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Internal friction in Fe–Mn–Cr–Si–Ni shape memory alloys

R.B. Pérez-Sáez[a], M.L. Nó[b] and J. San Juan[a,*]

[a]Dipartamento Física Materia Condensada, [b]Dipartamento Física Aplicada II, Facultad de Ciencias, Universita del Pais Vasco. Apartado. 644, E-48080 Bilbao (Spain)

Abstract

In this work we have carried out internal friction and modulus measurements on Fe–Mn–Cr–Si–Ni samples using an inverted torsion pendulum at 1 Hz. The internal friction peaks associated with the martensitic transformation are clearly observed in the obtained spectra. Analysis of the internal friction spectra allowed us to obtain a linear relation between the peak area and the heating or cooling rate during the direct and reverse transformations. The evolution of the transformation temperatures and the hysteresis of the cycle as well as the area of the internal friction peak have been studied *vs.* the cycling. A general explanation is discussed that allows us to interpret the whole set of experimental results.

1. Introduction

Historically, shape memory phenomena have been associated with alloys that exhibit a thermoelastic martensitic transformation (MT), such as Ti–Ni, Cu–Zn–Al, Cu–Al–Ni as well as some ferrous alloys such as Fe–Pt, Fe–Pd and Fe–Ni–Co–Ti. However, it is now known that some shape memory effect (SME) is possible without thermoelasticity [1, 2]. This is the case for Fe–Mn–Si alloys, which show an SME associated with the f.c.c. (γ-austenite)$\Leftrightarrow$h.c.p. (ϵ-martensite) non-thermoelastic MT. Sato *et al.* [3, 4] found that Fe–Mn–Si single crystals exhibit a perfect shape recovery when they are deformed in a specific direction. Murakami *et al.* [5] obtained a complete SME in the same polycrystalline alloy. This is why a new Fe–Mn–Cr–Si–Ni family of alloys has been developed. The Cr improves the corrosion resistance and the Ni stabilizes the γ phase, avoiding the nucleation of δ-ferrite [6]. After a suitable training process, Moriya *et al.* [7] obtained a very good shape recovery as high as 3% in these alloys.

The aim of this work is to study by means of internal friction measurements the evolution of the martensitic transformation as a function of the cycling and the heating–cooling rate in an Fe–Mn–Cr–Si–Ni alloy.

2. Experimental methods

An ingot of Fe–16Mn–9Cr–5Si–4Ni (weight per cent) was elaborated at Ugine-Savoie by the usual melting and casting process under an argon atmosphere. The ingot was hot rolled into a plate 1.7 mm thick and subsequently cold rolled to 0.5 mm at room temperature. From this plate a sample of dimensions 50 mm$\times$5 mm$\times$0.5 mm was cut for the internal friction measurements. The sample was annealed for 1 h at 900 °C in a helium atmosphere and ice-water quenched. According to Federzoni *et al.* [8], the annealing at 900 °C is above the recrystallization temperature and consequently the γ phase grains should contain a very low density of dislocations.

The internal friction was measured in an inverted torsion pendulum at about 1 Hz in a temperature range from 110 to 600 K and at a strain amplitude of 5×10^{-6}. The standard constant heating–cooling rate was 100 K h^{-1}, except for the spectra corresponding to the study as a function of the temperature rate.

3. Experimental results

In Fig. 1 the logarithmic decrement (δ) and the square of the oscillation frequency are plotted *vs.* the temperature. These are the internal friction spectra and modulus variation curves corresponding to the direct and the reverse MT obtained during cooling and heating respectively. We can point out the large thermal hysteresis characteristic of the non-thermoelastic MT. The internal friction background in the martensitic phase is as low as in the austenitic phase. This fact is evidence of the low mobility of the martensitic interfaces or the small quantity of such interfaces [9]. The square fre-

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[*] Author to whom correspondence should be addressed.

