Effect of Nitrogen Addition on Shape Memory Characteristics of Fe–Mn–Si–Cr Alloy

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Nitrogen-microalloying and partial substitution of Cr for Mn have been employed to enhance the shape memory effect and corrosion resistance of Fe–Mn–Si based alloys. Typically, the tested alloys with nominal composition Fe–25Mn–6Si–5Cr–(0.12–0.14)N in mass% exhibit perfect shape recovery for a 3% pre-strain after only one cycle of thermomechanical training. The related mechanism has been discussed, taking account of the effect of nitrogen on the stacking fault energy (SFE) or the stacking fault probability ($P_d$) of the alloy and the strengthening of the austenite matrix. Thermodynamic calculation and $P_d$ measurement showed that the SFE increases with increasing N-content in the concentration range investigated, e.g. less than 0.3 mass%. Thus, the critical stress for the formation of stress-induced martensite increases with N-content. It is believed that the interstitial strengthening of the matrix by nitrogen predominantly contributes to the improvement of shape memory effect. Besides, nitrogen-microalloying remarkably improves the corrosion resistance of the alloys in aqueous solutions containing NaOH and NaCl, but not in HCl solution as indicated by the long-term immersion tests.

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1. Introduction

Since a pronounced shape memory effect (SME) was discovered in a single crystal of Fe–30Mn–1Si in the early 1980s,1) Fe–Mn–Si based alloys have been subjected to extensive studies although the SME is only in one-way. These shape memory alloys have been regarded for a long time a promising potential to be used as tightening or pipe couplings2) due to their low cost and good workability. However, unlike the other shape memory alloys (SMA) such as Ni–Ti and Cu-based, it is necessary for the Fe–Mn–Si based alloys to perform at least three or four cycles of the thermomechanical training for achieving the complete (100%) shape recovery.3) Such a number of training cycles definitely causes significant energy consumption and fails to provide easy dimensional control of the resultant SMA products. Therefore, it has long been desired to reduce the required number of training cycles for their practical applications in industry.

It has been well acknowledged that the SME in Fe–Mn–Si based alloys is associated with the $\gamma$ (fcc) $\rightarrow$ $\varepsilon$ (hcp) martensitic transformation and its reverse process, and is originated from the reversible motion of the $1/6(112)$ Shockley partial dislocations in the fcc structure.4–7) Many efforts have been made to improve the alloy properties including the SME and corrosion resistance through various alloying methods such as that of the substitutional elements Cr, Ni8) or the interstitial ones C, N etc. In particular, the effect of nitrogen-microalloying on the SME of Fe–Mn–Si based alloys has been investigated by several investigators.9–13) Jiang et al.9,10) observed a slight improvement of SME in Fe–30Mn–6Si by adding 0.047 mass% nitrogen and found that nitrogen lowers the stacking fault probability $P_d$ or, inversely, raises the stacking fault energy (SFE) of the alloy as determined by XRD measurements. Ullakko et al.11) reported that addition of 0.2–0.22 mass% nitrogen existing both in solid solution or precipitate improves the SME, which is attributed to the matrix strengthening, easier motion of the $\gamma/e$ interface and suppression of permanent slip by perfect dislocations. Ariapour et al.12) investigated the influence of nitrogen in Fe–Mn–Si–Cr–Ni alloys and concluded that 0.25 mass% nitrogen in solid solution degrades its SME by about 80% as tested in compression. They suggested that the increased SFE and the pinning of partial dislocations could be the reasons. Besides, Soderberg et al.13) carried out a study on the effect of thermomechanical training (by rolling) on the corrosion resistance of the Fe–Mn–Si based steels containing 0.12–0.23 mass% nitrogen by means of immersion tests and anodic polarization measurements.

In the present paper, the effect of nitrogen addition ranging in 0.007–0.14 mass% on the mechanical and thermodynamic properties of an Fe–25Mn–6Si–5Cr based alloy was investigated, and it was found that an alloy containing nitrogen more than 0.12 mass% achieves complete shape recovery by only one cycle of training for 3% prestrain.

2. Experimental Procedures

The alloys investigated were induction melted in argon with high purity iron, manganese, silicon and chromium. Nitrogen was introduced by adding a proper amount of Cr–N iron. The analyzed composition of the alloys is listed in Table 1. In fact, a very small amount of nitrogen, 0.007 mass%, in Alloy No. 1# was contaminated from raw elemental metals and the processing. The ingots were annealed at 1373 K for 11 h and then hot rolled into 1.5 mm thick sheets. The samples with dimensions $5 \times 5 \times 1.5 \text{ mm}^3$ were cut from the sheets by spark erosion and austenitized at 1073 K for 30 min followed by water quenching. The surface layer about 0.06 mm thick was removed by chemical polishing to diminish the influence of demanganization for all the samples.

