Micro-parameters and micro-characteristics related to the formation of ϵ -martensite in Fe-based shape memory alloys

BOHONG JIANG* and XUAN QI

Open Lab of State Education Commission for High-Temperature Materials and Testing, Shanghai Jiao Tong University, Shanghai 200030, China

Abstract. The influence of some microstructure parameters and characteristics of γ -phase e.g. Stacking fault probability, grain size and texture etc on ϵ -martensitic transformation, shape memory effect and other macro-behaviours in Fe–Mn–Si based alloys are reviewed.

Keywords. Fe–Mn–Si; shape memory effect; ϵ -martensitic transformation; stacking fault probability; grain size; texture.

1. Introduction

Recently Fe–Mn–Si based alloys, a newly developed shape memory alloy system, are attracting great attention both in theory and practice owing to their good shape memory effect (SME) and cheap cost as well as fine workability (Sato *et al* 1982; Otsuka *et al* 1990). As in TiNi, Cu-based and other SMAs, we can find some microstructure parameters, which closely relate to the martensitic transformation, SME and other macro-behaviour of alloys. By virtue of the particularity of the phase transformation there are distinguishing micro parameters peculiar to the different alloy systems. For example, in Cu–Zn–Al alloys the ordering of parent phase is one of the necessary conditions for obtaining a good SME. We have deduced that the M_s temperature is a function of ordering parameter ξ^2 in Cu–Zn–Al alloys (Wu *et al* 1988) and the SME is closely related with the ordering degree (Jiang and Hsu 1990). However, it is not the case in Fe-based alloys because there is no ordering transformation in these alloys. In this paper several of our recent works dealing with the effect of micro-parameters and characteristics on the macro-behaviours related to the ϵ -martensitic transformation and SME in Fe–Mn–Si based alloys are summarily reviewed.

2. Stacking faults

It is well known that Fe–Mn–Si based alloys undergo a phase transformation from γ (fcc) to ϵ (hcp) structure, and the ϵ -phase can be formed by means of stacking faults which are introduced on every second layer of the {111} planes in austenite. The ϵ -martensite can be formed thermally-induced and stress-induced. In both

cases the stacking faults will play an important role. For example, the nucleation of ϵ -phase can be realized by the multiplication of stacking faults through the sweeping of the partial dislocation around a pole dislocation (Seeger 1956; Hoshino *et al* 1990) or directly by the overlapping of stacking faults (Olson and Cohen 1976; Hsu 1980), which will affect the characteristics of the phase transformation, e.g. M_s temperature, the critical stress required for inducing ϵ -martensite, σ_M , as well as mechanical behaviour and SME.

The characteristics of stacking faults in Fe–Mn–Si based alloys are extremely wide usually extending from one side of a parent grain boundary to the other side as observed in TEM, because of relative low level of the stacking fault energy in these alloys. The extending dislocations with limited width and the extending nodes of stacking faults which are easily observed in stainless steels, Ni-based and other alloys can not be found in Fe–Mn–Si based alloys. Therefore, it is difficult to evaluate the stacking fault energy by measuring the width of extending dislocations or the extending node radii from TEM.

By means of an X-ray diffraction profile analysis the stacking fault probability can be determined and then the stacking fault energies can be estimated for several metals (Reed and Schramm 1974).

2.1 Stacking fault probability

Fourier analysis of X-ray diffraction profile for polycrystal with stacking fault indicates that there are three diffraction effects of stacking fault: the broadening and asymmetry of profile as well as the displacement of diffraction peak (Warren 1969). In our works, the stacking fault probability, P_{sf} , was determined by the broadening effect of diffraction profile (Qi *et al* 1998).

*Author for correspondence

The stacking fault energy SFE can be estimated by following approximate equation (Noskova and Pavlov 1962):

$$\text{SFE} = \frac{G \cdot a_0^2 \cdot d \cdot \rho}{24\pi \cdot P_{\text{sf}}}, \quad (1)$$

where G is the shear modulus, a_0 the lattice parameter, d the lattice space of determined crystal plane and ρ the dislocation density. The error of above (1) is relatively large, because the calculation of ρ needs several hypothesis models. Another equation for estimating SFE from stacking fault probability (Reed and Schramm 1974) is also an approximate one because of the arbitrary nature of the selection in the proportional constants.