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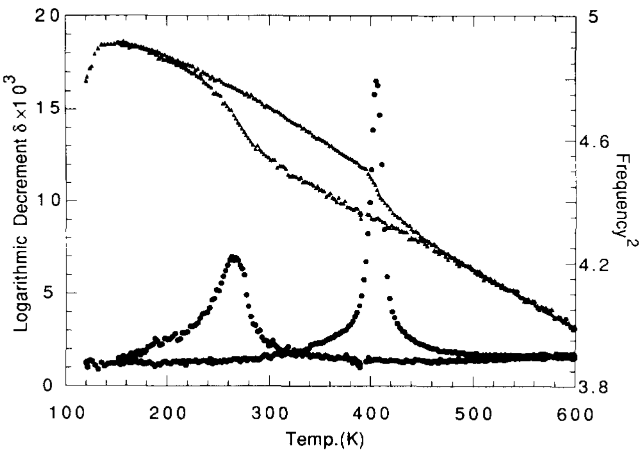

Fig. 1. Logarithmic decrement δ (●) and square frequency (▲) *vs.* temperature during second cycle of transformation (heating–cooling rate 100 K h^{-1}).

quency curves show an increase in the modulus during the γ–ϵ transformation. In addition, a strong decrease in the modulus linked to the paramagnetic–antiferromagnetic transition that the γ phase undergoes, which inhibits any further MT, is clearly observed around 130 K.

It is well known that the internal friction peaks linked to the MT show a strong dependence on the heating–cooling rate, but no work has been performed on this kind of alloy. We have carried out a study of the peak height behaviour for heating–cooling rates between 60 and 220 K h^{-1}. The evolution of the peaks with the temperature rate will be analysed later.

The evolution of the internal friction peaks with the thermal cycling has also been studied. We have observed a decrease in the peak temperatures during the direct transformation (γ–ϵ) as well as during the reverse transformation (ϵ–γ), as seen in Fig. 2A. The shift of the peak temperature after 20 cycles is about 10 and 25 K for the direct and the reverse transformation respectively, leading to a decrease of 15 K for the transformation hysteresis (Fig. 2B). It is interesting to note that the temperature displacement is produced in a global way, shifting the whole internal friction peak; this shift can also be observed in the modulus change linked to the MT. In contrast, no shift at all is observed in the modulus change due to the magnetic transformation at the Néel temperature.

The evolution of the height and area of the direct transformation peak *vs.* the number of cycles is shown in Fig. 3. The increase in the height and area of the peak is accompanied by a sharpening of the peak shape. Both behaviours (the shift of the peak temperature and the increase in peak size) are stronger during the first cycles and show a slow tendency to a further stabilization.

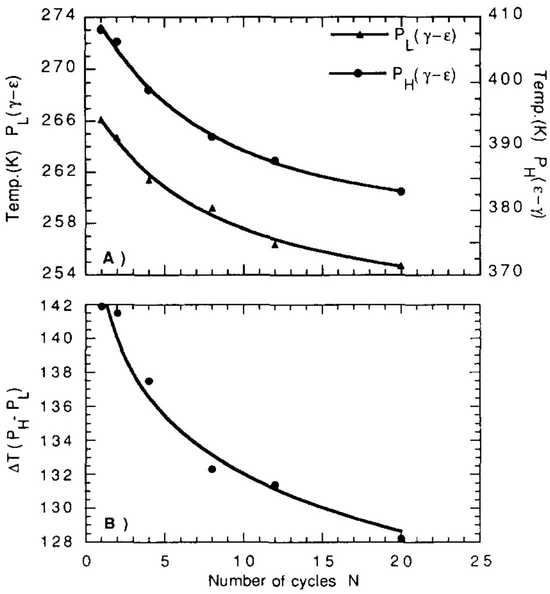

Fig. 2. Evolution of transformation temperatures during thermal cycling: A, shifts of direct transformation peak $P_L(\gamma$–$\epsilon)$ and reverse transformation peak $P_H(\epsilon$–$\gamma)$; B, evolution of hysteresis (temperature difference between peaks, $\Delta T(P_H - P_L)$).

