improve shape recovery. It was observed in the aged samples by transmission electron microscope (TEM) that there exist very fine NbC precipitates of 10-20 nm in size accompanying large strain contrast in the austenite. Furthermore, our preliminary experiments with TEM and AFM (atomic force microscope) [9, 10] strongly indicate that the resulting deformation structures in those NbC containing alloys are exactly what we have expected, that is, it was observed by TEM that very thin stress-induced martensite plates with about 1 nm are uniformly distributed and most of martensite plates observed by AFM have the same variant. An example of the AFM micrographs is shown in Fig. 5. Thin martensite plates with the same contrast are seen in this micrograph. These martensite plates have the same color in the original AFM color picture, which means that they are the same variant. It is also noted that the martensite plates are uniformly distributed. These characteristics on the stress-induced martensite plates revealed by AFM are exactly the same as our recent AFM observations on the "trained" sample in Fe-Mn-Si based shape memory alloys [6, 7]. These preliminary results convince us that fine NbC precipitates in austenite can produce almost the same deformation structures as those of the "trained" sample as predicted by Kajiwara [4], which results in very good shape memory effect in Fe-Mn-Si based shape memory alloys. It is expected that these NbC precipitates will also increase the strength of austenite and, then, effectively prevent slip deformation when external stress is applied for shape change. This would be another factor to improve SME in the NbC containing alloys. It should be noted that the recovery strength of the new alloys is significantly increased as seen in Fig. 4 although it cannot still reach that of the "trained" sample

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