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Non-equilibrium martensitic transformation in metamagnetic shape memory alloys

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ABSTRACT

The martensitic transformation (MT) in ferromagnetic and metamagnetic shape memory alloys can be induced by changing the temperature or stress but also by applying a magnetic field. In this work, some non-equilibrium processes that take place in a Ni–Mn–In–Co metamagnetic shape memory alloy will be analyzed. The retained austenite at low temperatures under a magnetic field evolves to martensite as soon as the field is removed or reduced. The reduction in the applied field, apart from an instantaneous phase change, leads to a time dependent evolution of the transformed fraction. In addition to the field-related evolution of retained austenite, the cyclic magnetic field induced reverse MT will be analyzed as a function of temperature. The magnetic field induced martensitic transformation (MFIMT) fraction induced at constant temperatures depends on the distance to the equilibrium state: states farther from equilibrium promote larger MFIT fractions.

1. Introduction

The magnetic-field-induced strains (MFIS) in ferromagnetic shape memory alloys (SMA) are associated with the rearrangement, under an applied magnetic field, of the crystallographic domains (twin variants) formed as a result of a martensitic transformation (MT). The MT takes place from a high symmetry high temperature phase (austenite) to a lower symmetry low temperature phase (martensite) [1]. In order to get MFIS, the appearing martensitic phase must be strongly ferromagnetic with high values of the saturation magnetization and anisotropy field. The maximum achievable MFIS is determined by the crystal structure of the martensitic phase, which mainly depends on the alloy composition [2,3]. However, practical applications based on MFIS are limited since only a relatively low level of output stress, less than about 3–4 MPa, can be expected [4,5]. The origin of such (a) low values of the output stress lies on the limited driving force achievable from the magnetocrystalline anisotropy energy of the martensitic phase, which limits the generated stress. On the other hand, the MT can also be induced by applying a magnetic field. Larger generated stresses could be expected in a magnetic field induced martensitic transformation (MFIMT) [6]. Unfortunately, in conventional ferromagnetic alloys the MT cannot be induced by moderately low magnetic fields [7–10].

Nevertheless, MFIMT under reasonable magnetic fields has been reported in Ni–Co–Mn–In [11], Ni–Mn–In [12], Ni–Mn–Sn [13], Ni–Co–Mn–Sn [14], Ni–Mn–Sb [15], Ni–Co–Mn–Al [16] and Ni–Co–Mn–Ga [17] alloys. These alloys, unlike the conventional ferromagnetic SMA, transform from a ferromagnetic austenite into a weak magnetic martensitic phase. Due to the lower magnetization of martensite with respect that of austenite, the application of a magnetic field shifts the transformation range to lower temperatures and thus enables inducing the reverse MT (magnetic shape memory effect). It is worth to note that in this case the recovery stresses are much higher than the magneto-stresses associated with the variant reorientation mechanism. These peculiar ferromagnetic SMA are usually described as metamagnetic SMA. Together with the MFIS effect, several interesting properties are being investigated in metamagnetic SMA because of their potential applications, namely the magnetocaloric effect and the magnetoresistivity.

Large magnetoresistance values related to the MT have been reported in some metamagnetic SMA [18–21]. In these alloys, the MFIMT is responsible for the large magnetoresistance taking place across the MT. Due to the giant inverse magnetocaloric effects ($S(T, H) - S(T, 0) = \Delta S_m > 0$) in metamagnetic SMA [22–34] alloys, they can be adiabatically cooled by application of a magnetic field. This behavior is a direct consequence of the strong temperature variations of the magnetization around the MT. According to theoretical models [35–37], the MFIMT, or equally the change of martensitic transformation temperature (T_m) as a function of the applied magnetic field, is responsible for the large magnetocaloric values.

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Therefore the characterization of the features of the MT under a magnetic field is crucial in order to improve properties like magnetoresistance and magnetocaloric effect.

In this kind of alloys, the transformation temperature decreases with increasing magnetic field but, simultaneously, the direct MT can be inhibited (arrested) by the application of a field [38,39]. In this work, some non-equilibrium processes that take place in a Ni–Mn–In–Co metamagnetic SMA will be analyzed. The austenite retained at low temperatures under a magnetic field evolves to martensite as soon as the field is removed or reduced. The reduction in the applied field, apart from an instantaneous phase change, leads to a time dependent evolution of the transformed fraction. In addition to the field-related evolution of retained austenite, the cyclic magnetic field induced reverse MT will be analyzed as a function of temperature. The results reveal how the MFIMT fraction induced at constant temperatures depends on the distance to the equilibrium state: states farther from equilibrium promote larger MFIT fractions.

2. Experimental procedure

A $Ni_{45}Mn_{36.7}In_{13.3}Co_5$ alloy was produced by arc-melting followed by several consecutive re-melting in order to homogenize the ingot. After 24 h homogenization at 1170 K under vacuum, samples were annealed at 1070 K for 1800 s and slowly cooled in air. Differential scanning calorimetry (DSC) analysis reveals that in zero field the martensite to austenite transition peak maximum is at A_p = 258 K. The transformation entropy, estimated as the latent heat ΔH (2.6 J/g) divided by DSC peak temperature, A_p, is $\Delta S_{tr} = 10 \pm 1$ J/(kg K) and the Curie temperature, T_c = 386 K. The temperature dependences of the magnetization $M(T)_H$ at different applied magnetic fields after zero field cooling (ZFC) and field cooling (FC), and the field dependence of the magnetization $M(H)_T$ were determined using a Quantum Design MPMS XL-7 SQUID magnetometer [40].

