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On the origin of the improvement of shape memory effect by precipitating VC in Fe–Mn–Si-based shape memory alloys

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ABSTRACT

We studied the role of VC precipitation in improving the shape memory effect (SME) of the as-solution treated Fe–Mn–Si-based shape memory alloys by examining the microstructures developed during aging and deformation using transmission electron microscopy and electron channeling contrast imaging. Our results suggest that VC particles are not the only product of aging. Upon aging at 650 °C, the precipitation of VC particles is accompanied by the formation of profuse dislocations ($2.26 \pm 0.098 \times 10^{13}$ m^{-2}). In this case, the SME is not improved compared to the as-solution treated reference state. Upon aging at high temperatures (700–900 °C), a number of stacking faults are formed accompanying the VC precipitation and the SME is significantly improved, where the recovery ratios reach almost twice that of the as-solution treated state (<50%). For these high-temperature aged states, in situ straining experiments reveal that the stacking faults rather than the VC particles play an important role in the stress-induced martensitic transformation, leading to the formation of very thin (<3 nm) martensite plates with a single crystallographic variant within each grain. These martensite plates are in contrast to the very thick (from tens to hundreds of nanometers) and multi-variant martensite plates that prevail in the as-solution treated state. By comparing the characteristics of the martensite plates between the as-solution treated and the high-temperature aged states, the reasons for the improvement of SME by precipitating VC were discussed.

1. Introduction

Shape memory alloys are characterized by reversible diffusionless/martensitic transformation, i.e., stress-induced martensitic transformation upon loading and its reverse transformation upon unloading or heating [1,2]. In deformed shape memory alloys, a certain portion of the non-linear strain can be recovered upon unloading and further recovery can be attained by heating above a critical temperature. The former phenomenon is referred to as superelasticity and the latter shape memory effect (SME) [3]. Both phenomena arise from the reverse martensitic transformation. In the past half century, Ti–Ni-based alloys have attracted the most extensive research efforts among all shape memory alloys owing to their excellent superelasticity and SME (recovery strain up to 8%) as well as the associated complicated martensitic transformations [4–6]. Numerous applications such as pipe couplings, coronary stents and micro-actuators [7–10] have been found for Ti–Ni-based shape memory alloys. Nevertheless, these alloys suffer from high alloying costs and low workability, limiting their wider application.

In 1982, Sato et al. [11] observed a large recovery strain (up to 9%) comparable to that of Ti–Ni-based shape memory alloys in single-crystalline Fe–30Mn–1Si alloy, opening up the possibility of developing commercially more attractive ferrous shape memory alloys with lower alloying costs and better workability. However, subsequent studies [12–14] revealed that the as-solution treated polycrystalline Fe–Mn–Si-based alloys suffered from a low recovery strain. Even the three alloys, Fe–28Mn–6Si–5Cr, Fe–20Mn–5Si–8Cr–5Ni and Fe–16Mn–5Si–12Cr–5Ni, which were claimed to have a combination of good corrosion resistance and good SME, exhibited a recovery strain <2.5% [13]. In the past three decades, considerable effort has been devoted to improving the SME of these alloys and their derivatives [13–32].

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Given that the SME of the Fe–Mn–Si-based alloys arises from the reversible transformation between face-centered cubic (fcc) γ austenite and hexagonal close-packed (hcp) ε martensite, all factors that promote the $\gamma \rightarrow \varepsilon$ martensitic transformation during straining or the reverse $\varepsilon \rightarrow \gamma$ transformation during heating are likely to improve the SME. In addition, the factors that increase the yield strength of the parent austenite are also considered effective in terms of preventing the undesired intrusion of irreversible slip deformation during martensitic transformation. The majority of the initial attempts to realize these beneficial factors were focused on thermomechanical treatments: (i) ausforming, i.e., performing slight tensile deformation above the temperature for martensitic transformation [15,17,19]; and (ii) training, i.e., imposing a few cycles of slight deformation at room temperature and subsequent recovery annealing [13,16,18]. These two types of treatment have indeed led to increased recovery strains, e.g., 3.8% in an ausformed Fe–29.9Mn–6Si alloy [19] and 5.4% in a trained Fe–20Mn–6Si–7Cr–1Cu alloy [18]. Such improvements in the attained SME were initially attributed to the enhancement of the yield strength of the austenite as well as to the reduction of the critical stress for martensitic transformation [13,19].

By correlating the SME to the characteristic features of the stress-induced martensite plates, Kajiwara et al. [33–36] proposed that in trained Fe–Mn–Si-based alloys the improvement of SME was governed by the formation of (i) uniformly distributed, (ii) very thin (~1 nm in thickness) and (iii) single-variant martensite plates within each grain. The training-induced increase in the yield strength of the austenite and decrease in the critical stress for martensitic transformation were regarded as a necessary but not sufficient condition for improving the SME. The characteristic microstructures developed during training were identified as high densities of uniformly distributed stacking faults (SFs) [33,36,37] and very thin hcp plates [36] on the primary slip planes of the austenite. These microstructures were considered indispensable for the formation of the specific martensite plates mentioned above upon mechanical loading to reach a shape change [33–36]. In the alloys subjected to ausforming, uniformly distributed SFs have also been observed [20] and the formation of thin martensite plates with the same variant has also been considered to play the dominant role in improving the SME [38].