Therefore, the SFE can only be estimated approximately by above equations. Actually in most cases we need only the relative variation rule of SFE in matrix with various external conditions such as alloying elements, heat-treatments etc. Accordingly in present work we only measure the P_{sf} for relative comparison, since the P_{sf} is inversely proportional to SFE, i.e. $\text{SFE} \propto 1/P_{\text{sf}}$.

2.2 Effect of alloying composition on P_{sf}

The stacking fault probability, P_{sf} of Fe–Mn–Si specimens with various alloying compositions were determined and the starting temperature of $\gamma \rightarrow \epsilon$ transformation, M_s , of alloys are measured. The results are listed in table 1. It is shown that the addition of Cr and N reduces P_{sf} and correspondingly decreases M_s as comparing alloy 0 with M3 as well as N1, respectively. While comparing alloy M1 to M4, the P_{sf} and M_s run lower with increasing content of Mn.

Recently we have measured the stacking fault probability in stainless steel type SMAs i.e. Fe–14Mn–6Si–13Cr–5Ni with different contents of cobalt and found that the P_{sf} increases with increasing Co. The results agree with that reported in literature as the stacking fault energy measurement.

2.3 Relationship between M_s and P_{sf}

We sum up the results of M_s points and P_{sf} from different heat treatments in various alloys listed in table 1 (Jiang

et al 1998). While plotting M_s vs $1/P_{\text{sf}}$, a linear line is obtained by linear regression as shown in figure 1:

$$M_s(K) = 372 - 0.113/P_{\text{sf}}. \quad (2)$$

The above relationship can be deduced from thermodynamics. The change in the total free energy per unit volume associated with the γ (fcc) $\rightarrow \epsilon$ (hcp) martensitic transformation $\Delta G^{\gamma \rightarrow \epsilon}$, may be expressed as

$$\Delta G^{\gamma \rightarrow \epsilon} = \Delta G_c^{\gamma \rightarrow \epsilon} + \Delta U_{\text{str}} + s/v(a + \xi), \quad (3)$$

where $\Delta G_c^{\gamma \rightarrow \epsilon}$ and ΔU_{str} refer to the changes of chemical free energy and coherency strain energy per unit volume, respectively, a is the specific surface energy of hcp phase, ξ the SFE of austenite, s and v are area and volume of the hcp phase formed, respectively. A calculation of the coherency strain energy change for fcc $\rightarrow$ hcp transformation in Fe–Cr–Ni alloy (Olson and Cohen 1976) revealed that this energy is < 0.1 pct of the measured fault energy. Hence, the contribution of ΔU_{str} can be neglected here.

The M_s temperature can be defined as the temperature, T at which $\Delta G^{\gamma \rightarrow \epsilon} = 0$. Thus, at M_s (3) becomes

$$-\Delta G_c^{\gamma \rightarrow \epsilon} = s/v(a + \xi) = C + D/P_{\text{sf}}, \quad (4)$$

where C and D are constants.

Owing to that M_s temperature varies within a relatively small range, the changes in enthalpy $\Delta H^{\gamma \rightarrow \epsilon}$ and $\Delta S^{\gamma \rightarrow \epsilon}$ can be taken as constants independent of temperature. Thus the chemical free energy difference accompanying $\gamma \rightarrow \epsilon$ can be expressed as

$$\Delta G_c^{\gamma \rightarrow \epsilon} = \Delta H^{\gamma \rightarrow \epsilon}(1 - T/T_0), \quad (5)$$

where T_0 is the temperature at which $\Delta G_c^{\gamma \rightarrow \epsilon} = 0$.

When $T = M_s$, we obtain

$$M_s = T_0 + \frac{(C + D/P_{\text{sf}})T_0}{\Delta H^{\gamma \rightarrow \epsilon}}. \quad (6)$$

Owing to that $\Delta H^{\gamma \rightarrow \epsilon} < 0$, and for a given alloy, $\Delta H^{\gamma \rightarrow \epsilon}$ and T_0 are constants, thus

Table 1. Composition of the tested alloys (wt %) and measured P_{sf} , M_s .