The samples were deformed in tension at room temperature

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by various prestrains and then unloaded. Subsequently, they were heated to and held at 873 K for 30 min for shape recovery, i.e. the reverse transformation of stress-induced martensite.

The shape memory effect was evaluated from the change in gauge lengths of a sample at room temperature. The shape recovery ratio \( \eta \) is defined as

\[
\eta(\%) = \frac{(l_1 - l_2)}{(l_1 - l_0)} \times 100
\]

where \( l_0 \), \( l_1 \) and \( l_2 \) are the gauge lengths before and after deformation, and after shape recovery respectively. A prestrain of 3% was used in the training (see the text below).

The stacking fault probability \( P_{sf} \) was determined by XRD profile analysis for the 111 and 200 reflections of the parent phase.\(^{10}\) The characteristic transformation temperatures \( M_s \), \( A_s \) and \( T_K \) were measured by electric resistance method. The 0.2% proof stress, \( \sigma_{0.2} \), of the austenitic matrix at room temperature was obtained by extrapolation from the stress-strain curves tested at temperatures above \( M_d \). Immersion tests and potentiodynamic polarization measurements were implemented in 3 kmol-m\(^{-3}\) NaOH, 1 kmol-m\(^{-3}\) HCl and 3.5% NaCl aqueous solutions to compare their corrosion behavior with that of an 18-8 stainless steel.

### 3. Results

#### 3.1 Effect of prestrain on SME

The shape recovery ratios (\( \eta \)) of the alloys investigated were measured as a function of prestrain. The results are summarized in Fig. 1, indicating that the SME always becomes worse when the prestrain increases in a range from 1 to 6%. However, for a given prestrain the alloy exhibits an enhancing \( \eta \) with increasing N-content. It has been found that all the alloys containing more than 0.05 mass% nitrogen show rather good shape recovery characteristics, i.e. the \( \eta \) is higher than 80%, for an identical prestrain of 3%. Therefore, 3% was chosen as a constant prestrain for the training in the following experiments.

#### 3.2 Effect of training cycles

It has been well known that the SME of Fe–Mn–Si based alloys can be significantly improved by thermomechanical training.\(^3\) Figure 2 shows the dependence of \( \eta \) on the number of training cycles for various alloys with a 3% prestrain. It was very exciting to see that, for the alloys containing 0.12 and 0.14 mass% nitrogen, the shape recovery ratios become 100% at the second cycle of training. This clearly indicates a substantially beneficial effect of nitrogen-microalloying on the SME that only one preliminary training cycle is needed to make such materials to achieve a perfect recovery before their practical use. For instance, in the case of tightening or coupling purpose, the deformation of the fabricated products for fitting into certain dimensions in connection can be made after only one cycle of the training.

#### 3.3 Strengthening effect on \( \gamma \) matrix

At room temperature, which is between \( M_s \) and \( M_d \) for the present alloys (see Section 3.5), the stress applied to the water-quenched sample in austenitic state will induce the formation of \( \varepsilon \) (hcp)-martensite before it reaches its 0.2% proof stress. Therefore, in order to assess the strengthening effect of nitrogen for the matrix, it is necessary to measure the \( \sigma_{0.2} \) of various alloys at temperatures above \( M_d \) and then extrapolate them to obtain the value at room temperature. The results are shown in Fig. 3. It can be seen that a remarkable increase of 100 MPa in \( \sigma_{0.2} \) results from about 0.1 mass% nitrogen addition, presumably by its interstitial hardening effect.

#### 3.4 Stacking fault probability \( P_{sf} \)

The XRD measurements of \( P_{sf} \) for the alloys containing various amounts of nitrogen are summarized in Fig. 4. It is seen that the \( P_{sf} \) decreases with increasing N-content in the range concerned, being in good consistence with our previous results.\(^{10}\) In other words, nitrogen raises the SFE of Fe–Mn–Si based alloys and, thus possibly, there exists a negative influence on their SME improvement.
3.6 Corrosion behavior

The corrosion behavior of the alloy containing 0.14 mass% nitrogen was investigated by a long-term (140 h) immersion in various aqueous solutions, together with those of Fe–Mn–Si, Fe–Mn–Si–Cr and an 18-8 stainless steel for comparison. Figure 6 shows the rate of weight loss of the tested alloys immersed in 3.5% NaCl aqueous solution for 140 h.

