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Low-frequency elastic and thermomechanical analysis of Ni-Mn-In(Co) single crystals

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Abstract

Martensitic transformation (MT) in $Ni_{45.0}Mn_{36.7}In_{13.3}Co_{5.0}$ single crystals (SC) has been characterized by DSC and X-ray diffraction. Their elastic and thermomechanical properties have been investigated by a low-frequency dynamic-mechanical analysis in a tensile mode and by static mechanical compression made at different temperatures. The Young's modulus of the order of 10 GPa was measured in tensile tests along <100> crystallographic axis of austenite showing soft behavior in a broad temperature range whereby revealing a lattice instability similar to the classical Ni-Mn-Ga alloys. The compression tests along <100>, <011> and <111> directions have shown that despite a high brittleness the samples exhibit large martensitic plasticity, rubber-like behavior and superelasticity.

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Keywords: Ni-Mn-In(Co) Metamagnetic Shape Memory Alloy; Martensitic Transformation; Soft Modulus; Superelasticity

1. Introduction

The Heusler metamagnetic shape memory alloys (MetaMSMAs) such as Ni-Mn-X, X=In,Sn,Sb, where the magnetic field-induced transformation (MIT) was observed between a ferromagnetic austenite and a weakly

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magnetic martensite, have attracted a wide interest in the last years because MIT is accompanied by giant magnetocaloric and magnetoresistance properties. These properties are also well-pronounced in the polycrystalline state which is favorable for applications [1,2]. Particularly Ni-Mn-In(Co) alloys have been exploited for the detailed study of a metamagnetic shape memory effect [3], the influence of the magnetic field on MT and the entropy change at MIT [4,5]. It is worth noting that a giant magnetostrain effect was observed in textured polycrystalline samples [6]. Nevertheless the elastic, internal friction and thermo-mechanical behaviors of these alloys were rarely addressed in the literature while this is an important issue for the shape memory alloys to integrate the survey of the functional properties. This gap was intended to fill in this study by the thermomechanical testing of the Ni-Mn-In(Co) single crystalline samples in the vicinity of MT, the latter one was experimentally confirmed by calorimetric and structural methods.

2. Experimental results

The $Ni_{45.0}Mn_{36.7}In_{13.3}Co_{5.0}$ single crystal (SC) was grown by Czochralski process. Compression samples of 2x2x4 mm^3 labeled as A<100>, K<111> and I <011> were cut from different parts of SC with their long axes along the different orientations of the parent phase, while <100> tensile samples of 15x0.4x0.5mm^3 were prepared from part A of SC only. The samples were homogenized at 900 °C for 24h and quenched into water. The calorimetric measurements have been performed by DSC Q100 TA Instruments with rate of 10°C/min. The diffraction patterns were obtained by X-ray PANALYTICAL Xpert Pro using milled powder annealed at 600 °C for 1h in Ar/H_2 atmosphere. A dynamic mechanical analyzer DMA Q800 TA Instruments was used for the tensile measurements in dynamic (1 Hz, strain amplitude of 0.01%) and static regimes. In these measurements, the temperature rate was 2°C/min. The stress-strain investigation in compression (samples size of 3x3x5 mm^3) was carried out with a deformation rate of 0.1 mm/min by a MTS 2/M testing machine equipped by temperature chamber.

2.1. Transformation behavior

The DSC curves for all three samples are depicted in Figure 1.a. The temperatures of the forward, T_m, and reverse, T_a, martensitic transformations taken at onset of the peaks on DSC curves and enthalpies values are reported in Table 1. Figure 1.a and Table 1 show that the transformation characteristics vary appreciably in three samples reflecting their high sensitivity to some chemical inhomogeneity along the SC ingot still persisting after the employed heat treatment.

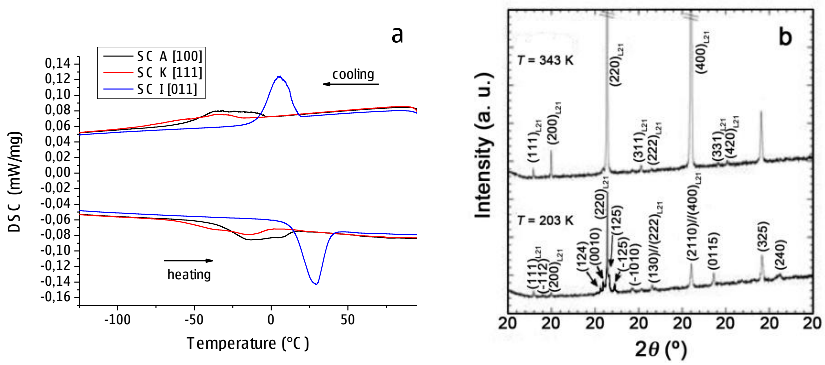

Fig. 1. (a) DSC analysis of all the single crystal A, K and I; (b) Xray diffraction pattern.