It should be noted that additional thermomechanical treatments raise the processing costs and they are not applicable for complicated shapes. In 2001, Kajiwara et al. [21,22] reported a remarkable increase in the recovery strain by precipitating fine NbC particles in Fe–Mn–Si-based alloys without applying any additional training. Subsequent studies suggested that the precipitation of VN [26,27], TiC [39,40] and VC [30,31] also resulted in the improvement of SME. All of these precipitates have a NaCl-type crystal structure, identical to that of NbC. In addition to increasing the yield strength of the austenite via precipitation hardening, these precipitates have been speculated (i) to act as the nucleation sites of stress-induced martensite [21,22,24–27,39,40], i.e., promoting the stress-induced $\gamma \rightarrow \varepsilon$ martensitic transformation, and (ii) to exert back stresses to the martensite tips that approach them [21,24,26,27]. Such back stresses, which result from the elastic strain field surrounding the precipitates, were supposed to assist the reverse movement of the Shockley partial dislocations at the martensite tips during recovery annealing, i.e., promoting the reverse $\varepsilon \rightarrow \gamma$ transformation. However, to date no direct experimental evidence is available to justify these speculations. On the other hand, the work of Stanford and Dunne [39,40] suggested that under certain circumstances precipitates did not necessarily lead to the improvement of SME, e.g., for rather small NbC precipitates (<5 nm) even a detrimental effect was observed. Therefore, a fundamental understanding concerning the influence of the precipitates on the SME, especially the origin for the improvement of SME by precipitation, remains to be developed.

Here, we investigate the role of VC precipitation in improving the SME of an as-solution treated Fe–28Mn–6Si–5Cr–0.764V–0.18C (wt.%) alloy. Aging treatments are carried out at various temperatures for precipitating VC and bending tests are performed to assess the SME. We examine the microstructures developed during aging and the stress-induced martensite plates formed during deformation using transmission electron microscopy (TEM). In situ observation of the evolution of the martensite plates during straining is made using electron channeling contrast imaging (ECCI) [41]. We discuss the contribution of the VC precipitation to the improvement of SME based on the comparison of the following three aspects between the as-solution treated and the aged samples: (i) the initial microstructures, (ii) the martensite plates and (iii) the evolution of these plates.

2. Experimental

The as-received hot-rolled alloy sheets were solution treated at 1140 °C for 6 h under argon atmosphere and subsequently water quenched to room temperature. Their chemical composition was analyzed by inductively coupled plasma optical emission spectroscopy, Table 1. For precipitating VC, a few of the as-solution treated sheets were aged at 650–900 °C for 2 h under argon atmosphere and then subjected to water quenching. All specimens for the following experiments were cut from the as-solution treated or aged sheets by electrical discharge machining.

The SME was measured using bending tests and recovery annealing. Flat specimens with their longitudinal direction parallel to the rolling direction of the sheets and a dimension of $100 \times 2 \times 1\ \mathrm{mm}^3$ were bent around various bend radii to produce a series of pre-strains. The bending pre-strain ε_p was determined by the following equation [39]:

$$\varepsilon_\mathrm{p} = \frac{t}{2R+t}, \qquad (1)$$

where t and R are specimen thickness and bend radius, respectively. The shape recovery of the bent specimens was accomplished by annealing at 450 °C for 15 min. Subsequently, the residual strain ε_r resulting from incomplete recovery was estimated using Eq. (1) as well. The recovery ratio was given by $(\varepsilon_\mathrm{p} - \varepsilon_\mathrm{r})/\varepsilon_\mathrm{p} \times 100\%$, where $(\varepsilon_\mathrm{p} - \varepsilon_\mathrm{r})$ is the recovery strain.

For characterizing the stress-induced martensite plates in detail, flat dog-bone shaped tensile specimens with a gauge section of $20 \times 5 \times 2\ \mathrm{mm}^3$ were cut along the rolling direction of the sheets. They were deformed to 4% total strain under tension at a cross-head speed of 0.6 mm/min (corresponding to an initial strain rate of $5 \times 10^{-4}\ \mathrm{s}^{-1}$) in a Zwick ZH 100 tensile testing machine. An extensometer was used to record the tensile strain. After deformation, round TEM disks with a diameter of 3 mm and a thickness of 0.5 mm were cut from the gauge section of the deformed tensile specimens. The evolution of the stress-induced martensite plates was examined by in situ three-point bending experiments performed in a scanning electron microscope (SEM), where flat specimens with a dimension of $7 \times 3.5 \times 0.8\ \mathrm{mm}^3$ were used. One $7 \times 0.8\ \mathrm{mm}^2$ surface of these specimens was polished prior to deformation. On such a surface sequential microstructural

Table 1
Chemical composition (wt.%) of the as-solution treated alloy.

Element	Fe	Mn	Si	Cr	V	C
Composition	Balance	27.9	5.68	5.16	0.773	0.212