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Influence of defects on the irreversible phase transition in Fe–Pd ferromagnetic shape memory alloys

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Abstract—In Fe–Pd ferromagnetic shape memory alloys a face-centered tetragonal (fct) martensite can be obtained when cooling the face-centered cubic austenite through the martensite transition. Nevertheless, further irreversible transformation on cooling into a body-centered tetragonal (bct) martensite needs to be prevented in order to retain the shape memory properties. Differential scanning calorimetry experiments demonstrate that high temperature thermal treatments stabilize the fct phase, reducing the fct–bct transformation temperature. A large misfit between the cell parameters of fct and bct phases was determined by neutron diffraction, pointing to the critical role of dislocations in the accommodation of both phases. The presence of dislocations and its dynamics was analyzed by mechanical spectroscopy, and a relaxation peak at ∼443 K related to the dislocation movement was identified. The driving force of the relaxation process can be proposed as a dislocation dragging mechanism controlled by the migration of vacancies without break-away. Defects such as dislocations and vacancies have been shown to play an important role in changing the irreversible phase transformation temperature. A reduction in the dislocation density reduces the irreversible transformation temperature and so increases the stability range of the alloy.

Keywords: Fe–Pd; Ferromagnetic shape memory alloys; Martensitic transformation; Dislocation dynamics

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) have attracted much scientific and technological interest owing to a broad range of possible engineering applications and highly stimulating fundamental physics related to the coupling between structural, mechanical, magnetic and thermodynamic properties [1,2]. Although the Ni_2MnGa Heusler alloys have received most attention [3], alternative materials systems with complementary properties have also become attractive due to their higher ductility, better corrosion resistance or biocompatibility [4,5]. Concerning the Fe–Pd system, the face-centered tetragonal (fct) martensitic phase allows the magnetic shape memory effect by the reorientation of martensite variants via twin boundary motion. The fct martensite can be obtained when cooling face-centered cubic (fcc) austenite through the martensite transition (MT) [6,7]. From the crystallographic point of view the fct martensite is indeed a bct structure; nevertheless, it is usual in the literature of FePd alloys to talk about fct when the Bain distortion of the initial fcc austenite is small. This structural transformation from fcc to fct takes place only in a very narrow compositional range ($29 < \text{at.\% Pd} < 32$) and the transformation temperatures lie typically below room temperature (RT) [8,9]. Nevertheless, further irreversible transformation on cooling into body-centered tetragonal (bct) and cubic (bcc) martensites needs to be prevented in order to retain the shape memory properties [10–20]. Once the irreversible bct is formed, the alloy must be annealed at temperatures above 1173 K and then quenched again in order to restore the martensitic transformation. The stability range of the thermoelastic martensite is therefore restricted to temperatures between the fcc–fct and fct–bct transformation zone. Both the fcc–fct and fct–bct transformation temperatures strongly depend on composition, and just a slight increase in the Pd content may cause an abrupt decrease of both transfor-

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mation temperatures [8,9]. The addition of a new element has been shown to be an effective way to control the MT temperatures of these alloys [21–28]. Nevertheless, there exist other different parameters such as internal stresses, point defects, dislocations and other bi-tri-dimensional microstructural defects that could play an important role in the characteristics of the different phase transformations and in its stability [29–36]. Epitaxial films show a tunable dependence on the strain that modifies the magnetic properties of the Fe–Pd alloys [37]. On the other hand, the motion of magnetic domains also depends on their interaction with structural defects [38]. It is the aim of the present investigation to address the impact of the intrinsic defects (in particular dislocations) on the stability of the fct martensite concerning their transition to the irreversible low temperature bct martensite.

2. Experimental

Polycrystalline ingots of nominal composition $Fe_{70}Pd_{30}$(at.%) were prepared from high purity elements by arc-melting under protective Ar atmosphere. The ingots were homogenized in vacuum quartz ampoules at 1273 K for 24 h. In order to retain the disordered γ(Fe, Pd) cubic structure, in which the MT occurs, the ingots were subjected to a 30 min annealing treatment at 1173 K in a vertical furnace, followed by quenching into iced water (AQ). Once treated, the composition of the elaborated alloys was analyzed by energy dispersive X-ray spectroscopy in a JEOL JSM-5610LV scanning electron microscope (SEM). Small samples for calorimetric measurements were obtained from disks previously cut from the center of the ingots by a slow-speed diamond saw. In order to determine the transformation temperatures, differential scanning calorimetry (DSC) measurements were carried out at a heating/cooling rate of 10 K $\min^{-1}$ in a TA Q100 calorimeter under a nitrogen protective atmosphere. Different thermal treatment cycles involving heating and cooling runs with different minimum and maximum temperatures within an interval of ~173 K and 623 K were performed. Neutron diffraction measurements were performed at the D1B installation at the Institute Laue-Langevin, Grenoble. The diffraction measurements were carried out from room temperature (RT) down to 10 K and again up to RT at a cooling/heating rate of 1 K $\min^{-1}$. The neutron wavelength was 1.28 Å. The Fullprof program [39,40] was used for performing the profile matching in order to determine the spatial groups and the cell parameters.