Table 1. MT temperatures and averaged transformation enthalpies obtained from DSC analysis for the samples A, K and I.

	A <100>	K <111>	I <011>
T_m (°C)	-3.4	-19.2	16.4
T_a (°C)	15.1	-0.7	38.3
ΔH (J/g)	3.2	2.2	6.2

Figure 1.b shows X-ray diffraction patterns of the powdered SC recorded at -70 °C and 70 °C that unequivocally confirm martensitic and austenitic phases, respectively. The pattern at 70°C corresponds to a single phase $L2_1$ Heusler structure with a lattice spacing of 0.599 nm. At -70 °C, the martensitic transformation is still not complete as far as powder sample consists of two phases. This is probably due to the milling process and the consequent stored mechanical energy which was not completely removed by the thermal treatment. The first phase is attributed to the austenitic cubic one with a cell parameter of a_0 = 0.592 nm, slightly smaller than at 70 °C, due to the thermal contraction. The second phase is a 10M modulated martensitic structure with a monoclinic unit cell described by the lattice constants of a = 0.419 nm, b = 0.563 nm, c = 2.142 nm and β = 86.71°. Basically the structure of this phase can be considered as orthorhombic with a shuffle periodicity of 10 lattice planes in the <110> direction.

2.2. Elastic and thermomechanical properties

The temperature variations in elastic modulus, E, and internal friction, tanδ, are depicted in Figure 2a. and Inset. They show anomalies produced by a reversible MT and an anomalously low value of E (~13 GPa) persisting over a wide temperature range in the cubic phase. Such modulus softening is typical for Ni-Mn-Ga alloys [7]. The enhanced value of tanδ in the martensitic phase is an intrinsic property of twinned martensite pointing to its high damping capacity.

Figure 2.b demonstrates a 2.7 % tensile strain obtained in the martensitic state at -100 °C. This is the first time this kind of result for MetaMSMA is presented: such a strain is produced by the detwinning process. Figure 2.a shows that this process is interrupted by a sample failure revealing its poor strength. The alloy shows also a high intergranular brittleness in austenitic state as follows from compression tests below. The poor ductility of the single crystal of the intermetallic compound in our case stems not only from the reduced amount of slip systems but also can be explained by the crystal defects, dendrites, composition gradients etc. Despite a high brittleness some results of compression tests depicted in Figure 3 indicate that MetaMSMA potentially can exhibit promising shape memory characteristics for applications. Figure 3.a shows that martensite of sample A<100> accumulates 6.6% of deformation at -40 °C which is due to reorientation of variants. After first compression cycle the sample was heated to austenite in a free state resulting in recovery of its original length due to ordinary shape memory effect. The second cycle at -10 °C led to resulting in recovery of its original length due to ordinary shape memory effect. The second cycle at -10 °C led to sample fracture. The shapes of the curves at loading start in the case of compression along <111> of sample K (Figure 3.b) are irregular which is manifestation of some complexity of the strain response of this sample. Nevertheless, further loading and subsequent unloading show almost closed loops produced by a rub-

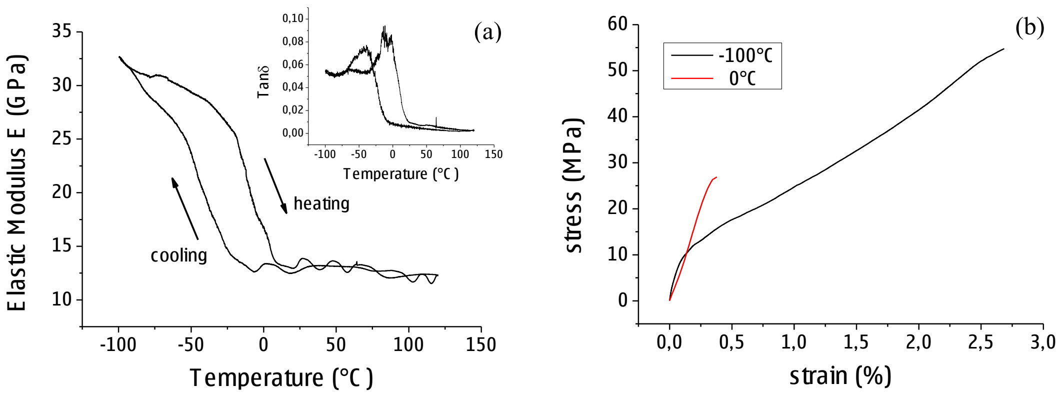

Fig. 2. (a) Dynamic-mechanical test of sample A <100>: main graph shows temperature dependence of elastic modulus, Inset shows concomitant behaviour of the internal friction; (b) tensile stress- strain curves in the martensitic state (-100 °C) and in austenite (0 °C) of the same sample where dependences end at failure points during first loading at -100 °C and second loading of the rest of sample at 0 °C.