Alloy	Mn	Si	Cr	N	Fe	$P_{\text{sf}}(\times 10^{-3})$	M_s (K)
0	30.3	6.1	–	–	balance	1.83	309
M1	26.4	6.2	5.2	–	balance	1.65	307
M3	30.0	6.0	5.3	–	balance	1.17	258
M4	32.2	6.4	5.2	–	balance	0.81	240
N1	30.0	6.0	–	0.05	balance	1.60	304

(Austenized at 1073 K for 0.5 h followed by water quenching)

$$M_s = A - B/P_{sf}, \quad (7)$$

where A and B are constants related to materials.

It is indicated from (7) that factors increasing P_{sf} will increase M_s and *vice versa*. Therefore in the present experiments, increasing the content of Mn or adding Cr or N in Fe-Mn-Si alloys will decrease M_s temperature.

2.4 Relationship between σ_M and P_{sf}

The proof yield stress $\sigma_{0.05}$ on the stress-strain curve obtained in extension test is taken as the critical stress required for inducing ϵ -martensite, σ_M . Owing to that the σ_M is usually lower than the real yield stress at room temperature in these tested alloys.

While summing up all the P_{sf} and σ_M resulting from various tested alloys and different treat conditions, a linear relationship between σ_M and $1/P_{sf}$ is obtained by linear regression as shown in figure 2:

Figure 1. Variation of M_s temperature vs reciprocal of stacking fault probability ($1/P_{sf}$) in Fe-Mn-Si based alloys.

Figure 2. A linear relationship between σ_M and $1/P_{sf}$ in Fe-Mn-Si-based alloys by linear regression as σ_M (MPa) = $29 + 0.212/P_{sf}$. The correlation coefficient is ≈ 0.98 .

$$\sigma_M (\text{MPa}) = 29 + 0.212/P_{sf}. \quad (8)$$

The Gibbs free energy per mole volume of $\gamma \rightarrow \epsilon$ transformation for stress-induction can be written as follows:

$$\Delta G^{\gamma \rightarrow \epsilon} = G_c^{\gamma \rightarrow \epsilon} + \Delta G_\sigma^{\gamma \rightarrow \epsilon}, \quad (9)$$

where $\Delta G_c^{\gamma \rightarrow \epsilon}$ is expressed as (13) and $\Delta G_\sigma^{\gamma \rightarrow \epsilon}$ is the mechanical driving energy supplied by applied stress which can be written as (Tamura 1982)

$$\Delta G_\sigma = \frac{1}{2} \sigma_a [\epsilon_\tau \sin 2\theta \pm \epsilon_n (1 + \cos 2\theta)], \quad (10)$$

where σ_a is the applied stress, ϵ_τ and ϵ_n are the shear strain and normal strain of phase transformation respectively; and θ is the orientation angle between stress-induced martensite and applied stress.

While the applied stress at deformation temperature, which is room temperature in the case of the present study, reaches a certain value, the total free energy $\Delta G^{\gamma \rightarrow \epsilon}$ just equals to zero so that the motion of Shockley partial dislocations are activated and the stacking faults are extended and overlapped, thus a first plate of ϵ -martensite is induced, in which the applied stress is the critical stress required for inducing transformation, σ_M . Thus, we obtain

$$-[C + D/P_{sf}] + \frac{1}{2} \sigma_M \Phi = 0. \quad (11)$$

Then

$$\sigma_M = M + N/P_{sf}, \quad (12)$$

where Φ , M and N are constants. Therefore the critical stress required for inducing martensite is proportional to the reciprocal of stacking fault probability, being in good agreement with the experimental results.