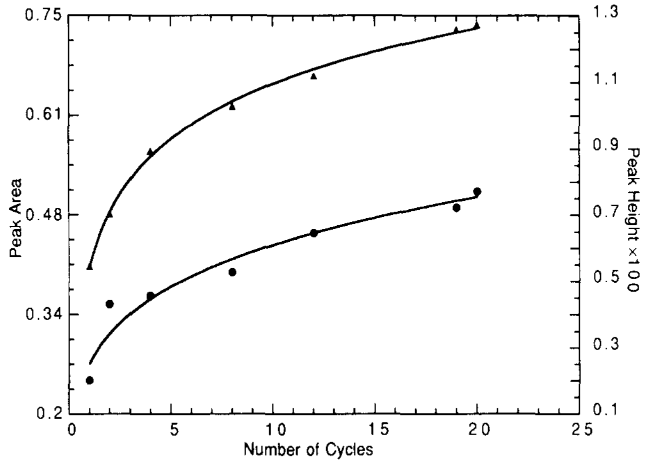

Fig. 3. Changes in height (▲) and area (●) of direct transformation peak during thermal cycling.

4. Discussion

The internal friction (IF) spectrum of a first-order phase transformation shows three contributions: the transient IF, the transformation IF and the intrinsic IF [9].

In this work we study the behaviour of the transient IF contribution, which is the most important in the frequency range in which we have carried out the measurements. Among the several models proposed to explain this IF contribution, we can point out those of Delorme *et al.* [10], Dejonghe *et al.* [11] and Gremaud *et al.* [12]. In these three models the transient logarithmic decrement δ_{Tr} shows a relation

$$\delta_{\mathrm{Tr}} = \text{const.} \times \frac{\partial f}{\partial t} = \text{const.} \times \frac{\partial f}{\partial T}\dot{T} \qquad (1)$$

where f is the volume fraction of the transformed material. Thus the height of the IF peak is linearly proportional to $\dot{T}$. In addition, the integral of the IF spectrum allows us to obtain the peak area A_P, and taking into account that $\dot{T}$=const., a linear relation of the peak area with $\dot{T}$ and f is obtained:

$$A_P = \int_{\mathrm{Peak}} \delta_{\mathrm{Tr}} \mathrm{d}T = \text{const.} \times f\dot{T} \qquad (2)$$

In Fig. 4 the area of the peaks is plotted *vs.* $\dot{T}$ for the various measured spectra. We can see that the experimental results fit a straight line as predicted by the models. The reason why the points corresponding to the direct transformation (cooling) and to the reverse transformation (heating) can be fitted by the same straight line is that the same fraction of martensite that appears during the direct transformation is converted into the γ phase during the reverse transformation. This is evidence of the good reversibility of the martensitic transformation in such iron-based alloys.

Concerning the cycling behaviour, a decrease in M_s with cycling has been observed by several authors in Fe–Mn–Si [13] and Fe–Mn [14] as well as an increase in A_f in Fe–Mn–Si [13, 15] and Fe–Mn [14]. Our results are in contradiction with the results reported in the literature and seem to indicate that the Fe–Mn–Cr–Si–Ni alloy shows a different cycling behaviour than the Fe–Mn–Si alloys.

The whole set of results can be interpreted as follows. During the direct transformation the appearance of martensite variants produces local stresses strong enough to create dislocations in the γ phase. These dislocations should be mainly of the [101] type and will be in the same (111) plane as the martensite variant that creates them. This effect will be enhanced at the Néel temperature where an intrinsic softening of the γ phase takes place, making dislocation creation easier. Thus in the next cycle there will exist a higher number of martensite nucleation points ([101] dislocations) and a higher volume fraction of martensite will be produced in each cycle. This mechanism allows us to explain, according to eqn. (2), the increase in the peak area with cycling during the direct transformation (Fig. 3). The increase in the height of the peak can be attributed to an increase in the transformation rate, because a greater amount of martensite is transformed in the same interval of temperature. We have to point out that the total amount of transformed martensite is only about 10% according to the work of Federzoni *et al.* [8] on this same alloy annealed at 900 °C.