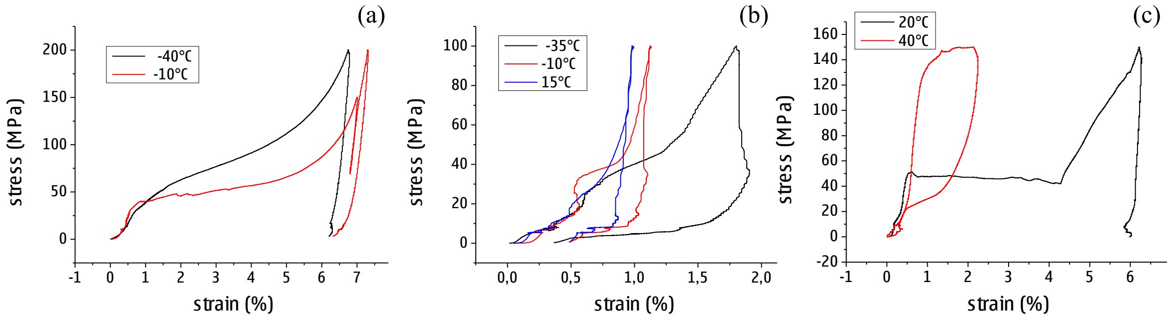

Fig. 3. (a) Stress-strain test in compression configuration for the A<100> sample; (b) Stress-strain test in compression configuration for the K<111> sample; (c) Stress-strain test in compression configuration for the I <011> sample.

ber-like behavior in the martensitic state and superelastic behavior in austenite (T=15 °C). The superelastic loop in austenite is also obtained for the I<011> sample (Figure 3.c); after compression test at 20 °C in martensite the full unloading resulted in the sample disintegration. The complete study of superelasticity has been managed in Ref. [8]

As a summary, in this work we have studied transformation behavior, elastic and thermoelastic properties of single crystalline samples of $Ni_{45.0}Mn_{36.7}In_{13.3}Co_{5.0}$ MetaMSMA. The experimental evidences have been obtained for the first time in the following items. The soft low-frequency elastic modulus behavior is found signaling similar mechanism of lattice instability of high temperature phase as in the case of Ni-Mn-Ga alloys. The internal friction in martensite reveals also similarities to Ni-Mn-Ga behavior. A 2.7% of tensile strain is obtained in the martensitic state at -100 °C. The stress-strain evolution of martensite for one of the samples has shown phenomenon similar to the rubber-like behavior. Despite the large brittleness of the alloy, the superelastic properties are confirmed.

References

[1] R. Kainuma, Y. Imano, W. Ito, Y. Sutou, H. Morito, S. Okamoto, O. Kitakami, K. Oikawa, A. Fujita,T. Kanomata, K. Ishida, Nature 439 (2006) 957.
[2] M. Acet, L. Mañosa, A. Planes, in: K.H.J. Buschow (Eds.), Handbook of Magnetic Materials, Vol. 19, Elsevier, Amsterdam 2011, pp. 231.
[3] J. Pons, E. Cesari, C. Seguì, F. Masdeu, R. Santamarta, Mater. Sci. Eng A 481-482 (2008) 5765.
[4] V. Recarte, J.I. Pérez-Landazàbal, S.Kustov, E. Cesari, J. Appl. Phys. 107 (2010) 053501.
[5] J.I. Pérez-Landazàbal, V. Recarte, V. Sánchez-Alarcos, C. Gómez-Polo, S. Kustov, E. Cesari, J. Appl. Phys. 109 (2011) 093515.
[6] J. Liu, S. Aksoy, N. Sheerbaum, M. Acet, O. Gutfleisch, Appl. Phys. Lett. 95 (2009) 232515.
[7] V.A. Chernenko, J. Pons, C. Segui, E. Cesari, Acta Mater. 50 (2002) 53.
[8] H.E. Karaca, I. Karaman, A. Brewer, B. Basaran, Y.I. Chumlyakov, H.J. Maier, Scr. Mater. 58 (2008) 815.