2.5 Effect of thermally mechanical training on P_{sf}

It has been pointed out by many investigators that thermal mechanical training can effectively improve the shape memory effect of the Fe-Mn-Si based alloys (Otsuka *et al* 1990; Inagaki 1992), but the mechanism is still not consistent. In our work the increase of stacking faults probability by training has been irrefutably proved by the X-ray profile analysis data as shown in table 2. Correspondingly the data of shape recovery degree η are also listed in table 2. We suggest that the essential cause of improvement of SME by thermal mechanical training may be the increase of stacking faults, which will not only provide the nucleation sites for SIM on the next deformation that leads to the decrease of σ_M and the increase of the amount of stress-induced ϵ -martensite on the same strain level, but also lead to the increase of

strain-hardening exponent that causes γ -phase strengthening homogeneously, resulting in the decrease of permanent strain; and on the other side promote the formation of finer lamella structure consisting of ε -martensite and residual austenite that will make the reverse transformation complete. All these facts will improve the shape recovery ability.

3. Grain size of γ -phase

Normally the grain size of γ -phase is an important microstructure parameter affected by phase transformations and mechanical properties. In Ni-Ti and Cu-based SMAs, the M_s temperature closely depends on the grain size. For example we have deduced that M_s is linearly related to the reciprocal of the square root of the grain size d as,

$$M_s = M_s^* - Kd^{-1/2}, \quad (13)$$

where M_s^* is a constant instead of the M_s temperature of a single crystal of the concerned alloy, and K a constant related to the materials (Wu *et al* 1988). However the above relation is not found in Fe-Mn-Si based SMAs. We have tested the M_s of ε -martensitic transformation for treatment of different austenitizing temperatures, as shown in table 4 (Jiang *et al* 1996).

The results of table 3 indicate that the change in grain size of γ -phase has no marked influence on M_s . The reason may be that in alloys with lower stacking fault energy, the nucleation of ε -martensite occurs by means of the pre-existed stacking faults rather than through nucleates at grain boundaries (Hsu 1980), which is quite different from the result. In Cu-based alloys, the item of elastic strain energy becomes a main resistance against the chemical driving force in the thermodynamic equilibrium equation. The shear stress required for the formation of α -martensite increases with decreasing the

grain size which is related to the strength of the parent phase through the Hall-Petch relation (Wu *et al* 1988). However the item of elastic strain energy for fcc $\rightarrow$ hcp transformation is so small as to be neglected as mentioned above. The main resistance becomes SFE, which is independent of the grain size.

4. Texture of γ -phase

The origin of SME of Fe-Mn-Si alloys is the reversion of macro deformation during heating, which is produced by the preferred stress-induced martensite or the preferred orientation of martensitic variants under applied stress. Obviously the preferred alignment of martensites is a texture problem in phase transformation. The component extent of texture will directly relate to SME. For example, extending a single crystal of Fe-Mn-Si alloy along $\langle 414 \rangle$ direction a maximum recoverable strain of 20% can be obtained (Sato *et al* 1982). Normally, however, polycrystal materials industry used FeMnSi, the recoverable preferential strain ε_R only reached 2%. Evidently it is related to the preferential extent of the stress-induced martensite. Otsuka *et al* (1990) have presented a formula for evaluating ε_R

$$\varepsilon_R = 20 \cdot f(V_\varepsilon \%), \quad (14)$$

where f is a preferred factor and $V_\varepsilon \%$ is the amount of SIM.

Recently we have studied the textures of γ -phase in an annealed Fe-27Mn-6Si-5Cr alloy wire by ODF analysis and connect with shape memory degree (Qi *et al* 1998). It is found that both the component and extent of fibre texture are variable with different annealing temperatures. For example, there are four kinds of texture i.e. $\langle 001 \rangle$, $\langle 111 \rangle$, $\langle 011 \rangle$ and $\langle 221 \rangle$ for annealing at 873 K. The intensity of these texture components is nearly the same except that of $\langle 221 \rangle$ which is lower. However, after annealing at 973 K the $\langle 001 \rangle$ texture becomes very strong, and the $\langle 011 \rangle$ and $\langle 221 \rangle$ components disappear while the $\langle 111 \rangle$ one only remains a trace. For annealing at 1073 K the above four components appear together again, while the intensities are all lower. After annealing at 1123 K only $\langle 001 \rangle$ and $\langle 011 \rangle$ can be detected.