As seen in this figure, the Fe–Mn–Si–Cr–N alloy exhibits an excellent corrosion resistance in NaCl solution. It was also found that this N-containing alloy shows fairly good corrosion resistance even in NaOH and HCl solutions compared to the other alloys except the 18-8 stainless steel. The detailed results will be published elsewhere.14)

4. Discussion

From the previous investigations it is presumed that a good SME in Fe–Mn–Si based alloys can be achieved through lowering the SFE, strengthening the γ matrix and forming a large amount of the stress-induced ε-martensite (SIM) with high fraction in a single variant.15, 16) When Otsuka et al.3) first reported that the SME in Fe–Mn–Si based alloys was greatly improved by “training”, they attributed it to the increased yield stress of austenite and the concurrent decrease of the critical stress to induce martensitic transformation. However, Kajiwara and his coworkers7, 17) noticed that this is not the only factor for the improvement in SME. They studied in detail the microstructure of SIM by high resolution microscopies (differential OM, CTEM and TEM) and concluded that the existence of uniformly distributed martensite plates with extremely small widths (less than 1 nm) is most important for attaining the perfect SME. Furthermore, it was found very recently by atomic force microscopy study that several cycles of the training are necessary to create a high fraction of the single variant martensite in the Fe–Mn–Si based alloys.16) Obviously, such a “training” treatment would not be easy for most conceivable applications and, then, would certainly raise the cost of processing and the difficulty of dimensional control in fabrication of the applicable materials and products. Therefore, it is desired to develop new Fe–Mn–Si based shape memory alloys that need only few cycles of training or even do not need any training. The present work has made a considerable progress in reduction of the required number of training cycles for achieving a perfect recovery rate in such alloys through nitrogen-microalloying.
Of course, it is self-evident that the total amount of the SIM depends on the alloy composition, the deformation temperature and the amount of deformation, i.e. the prestrain, in the present case. As the SME in the present alloys was determined at room temperature by a given prestrain (3%), the effect of nitrogen content on the SFE and the strengthening of matrix are mainly discussed in the following.

The SFE of the present alloys was calculated also in this paper after the thermodynamic model proposed by Yakubtsov et al.\(^{18}\)

\[
\gamma = \gamma_b + \gamma_s + \gamma_m
\]

where \(\gamma_b\) is the difference in Gibbs free energy between fcc and hcp phases per unit area, \(\gamma_s\) the energy change due to nitrogen segregation at stacking fault and \(\gamma_m\) the contribution of magnetism. The result is shown in Fig. 7, which indicates that nitrogen results in an increase of the SFE in Fe–25Mn–6Si–5Cr based alloys. Considering a relationship suggested by Noskova and Pavlov\(^{19}\) that the \(P_{sf}\) is inversely related to SFE, it agrees with the measured dependence between \(P_{sf}\) and nitrogen content in the present work (Fig. 4). Furthermore, a thermodynamic calculation carried out by the present authors\(^{20}\) has also proved a similar tendency for the Fe–30Mn–6Si–xN alloys, but it predicts that SFE will decrease if nitrogen raises the SFE in the investigated alloys and therefore may cause a slight increase in the critical stress for the formation of SIM, it seems that it has been more compensated by the strengthening effect. Besides, the increase in SFE could also be a reason why the \(M_s\) is lowered by about 40 K as seen in Fig. 5, suppressing the possible formation of thermal-induced \(\varepsilon\)-martensite (TIM) to some extent during quenching. This could be another favorable factor for obtaining better SME in the present alloys, for these alloys may need only a very few training cycles to transfer those TIM into single variant to achieve a perfect SME. Therefore, the net effect of nitrogen-microalloying in Fe–Mn–Si based alloys is substantially to improve the SME as shown in Figs. 1 and 2. However, a question still remaining to answer is whether or not there exists an optimum nitrogen content for the best SME in the present alloys. Perhaps it can be expected if lower SFE is attained when containing more nitrogen.\(^{20}\) A semi-empirical prediction of the SME in Fe–Mn–Si based alloys has been proposed in our recent paper.\(^{23}\) The recovery rate \(\eta\) is expressed as a function of various parameters including the strengthening effect of \(\gamma\) matrix (the c.r.s.s. of perfect dislocation slip, \(\tau_0\)), grain size \((R)\), stacking fault probability \((P_{sf}\) or the SFE) and the number of training cycles \((n)\):

\[
\eta = \frac{1}{\varepsilon} \left[ 2 \left\{ \frac{C_1 (1 - \frac{2A}{R}) + C_2 P_{sf}}{\pi} \right\} \arcsin \left( \frac{2(\tau_0 + k R^{-1/2})}{\sigma} \right) + 0.353A[\cos \beta + (1 - \cos \beta)(q_0 + q_1n + q_2n^2 + q_3n^3)][1 - \exp(-k_1e^{k_2})] \right] 
\]

where \(\beta\) is the angle between two variants, the other parameters should be determined by experiments. According to a thermodynamical calculation,\(^{20}\) SFE approaches a maximum when the nitrogen content \((x_N)\) equals to about 0.25 mass% in
Fig. 8 Effect of nitrogen content on the shape recovery ratio of Fe–Mn–Si–Cr–N alloys based on a semi-empirical prediction.26}

\[ \eta = \frac{50}{\pi} \left( C_1 \left( 1 - \frac{2A}{R} \right) + C_2 \left( a_1(x_N - 0.25)^2 + a_2 \right) \right) \times \arcsin \left( \frac{2(d_1 x_N + d_2 + 70.0)}{90} + 33A \right) \]