3. Results and discussion

Fig. 1(a) shows the zero field cool (ZFC) and field cool (FC) DC susceptibility measured at 100 Oe. The magneto-structural martensitic transition between 200 K and 300 K can be identified by the hysteresis observed between cooling and heating curves. The DC susceptibility increases during heating in the MT range due to the higher magnetization of the austenitic phase. At low temperatures, susceptibility exhibits glassy features below 50 K were both curves split [41]. Fig. 1(b) shows the ZFC and FC magnetization measured at 60 kOe. The high field magnetization in ZFC and FC curves shows a much stronger difference which has been attributed to the arrest of the austenitic phase during the FC process [38,39]. The degree of magnetization change produced during cooling (FC) due to the MT is reduced with respect to the change observed during heating (ZFC) indicating a lower fraction of transformed volume. Besides, the shift of the MT temperature (T_m) to lower temperatures, at high applied magnetic field, indicates that the magnetic field stabilizes the austenite – the higher magnetization phase – with respect to the martensite. The observed shift agrees with that given by the Clausius–Clapeyron equation [34].

The transformation entropy in non-magnetic SMA has mainly a vibrational origin [42,43]. An excess of vibrational entropy of the austenite with respect to the martensite, $\Delta S_{vib}^{p\to m} < 0$ related to a low energy TA_2[1 1 0] phonon branch is at the origin of the stability of the austenite at high temperature and its instability towards a martensitic transformation at low temperatures. When one or both phases show magnetic ordering, the magnetic contribution, due to the different magnetic exchange interactions in each phase, must be taken into account in the entropy variation, i.e. $\Delta S = \Delta S_{vib} + \Delta S_{mag}$ [44–46]. In metamagnetic SMA, the martensitic phase shows lower values of the saturation magnetization and Curie temperatures than the austenite, so the magnetic entropy of the system increases during the forward MT and consequently $\Delta S_{vib}^{p\to m}$ is negative and $\Delta S_{mag}^{p\to m}$ is positive on cooling. Therefore, the absolute value

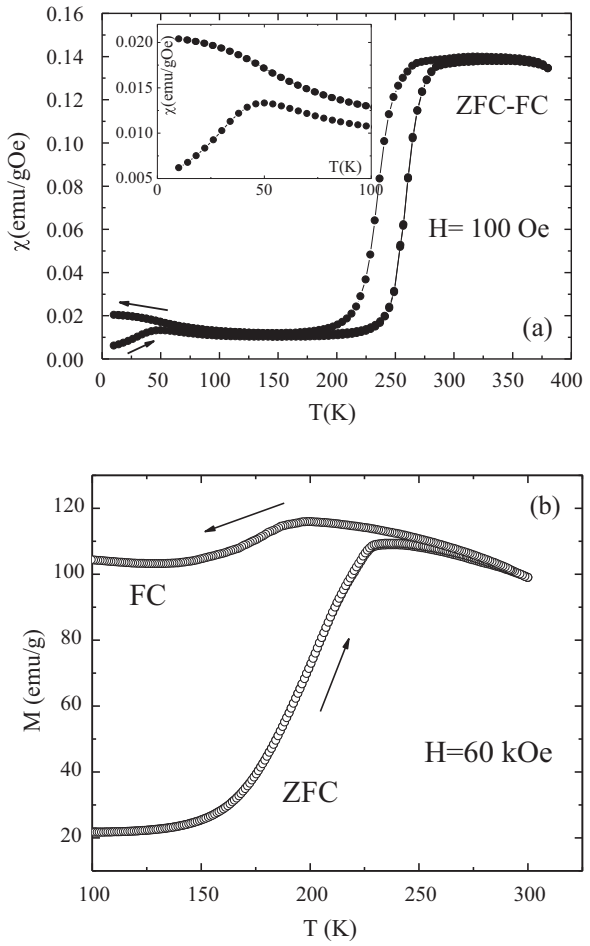

Fig. 1. Zero field cool (ZFC) and field cool (FC) DC susceptibility measured at 100 Oe (a) and ZFC and FC magnetization measured at 60 kOe (b).

of $\Delta S^{p\to m}$ diminishes as T_C–T_m increases and the vibrational driving force ($\Delta G_{vib}^{p\to m} = -\Delta T \cdot \Delta S_{vib}^{p\to m}$) to induce the MT is opposed by the magnetic contribution ($\Delta G_{mag}^{p\to m} = -\Delta T \cdot \Delta S_{mag}^{p\to m}$) promoting the arrest of the MT [38,39]. The application of an external magnetic field at high temperatures reduces the magnetic entropy of the parent phase and increases the magnetic contribution (positive) to the MT entropy change. The arrest of the MT will take place in the temperature range where the lattice and magnetic contributions to ΔS compensate each other. Indeed, it has been observed that ΔS goes to zero at low temperatures [38,44,47].

Fig. 2 shows the difference in the magnetic hysteresis loops obtained at 50 K after ZFC and FC (at 70 kOe) from room temperature. The ZFC M(H) curve (solid circles) shows a maximum magnetization of around 30 emu/g and a hysteresis between 10 kOe and 70 kOe linked to the energy losses (E_l) produced during the MFIMT [48]. The area of the loop and the fraction of MFIMT are very small (see inset). After zero field cooling the sample transforms to 100% martensite but the application of a magnetic field at 50 K promotes the MFIMT. Since the MFIMT appears at high fields, the value of the magnetization of the martensitic phase at 70 kOe, M^{mar} (70 kOe) can be evaluated [48] using a linear extrapolation of the magnetization values at moderate fields as shown in inset in Fig. 2 (full line).

On the other hand, when cooling the sample from 300 K keeping constant the applied field (H = 70 kOe), the magnetization reaches a large value of around 120 emu/g at 50 K (open circles). This large value is linked to the austenite retained during the FC process. Removing the field allows the transformation of the retained