On the Nature of the Variation of Martensitic Transformation Hysteresis and SME Characteristics in Fe-Ni-Base Alloys

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Abstract. The purpose of this paper is to summarize the various investigations, both by the authors and other works, concerning with the martensitic transformation and SME in Fe-Ni-base alloys. The thermal hysteresis dependence on the alloying elements and thermal treatments are surveyed. The contribution and effect on SME characteristics of widely used alloying elements such as Ti, Nb, Ni, Al, Co, Ta and peculiarities of thermal treatment are discussed. It is noted the main goal of these treatments is to reduce the symmetry of transformation by the ordering or precipitation of a fine coherent phase. The physical principles of transformation hysteresis manipulation in Fe-base alloys is discussed and it concluded that the thermal cycling behavior of Fe-base alloys is very complex and is not clearly understood at present. On the other hand, it is pointed out that thermal cycling is an effective method for control and improvement of SME in these alloys. It is concluded that Fe-base alloys are highly evolved shape memory materials having a wide working range, good workability and are relatively cheap. In addition, the properties are easily controlled by suitably alloying, aging and thermal cycling.

1. INTRODUCTION

Recently, serious progress has been achieved in the development of Fe-based Shape Memory Alloys with a FCC-BCC(T) martensitic transformation (MT). As reported at [1] a high tetragonality of the martensite lattice, a decrease of the thermal hysteresis, the presence of a thin-plate morphology of the martensite and a change of type from non-thermoelastic to thermoelastic all have been observed in Fe-Pt alloys near the composition Fe₃Pt with an increase in the degree of long order of the austenite. In Fe-Ni-Co-Ti alloys it has been shown that similar effects are caused by fine coherent precipitates which also possess a L1₂ structure[2]. In our laboratory, significant attention has been paid to the investigation of Fe-Ni-(Ti, Nb, Ta, Al)-based (FNB) alloys in the last decade [3,4,5,6]. The aim of this report is to discuss some peculiarities of MT and SME in aged Fe-Ni-based alloys, namely:

- effect of the aging on the hysteresis, martensitic points and SME
- particles and martensite structures
- precipitated particle deformation mechanism
- perfect SME induced by aging
- thermal hysteresis behavior and shape of hysteresis loop
- thermal cycling mechanical behavior

2. ALLOY PREPARATION AND EXPERIMENTAL PROCEDURES

The ranges of chemical composition of the alloying elements and their effect on the various properties of FNB alloys are given in Table 1. The basic elements of FNB alloys are Fe and Ni. Ti, Al and Nb, Ta are

elements that supersaturate the solid solution. Due to these elements two systems of precipitates can form during annealing. These are γ' in the former pair and γ'' in the later (figure 1). Both systems decrease the

Table Effect of the element on alloys properties

Alloying element	at. %	Effect on M_s	Effect on hysteresis	Effect on hardness	Minimal hysteresis	Precipitates system	Contribution of element
Fe	ball	$\pm$	$\pm$				base
Ni	26-32	$\downarrow$	$\pm$	$\uparrow$			base
Ti	<5	$\downarrow$	$\uparrow$	$\uparrow$	50 K	γ' [2,8]	saturated element
Al	<4	$\downarrow$	$\uparrow$	$\pm$	?		saturated element
Nb	<4	$\downarrow$	$\uparrow$	$\uparrow$	180 K	γ'' [3,4,7]	saturated element
Ta	<3	$\downarrow$	$\uparrow$	$\uparrow$	180 K		saturated element
Co	<12	$\uparrow$	$\pm$	$\pm$			modifier

$\uparrow$ - increase; $\downarrow$ - decrease; $\pm$ - effect is small or absent.

Figure 1: γ' at left hand and γ'' at right hand. At left alloy Fe-Ni29-Co10-Ti-5 aged at 750°C 3 hours and at right alloy Fe-30-Nb-6.8 aged at 650°C 12.5 hours is shown. Dark field in (100) superlattice spot for both alloys is shown.

M_s point down to liquid nitrogen temperatures and increase the hardness of alloys (figure. 2). To achieve the perfect SME alloys with γ' phase are aged at higher temperatures for a shorter time than the alloys with γ'' phase. Therefore, the decomposition process in Fe-Ni-Nb(Ta) alloys is more controllable It is only Co that increases the M_s point up to environment temperatures and makes the utilization of these alloys very possible. Another peculiarity of the Co addition is accelerating the decomposition processes[9]. The composition inhomogeneities of the samples was no more than 0.4 at.% after the ingots were hot forged and homogenized at 1473K for 360 ks. In the solution treatment state, the FNB alloys were hot forged and rolled. Further aging at appropriate temperatures control of the required hardness and SME properties by choosing a suitable aging time.