During the cycling the dislocation density in the γ phase increases and the stress field makes the nucleation of martensite more and more difficult. Thus a higher driving force is needed, producing a decrease in the direct transformation temperature (Fig. 2A). In addition, the increment of the amount of transformed martensite with cycling raises the stresses due to the martensite variants and therefore the free energy of the transformed microstructure becomes higher in comparison with the γ microstructure. Thus a decrease in the reverse transformation temperature is expected with cycling, in good agreement with the experimental results (Fig. 2A).

The presented schema of the mechanisms controlling the behaviour of these alloys is also supported by the evolution of the modulus with cycling. The decrease in the modulus in the γ phase with cycling at 340 K (Fig. 5) confirms that mobile dislocations in the γ phase ([101](111)) are created during cycling.

During transformation the modulus increases owing to the appearance of martensite and the internal stresses produced by the martensite variants. These hinder the

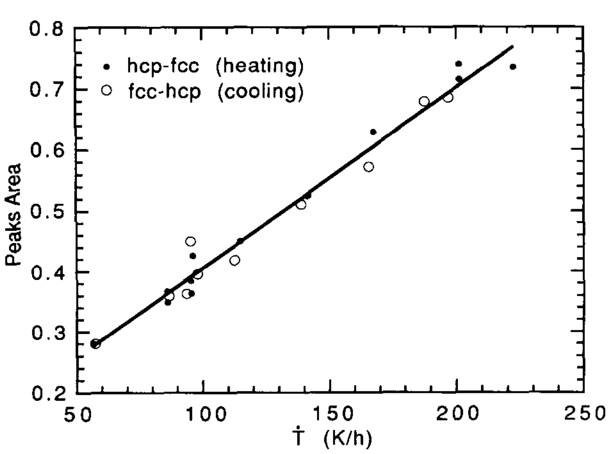

Fig. 4. Linear relationship between peak area and heating–cooling rate ($\dot{T}$).

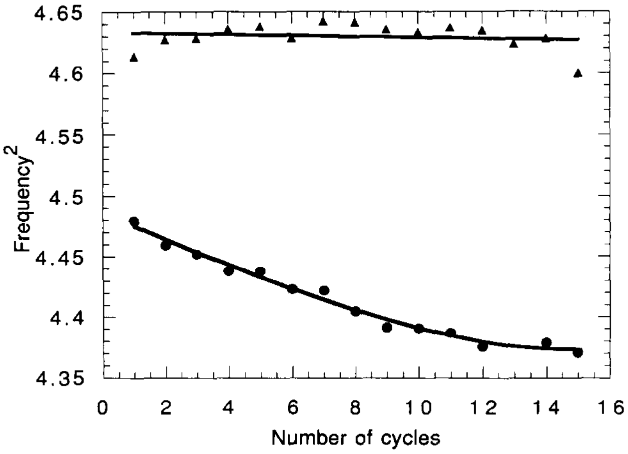

Fig. 5. Evolution of square frequency during thermal cycling at 340 K: ●, γ phase; ▲, $\gamma+\epsilon$ phase.

movement of the γ phase dislocations and as a consequence a hardening of the whole microstructure occurs. Here we have to remark that the main part of the sample is in the γ phase even after transformation. Thus the modulus of the $\gamma+\epsilon$ microstructure at 340 K (Fig. 5) remains constant with cycling despite the softening of the γ phase. Therefore the γ microstructure becomes softer and softer than the $\gamma+\epsilon$ microstructure, giving rise to an increase in the difference between the free energies of the two microstructures.

Finally, we have to note that the observed evolution of the peak area and the transformation temperatures shows a tendency to stabilization. For a higher number of cycles the behaviour of the alloy could evolve in a different or even in an opposite way. Long-term cycling needs further research that is at present under way.

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