Typically, \( \epsilon = 3\% \), \( \sigma = 90 \text{ MPa} \), \( k_1 = 2 \) and \( k_2 = 0.4 \), a relationship between \( \eta \) and \( x_N \) can be drawn out and is shown in Fig. 8:

\[ \eta = [1.0 + 250(x_N - 0.25)^2] \arcsin(0.8 x_N + 0.001) + 0.45 \]

It is clear that by adding an appropriate amount of nitrogen, e.g. around 0.11 mass%, the shape memory effect of Fe–Mn–Si based alloys could be improved to its best level. By chance, the (0.12–0.14)mass%N-containing alloy investigated in the present work seems to have just taken the maximum favorable effect of nitrogen-microalloying on the SME.

On the other hand, adding more nitrogen may result in the formation of nitride precipitates in the alloys, which can also strengthen the matrix and probably provide more nucleation sites for the formation of \( \varepsilon \)-martensite. Furthermore, there would be more strain energy stored in the matrix surrounding those fine precipitates, making the reverse transformation possibly easier. However, the corrosion resistance of the alloys might be deteriorated due to the presence of such precipitates although not tested yet.

Finally, it is worthy to note a successful achievement, aiming at the similar objective as was accomplished in the present work, in remarkable improvement of the shape memory effect of the Fe–Mn–Si based alloys and, meanwhile, in reduction of the necessary number of training cycles. Kajiwara et al.26) reported recently that they added small amounts of Nb and C into the current Fe–Mn–Si–Cr–N alloys. The key point of this alloy composition design is to produce fine NbC precipitates in austenite by aging. In the as-solution treated state, the Fe–28Mn–6Si–5Cr (in mass%) alloys containing (0.47–0.93) Nb and (0.06–1.0) C show the same shape recovery rates (around 50%) for about 4% bending strain as that of the NbC free alloys. By aging at 1070 K/2 h, their recovery rates are enhanced to 80–100% for 1–4% tensile strains without any training treatment. From the TEM micrographs of the aged alloys, the size of the formed NbC precipitates in a cubic-to-cubic orientation relationship with austenite matrix is estimated to be about 20 nm. It was found that there exists a large strain field with dislocations associated with each precipitate, which will provide a preferential nucleation site for the stress-induced martensitic transformation from fcc to hcp. Those fine precipitates will also strengthen the austenite matrix and, then, effectively prevent the permanent deformation by slip of perfect dislocations when making shape change of the specimen. Furthermore, they are possible to be obstacles for martensite growth and generate a back stress at the tip of the martensite plates, helping the reverse motion of the Shockley partial dislocations and resulting in good shape recovery. A rather large recovery force of about 160 Mpa was also obtained for the aged alloys, which is almost the same as that of the “trained” sample of the corresponding alloy containing free of NbC.

If a comparison is made between Fig. 1 of the present paper and their results (Fig. 3 of Kajiwara et al.26), it is very interesting to find that the Fe–Mn–Si–Cr alloys containing more than 0.05 mass% nitrogen (Alloy Nos. 2#–5#) in the as-solution state exhibit excellent SME, which is very close to that of the aged alloy with about 1.0 mass%NbC (Alloy No. 2) in the same tensile prestrain range 1–4%.

5. Summary

Effect of nitrogen on properties including shape memory effect, mechanical behavior and corrosion behavior of Fe–Mn–Si–Cr based alloys has been investigated in the present paper. It is summarized as follows:

(1) The shape memory effect is markedly improved by adding a small amount of nitrogen in Fe–25Mn–6Si–5Cr alloys.

(2) The tested alloys containing more than 0.12 mass% nitrogen show an excellent SME to achieve the complete shape recovery (\( \eta = 100\% \)) after only one cycle of training for a prestrain 3%.

(3) The most important factor for improving the SME is the strengthening of austenite matrix caused by the interstitial solution hardening of nitrogen, which remarkably raises the critical stress for the offset of slip by perfect dislocations.

(4) Nitrogen-microalloying enhances the corrosion resistance of Fe–Mn–Si–Cr based alloys in aqueous solutions containing NaOH and NaCl, but it seems not the case in HCl solution.

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