Mechanical spectroscopy (MS), referred to as the internal friction method in the early literature, involves the simultaneous measurement of damping, Q^{-1} (or internal friction) and natural frequency (f) as a function of temperature and/or strain [41–45]. Measurements were performed in a mechanical spectrometer based on an inverted torsion pendulum under Ar at atmospheric pressure. The maximum strain on the sample surface was 5×10^{-5}. The measurement frequency was ~4 Hz (except for measurements performed to obtain the activation energy of the relaxation processes). The heating and cooling rates employed in the tests were 1 K $\min^{-1}$. Damping can be calculated from the slope of the natural logarithm of the decaying amplitudes vs. time, such that [41,42].

$$\ln(A_n) = \ln(A_0) - \pi Q^{-1} n \tag{1}$$

where A_n is the area of the nth decaying oscillation, A_0 is the initial area of the starting decaying oscillation and n is the period number. For all these measurements the same initial and final values of the decaying amplitudes were used to avoid distortions linked to the appearance of amplitude-dependent damping (ADD) effects [45]. ADD, i.e. damping as a function of the maximum strain on the sample, ε_0, was calculated from Eq. (2) [45–47]:

$$Q^{-1}(\varepsilon_0) = -\frac{1}{\pi}\frac{d(\ln(A_n))}{dn} \tag{2}$$

The decaying of the oscillations was performed at constant temperature ($T \pm 0.5$ K). Polynomials were fitted to the curve of the decaying areas of the torsional vibrations as a function of the period number by means of chi-square fitting. Subsequently, Eq. (2) was applied. Polynomials of degree higher than 1 indicate that Q^{-1} is a function of ε_0, leading to the appearance of ADD effects, as can be inferred easily. This procedure allows us to obtain damping as a function of the maximum strain (ε_0) from free decaying oscillations [45–47]. The strength of the ADD behavior can be determined through the average slope of the $Q^{-1}(\varepsilon_0)$ curve using the S coefficient [45–47]:

$$S = \frac{\Delta Q^{-1}}{\Delta \varepsilon_0} \tag{3}$$

where ΔQ^{-1} is the damping change corresponding to the full amplitude changes $\Delta\varepsilon_0$ measured in the whole oscillating strain range. Depending both on the oscillating strain level (usually higher than 10^{-6}) and on the measuring temperature, the damping can be either amplitude-independent or amplitude-dependent. ADD is usually a consequence of interaction processes involving mobile dislocations through thermally activated mechanisms. The thermally assisted break-away of dislocations from weak pinning points is one such example. Mechanisms involving the dragging of jogs by screw dislocations, or the pinning by large precipitates or other blocked dislocations, lead to nearly amplitude-independent damping processes [48,49].

The elastic shear modulus, G, was calculated from the proportionality relationship with the square of the natural oscillating frequency (f). This relation for the case of a bar of rectangular section is [45,50,51]:

$$G = \frac{(2\pi)^2 f^2 l\, II}{ka^3 b} \alpha f^2 \tag{4}$$

where k is a constant which depends on the ratio b/a, II is the moment of inertia of the oscillating system, l is the length of the sample and a and b are the half thickness and width of the sample, respectively.

3. Results and discussion

The structural transformations have been studied by DSC measurements. Fig. 1a shows DSC thermograms for the sample in the as-quenched state. The exothermic (endothermic) peak observed on cooling (heating) corresponds to a direct (reverse) thermoelastic MT. The measured enthalpy is 0.8 J g^{-1} and corresponds to the full transformation from fcc austenite to fct martensite [28]. In order to determine the stability of the fct phase, the next measurement was performed down to a lower temperature limit, as shown in Fig. 1b. As expected, the thermogram exhibits two exother-