3. DISCUSSION

3.1 Effect of the aging on the hysteresis, martensitic points and SME

The common method for the achievement of good SME in the FNB alloys consists of suitable aging of the alloy which initially demonstrates no perfect SME. So, as a rule the typical values of the shape recovery and hysteresis in the solution treatment state are correspondingly 30-60% and 723-1023 K depending on alloy composition. By ausaging the hysteresis decreases and perfect shape memory effect takes place. Some analogies between the characteristics of MT and SME in alloys with γ' - and γ'' -phases are found. In figures 2, 3 typical aging curves are shown. According the Hornbogen model [11] describing aging

behavior of Fe-Ni-Al alloys the M_s point is guided by two opposite trends. First is the increase in M_s owing to the depletion by the solute and Ni atoms during the aging. Second is the decrease in M_s due to the strong internal stresses induced by small untransformed coherent particles. It is supposed these stresses are the main reason for the decrease of hysteresis. The minimum value of hysteresis depends on the composition and system of precipitates formed during the aging (see table).

Figure 2: Hardness and hysteresis as a function of aging time for alloys with both systems of precipitates referred to as " γ' hardened" Fe-Ni29-Co10-Ti-5 and " γ'' hardened" Fe-Ni30-Nb6.8, respectively.

Figure 3: Shape recovery and M_s point as a function of aging time for alloys with both systems of precipitates referred to as " γ' hardened" Fe-Ni29-Co10-Ti-5 and " γ'' hardened" Fe-Ni30-Nb6.8, respectively.

3.2 Particles and martensite structures

For an improvement in SME appears to be associated with high tetragonality of martensite in Fe-Pt and Fe-Ni-Co-Ti alloys, due to either the ordering in $L1_2$ as whole or in the precipitates, it could be concluded the high tetragonality of martensite is a necessary condition for a perfect SME in iron-base alloys with FCC-BCC(T) martensitic transformation. As for $L1_2$ long range order, the direct influence on the tetragonality of martensite has been clearly shown in Fe_3Pt alloys. What factor controls the martensite structure in alloys with the fine coherent particles?

The same $L1_2$ ordering of particles having different compositions suggests that the tetragonal distortion of

Figure 4: TEM microphotograph of Fe-Ni30-Nb6.8 alloys aged at 650 $^{\circ}C$.

- a γ'' particles deformed after martensitic transformation. Particles imbedded in martensite. Dark field;
- b morphology of martensite plates;
- c large crystals of martensite remaining after heating to 973K;

the martensite lattice is caused by the tetragonal symmetry of the atomic ordering in particles. To verify this suggestion, Fe-Ni30wt. %-NbX alloys where γ'' -phase precipitates have been examined. These particles are distinct from the γ' phase by the ordering, but are similar in all other features.

The γ'' -phase is formed as coherent plate-shaped fine particles with a DO₂₂ structure as shown in figure 1. Uniformly distributed fine particles of the γ'' -phase have an immediate effect on the nucleation and growth of the martensitic crystals because the γ'' -particles are inherited by the martensite. But they remain FCC after MT of the surrounding matrix. It was found [4] that the particles of the γ'' -phase initially having an orientation the same as the austenite undergo a disorientation relative to both the martensite and the untransformed austenite. Also it was observed that the γ'' -particles are deformed during MT (figure 4a). It is not clear whether the precipitates have been plastically sheared or twinned. The morphology of the martensite is a mixture of thin-plate and lenticular martensite (figure 4b). Twinned plate with midribs were observed, but the dislocations were not identified at the crystal's periphery. The tetragonality of the martensite achieved 2.5% for 90 ks and decreased during further aging.

3.3 Precipitated particle deformation mechanism

To accommodate the shear of the surrounding transformed matrix the particles may be plastically sheared. Thus rotation is provided by the dislocations aligned at the boundary between the martensite and γ'' phase. The observed solid rotation of the particles around the $[110]_\alpha$ axis by 5-6° can be also provided by the dislocation loops pinned to the particles. They are good obstacles for the dislocations introduced by the MT and carried out the complementary shear of the MT. Both proposed mechanisms are equivalent in terms of induced rotation. As was established in [4] the last mentioned mechanism is preferable. Thus, the rotation of particles is such that it accommodates the additional shear of the martensite rather than the shape deformation as a whole and, hence, the particles provide, to some extent, this complementary shear.