The shape recovery degree η , which is determined by extending the wire specimen followed by recovery heating to 873 K, varies with annealing temperature as shown in table 4.

Table 2. Effect of thermal mechanical cycling of alloy N1.

Cycle no	σ_M (Pa)	η (%)	P_{sf} ($\times 10^{-3}$)
1	177	43	1.60
2	153	79	1.92
3	135	90	2.08
4	126	99	—
5	108	100	2.31

Table 3. M_s of $\gamma \rightarrow \varepsilon$ for different austenitizing temperature in Fe-26.4 Mn-6.2Si-5.2Cr (wt %).

Austenitizing temperature (K)	1073	1123	1173	1223	1273
Mean grain size of γ (μm)	20.62	23.70	28.30	34.58	37.12
M_s temperature (K)	307	311	311	313	313

Table 4. Shape recovery degree at various annealing temperatures.

Temperature (K)	873	973	1073	1123
η (%)	47	65	40	38

It is indicated that the best shape recovery degree is obtained by annealing at 973 K corresponding to the heat treatment of getting nearly monomial texture. Obviously there is some connection between SIM and texture. The calculation of the angles between the fibre texture direction $\langle uvw \rangle$ and the moving direction of $1/6\langle 211 \rangle$ partial dislocations shows that extending along $\langle 001 \rangle$ direction the maximum shear stress direction will be the nearest one to the stress induced direction. Therefore the more the crystal grains align with $\langle 001 \rangle$, the easier the ϵ -martensites form.

5. Conclusions

There are some micro-parameters and micro-characteristics which affect the macro-behaviours such as the phase transformation temperature of ϵ -martensite and SME in Fe-Mn-Si based shape memory alloys and can be summarized as follows:

(I) Stacking fault probability P_{sf} as a micro-parameter takes an important effect on both M_s temperature and σ_M , the critical stress of SIM. The larger the P_{sf} , the higher the M_s and the lower the σ_M . The thermal mechanic cycling will increase P_{sf} so that it decreases σ_M .

(II) The grain size of parent phase has no obvious influence on the M_s temperature for the fcc to hcp transformation.

(III) The texture of parent phase acts as a non-negligible role on the shape memory effect.

References

- Hoshino Y, Nakamura S, Ishikawa N and Sato A 1990 *Mater. Sci. Forum* **56-58** 643
- Hsu T Y (Xu Zuyao) 1980 *Acta Metall. Sinica* **16** 430
- Inagaki H 1992 *Z. Metallkd* **83** 8097
- Jiang B H and Hsu T Y (Xu Z Y) 1990 *Mater. Sci. Forum* **56-58** 457
- Jiang B H, Qi X, Zhou W M and Hsu T Y (Xu Z Y) 1996 *Scr. Metall. et Mater.* **34** 771
- Jiang B H, Qi X, Yang S X, Zhou W M and Hsu T Y (Xu Z Y) 1998 *Acta Mater.* **46** 501
- Noskova N I and Pavlov V A 1962 *Phys. Metals & Metall.* **14** 899
- Otsuka H *et al* 1990 *Iron Steel Inst. Japan Int.* **30** 674
- Olson G B and Cohen M 1976 *Metall. Trans.* **A7** 1897
- Qi X, Jiang B H and Hsu T Y (Xu Zuyao) 1998 *Physical Testing and Chemical Analysis, Part A: Physica Testing*, **34** 16 (in Chinese)
- Reed R P and Schramm R E 1974 *J. Appl. Phys.* **45** 4705
- Sato A, Chishima E, Soma K and Mori T 1982 *Acta Metall.* **30** 1177
- Seeger A 1956 *Metallkunde* **47** 653
- Tamura I 1982 *Metal Sci.* **16** 245
- Warren B E 1969 *X-ray diffraction* (Reading, Mass: Addison-Wesley) pp 275-294
- Wu J X, Jiang B H and Hsu T Y (Xu Z Y) 1988 *Acta Metall.* **36** 1521