Effect of Si on the reversibility of stress-induced martensite in Fe–Mn–Si shape memory alloys

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Abstract

Fe–Mn–Si is a well-characterized ternary shape memory alloy. Research on this alloy has consistently shown that the addition of 5–6 wt.% Si is desirable to enhance the reversibility of stress-induced martensite vis-à-vis shape memory. This paper examines the effect of Si on the morphology and the crystallography of the martensite in the Fe–Mn–Si system. It is concluded that the addition of Si increases the c/a ratio of the martensite, reduces the transformation volume change and decreases the atomic spacing difference between the parallel close-packed directions in the austenite–martensite interface (habit) plane. It is proposed that, in addition to austenite strengthening, Si enhances reversibility by reducing the volume change and the interfacial atomic mismatch between the martensite and the austenite. Although shape memory is improved, transformation reversibility remains limited by the necessary misfit dislocations that accommodate the atomic spacing differences in the interface.
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1. Introduction

The shape memory properties of the Fe–Mn–Si-based alloy system are well documented [1–5]. The parent phase in these alloys is face-centred cubic (fcc) austenite, and deformation produces a hexagonal (hcp) martensite known as ε. The transformation from fcc to hcp occurs by the formation and overlap of stacking faults [1]. The stress-induced ε can be reversed to the parent phase by heating, and this imparts the shape memory effect (SME).

The pioneering work of Enami et al. [6] showed that limited shape memory can occur in binary Fe–Mn alloys and Sato et al. [1] subsequently demonstrated higher recovery strains in single crystals of Fe–Mn–1%Si alloys. However, the recovered strains were relatively low, and Murakami et al. [7] subsequently reported that higher concentrations of Si significantly increased the amount of recoverable strain. They carried out an extensive investigation to determine the optimum composition for the ternary Fe–Mn–Si shape memory alloy system and found that shape memory is optimized for a composition of approximately Fe–30Mn–6Si (wt.%). Shape memory increases with increasing Si, but above 6 wt.% alloys are too brittle. The other main alloying addition, Mn, can be used in concentrations from about 12% to 30% and has been combined with Cr, Ni and other alloying elements. For example, a "stainless" variant based on the elements Fe–Mn–Si–Cr–Ni has been developed [8]. Although the transformation temperatures are composition dependent, an appropriate choice of thermo-mechanical treatment and deformation temperature generally ensures that significant shape memory will be exhibited.

Even though silicon is now established as an important ingredient in this alloy system for good shape memory, the reason that it strongly promotes martensite reversibility is still uncertain [5]. The role of Si on the Fe–Mn–Si system has been studied by Maki and Tsuzaki [9], who clearly showed that the addition of Si to Fe–Mn alloys enhances

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the reversibility of thermally induced ε martensite, and that the same trend occurs for stress-induced ε martensite [7]. Maki and Tsuzaki [9] postulated that Si enhances reversibility because of: (i) solid solution strengthening; (ii) reduction in the stacking fault energy (SFE); and (iii) lowering of the Néel temperature (T_N) below M_S.

Although these three "silicon" factors are generally accepted as valid contributors to enhanced martensite reversibility, unambiguous experimental confirmation has been lacking, despite significant attention to the thermodynamics aspects of SFE and T_N. Moreover, in a recent publication, the present authors modified the SFE by alloying with Cr and Ni, and found no correlation between SFE and SME [10]. The effect of magnetic transition on the SME was also examined [10] and no significant decrease in SME was found for alloys with M_S below T_N. It was therefore concluded that T_N has little effect on shape recovery, consistent with the results of earlier work of Wayman et al. [11,12].

As a consequence of these conclusions, the role of Si on shape memory has been reconsidered, and the work of previous authors re-examined. This literature review indicated that two other factors could be important. One is that the addition of silicon enhances the reversibility of martensite by refining the martensite plate size. In the paper by Maki and Tsuzaki [9], micrographs of two alloys, Fe–24Mn and Fe–24Mn–6Si, are shown after cooling below the M_S. The microstructures are markedly different. The Si-containing sample exhibited significantly finer martensite plates compared to the Fe–Mn alloy. Finer plates are known to have better reversibility than thick plates [4,13] because the transformation strains associated with each plate, and their potential plastic accommodation, are more limited. The other factor is a favourable effect of Si on the crystallography of the transformation. Sato et al. [3] reported that Si increases the c/a ratio of the martensite, and results in enhancement of the shape recovery. The work reported in this paper addresses these two factors.

2. Experimental methods

The compositions of the alloys investigated are detailed in Table 1. The alloys were prepared by arc-melting in 50 g buttons under an argon atmosphere, using high-purity Fe, Mn and Si.

The arc-melted buttons were hot rolled at 1273 K from a thickness of 6 mm to 1.5 mm in six passes. For X-ray diffraction and shape memory testing, sections from the hot rolled strip with approximate dimensions of 20 mm × 40 mm × 1.5 mm were annealed at 1000 °C for 1 h before cold water quenching.

The SME was measured for selected alloys (A, B, D, G and H) using the bend test technique. The strain of the sample at the outer edge of the bend radius is determined by the equation:

$$\varepsilon = \frac{1}{(2R/h) + 1}$$

where ε is the conventional strain, R is the bend radius and h is the sample thickness.

To produce a range of pre-strains, samples with a thickness of about 0.8 mm were bent around rods with different radii. The bent samples were photographed and then recovery annealed at 773 K for 15 min for shape recovery. After recovery annealing, the residual strain ε_r was measured and used to calculate the percentage strain recovery: $100 (\varepsilon–\varepsilon_r)/\varepsilon$.

The transformation temperatures were measured using a TA Q100 differential scanning calorimeter (DSC) equipped with a refrigerative cooling system. The transformation behaviour of each of the samples was measured in the as-quenched condition after annealing at 1273 K. Before testing in the DSC, samples were immersed in liquid nitrogen to form thermal martensite, then heated in the DSC to measure the reversion of martensite to austenite. The samples were then cooled to determine M_S. The M_S, A_S and A_F temperatures are given in Table 1 for all alloys except alloy C, for which M_S was below the lower temperature limit of the instrument (223 K).

X-ray diffraction (XRD) was carried out using Cu Kα radiation and a scan rate of 0.5 or 1 deg. min^{-1}. Scanning electron microscopy was conducted using a Leica 440 scanning electron microscope (SEM). Before SEM and XRD, samples were electropolished in a solution of 5% perchloric acid in acetic acid. The electropolishing was carried out at 30 V for 2 min at room temperature.

Table 1
Compositions (in wt.%) of the alloys, measured by energy-dispersive spectroscopy, together with transformation temperatures for the formation and reversal of thermal martensite (DSC measurements).

Alloy	Fe (wt.%)	Mn (wt.%)	Si (wt.%)	M_S (K)	A_S (K)	A_F (K)
A	74.8	25.2	0.0	356	418	477
B	70.3	29.7	0.0	276	369	417
C	63.0	35.4	1.6	ND[a]	ND	ND
D	74.4	23.2	2.4	384	510	555
E	77.9	17.6	4.5	409	547	661
F	75.2	20.0	4.8	402	575	647
G	74.3	20.5	5.2	336	458	548
H	69.0	26.0	5.0	334	509	597

[a] ND, not determined.