3.4 Perfect SME induced by aging

The aligned dislocation loops around the particles or their elastic counteraction creates the reverse forces that are uniformly distributed in the martensite. The particles as memory elements are uniformly distributed into the martensite. The elastic energy stored by the particles may be estimated from following expression:

$$E = c \cdot \mu \cdot \varepsilon^2 / 2 \cdot (a/b),$$

where c , μ , a , b are volume fraction, shear module, thickness and length of the particles respectively; ε is the observed particle deformation that is difference between martensitic deformation and plastic relaxation of the particles. μ may be evaluated from the curves of hardening of FNB alloys. Assuming that hardness of particles is no less than hardness of aged alloy we can achieve $\mu \approx 500/0.002 = 2.5 \cdot 10^5$ MPa. ε can be estimated from the observed rotation of particles assuming that the observed deformation of particles is a simple shear. Thus $\varepsilon \approx 2 \cdot \sin(6^\circ) \approx 0.2$. Supposing $c = 0.1$, we have $E = 32$ cal/mole for plate shape particles ($(a/b)=0.2$) and 160 cal/mole for spherical particles. These values are comparable with energy of martensitic transformation [10] in Fe-Ni alloys. That is why the significant reduction of hysteresis is observed. In the framework of the proposed scheme, the deformation modes of the particles (elastic deformation, structural transformation, twinning or plastic shear) affect the level of the stored stresses and thus the value of tetragonality of the α phase. The higher the volume fraction of the particles, the higher the elastic energy stored by the particles. The shape factor (a/b) explains why the mentioned effects are stronger in alloys with spherical precipitates (γ' phase). The role of the particle dimensions is also important. It is likely that the characteristic scale at which the relaxation of the transformation stresses can be carried out elastically can not be much more than the characteristic scale of the complementary shear (e.g. the twin thickness).

3.5 Thermal cycling mechanical behavior

Thermal cycling behavior depends on the previous thermal treatment and, as a consequence, the substructure of austenite [5]. In the Fe-Ni30 alloy where the γ'' particles are not precipitated the effect of

the thermal cycling on the SME was negligible but the amount of deformation stored by the sample after MT increases with cycling. Contrariwise, in alloys with the precipitates of γ' - and γ'' -phase improvement of SME took place and the amount of permanent phase deformation decreases after cycling (figure 6). The decrement depends on the aging time.

When the heating took place to 973K the stored deformation decrement is due to the creation of the dislocation net pinned by the particles. This net is the physical realization of the additional slips occurring during the direct and reverse MT. The volume fraction of martensite decreases negligibly with the increasing of number of the cycles. Because the resulting force of the internal stresses fields arising due to pinned dislocations has a different direction to the external applied force, the component of the later in the initial load direction seems to be less than in the first cycle. Thus a decrement of stored deformation takes place. Under condition when the mobility of dislocations is relatively high, redistribution and annihilation of dislocations occur. The equilibrium between the pinning of the dislocation substructure during $\gamma \leftrightarrow \alpha$ MT and their annealing during heating determines the stored deformation behavior under thermal cycling.

3.6 Thermal hysteresis behaviour and shape of hysteresis loop

Figure 5: Relative deformation of Fe-Ni30-Nb6.8 alloy as function of temperature. The thermal treatment of the specimen is indicated in right top corner of each figure. Arrows on curves indicate the direction of process (loading, cooling, etc)

By aging the loop of thermal hysteresis is transformed in the same way in both systems of the alloys. The recovery of shape is accomplished in a few stages as shown in figure 5. The low temperature part of the recovery was detected in both solution treated and overaged states and in Fe-Ni30 alloy[6]. As it was found in [6] the direct MT continues during the heating in the internal stress field caused by the initially formed crystals of the martensite although the plastically relaxation of energy is not excluded [5]. Thus, the low temperature shape recovery is due to an accommodation mechanism other than the reverse MT.

The quota of every step in shape recovery depends on the aging time. By X-ray diffractometry and electrical resistivity, the 10-15% of α phase was found after heating up to a temperature at the end of the intermediate shape recovery part. The lowering of the intermediate temperature and decreasing of the thermal hysteresis associate with the elastic energy stored by the particles. As established from the TEM, only small and medium-size crystals of martensite disappear after the heating up to the intermediate stage. Large ones have been remained up to 973K (figure 4c). The austenite is formed within these martensite crystals by the nucleation and growth mechanism, with diffusion processes being involved since the austenite boundary is irregular and distorted[5].

4. CONCLUSIONS

It may be concluded that FNB materials are potential Shape Memory materials. Perfect SME can be achieved in these alloys due to the storage by the fine coherent particles of elastic energy. Opposition between the stored elastic energy and the annealing processes control the thermal cycling behavior in these alloys. The properties easily controlled by alloying, aging and thermal cycling. Other possibilities are opened by the complex character of the shape recovery path, allowing the use of FNB alloys in applications which require complex operations.

Figure 6: Sample deformation and SME thermal cycling behavior for Fe-Ni₂₉-Co₁₀-Ti₅ alloy.

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