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Martensitic transition, structure and magnetic anisotropy of martensite in Ni-Mn-Sn single crystal

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ABSTRACT

The structural and magnetic properties of $Ni_{50}Mn_{37.5}Sn_{12.5}$ single crystal were investigated. The alloy undergoes martensitic transformation at 308 K from the austenite phase to the structurally modulated tetragonal 4M martensite phase with lattice parameters $a_{4M} = 6.177$ Å, $c_{4M} = 5.669$ Å. The alloy shows 7.9% pre-strain upon uniaxial compression along the ⟨001⟩ direction, which is near the theoretical 8.2% maximum twinning strain. Magnetization measurements reveal that the magnetic anisotropy of the martensite phase is uniaxial with the easy magnetization axis corresponding to the shortest *c* axis of the tetragonally distorted unit cell, while its *a* axis is the hard magnetization direction. The magnetic anisotropy constant K_u saturates at low temperature around 7×10^4 J/m^3 and then gradually decreases with increasing temperature as the system approaches the Curie temperature of martensite at 215 K.

1. Introduction

Magnetic field induced reverse martensitic transformation (MFIRMT) is a phenomenon resembling the conventional shape memory effect due to heating with the exception that it is triggered by the action of a magnetic field [1]. It may then offer frequency response higher than conventional, which makes it interesting for actuation and sensing applications. MFIRMT is displayed by a special class of magnetic shape memory alloys (MSMA), often referred to as metamagnetic shape memory alloys such as Ni-Mn-(Sn, Sb, In) [1]. The transformation proceeds between the weakly magnetic martensite phase and ferromagnetic austenite [2,3]. The driving force for the transition along some contribution from the magnetocrystalline anisotropy energy (MAE) is predominantly the Zeeman energy ($ZE = \Delta M \cdot H$) arising from the different saturation magnetization between martensite and austenite [4]. Unlike MAE the ZE is less sensitive to the crystal orientation, it can continuously increase with the field and it can be maximized by enhancing the magnetization difference between the transforming phases for instance by doping with Co, which is known to increase the Curie temperature of the austenite phase (T_C^A) in ternary Ni-Mn-(In, Sn) based alloys [5,6]. Henceforth the *ZE* difference can yield considerable actuation stress on the order of 100 MPa greatly exceeding that of earlier MSMA such as Ni-Mn-Ga based alloys, which are capable of up to 12% recoverable magnetic field induced strain (MFIS) but at an order of magnitude lower output stress level (~2 MPa) [7,8]. This is associated with a different mechanism of MFIS in the latter, which is based on the twin boundary motion governed by MAE [9–11]. Similar to conventional SME an introduction of a pre-strain to the martensite phase is a prerequisite for large MFIS (due to MFIRMT). An almost full recovery of such a 3% deformation has been reported under 7 T in a single crystalline Ni-Co-Mn-In alloy, which aroused some attention [1]. A transformation strain of 5.4% under 125 MPa thermal cycling was reported in the same system [12] and more recently a 3.1% completely recoverable MFIS due to MFIRMT was noted in single crystal of $Ni_{45}Co_5Mn_{36.5}In_{13.5}$ alloy [13,14]. A lower recovery strain amounting to 77% of the initial 1.3% pre-strain was observed in

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polycrystalline $Ni_{43}Co_7Mn_{39}Sn_{11}$ alloy. Simultaneously this system showed a spontaneous 0.3% length change upon removal of the magnetic field, which indicated a two way shape memory effect not detected previously in single crystalline Ni-Co-Mn-In. This effect was ascribed to the presence of constraint stress at grain boundaries acting as nucleation sites for strained martensite [15]. Despite this initially encouraging results there are still pertaining issues *e. g.* the reduction of the critical magnetic field, and shortening of the transformation hysteresis etc., which need to be addressed in order to advance the dawn of practical applications [16,17]. These challenges are also relevant to other functional properties shown by MSMA such as giant magnetoresistance [18], exchange bias [19] and magnetocaloric effect [20], the potential of which could be harnessed in combination with magneto mechanical response of MSMA resulting in effective multiferroic systems [21]. For example lately a large elastocaloric effect (4 K) was found during loading polycrystalline $Ni_{45}Mn_{44}Sn_{11}$ alloy at 291 K with a 1.3% transformation strain [22]. In the early reports it was suggested that Ni-Mn-Sn with modulated orthorhombic (4O) martensite structure should show low twinning stress ($\beta = 90^\circ$) yielding considerable twin mobility and therefore a considerable pre-strain critical for MFIS [23]. Up to date this was not, however, verified experimentally largely due to difficulty in obtaining single crystalline Ni-Mn-Sn specimen [24]. In this letter we report on the microstructure, martensitic transformation, pre-strain and magnetic anisotropy of martensite in $Ni_{50}Mn_{37.5}Sn_{12.5}$ single crystalline alloy. This contribution should enhance the fundamental understanding of the unique properties of these systems and henceforth should aid the control of their functionalities in the future.

2. Experimental procedures

$Ni_{50}Mn_{37.5}Sn_{12.5}$ single crystal was grown using the Bridgman method from an ingot prepared in advance by induction melting from high purity Ni, Mn, Sn (99.99%). It was then annealed at 1220 K for 72 h to ensure chemical homogeneity. The composition of the single crystal was $Ni_{49.5\pm1}Mn_{38.4\pm0.8}Sn_{12.2\pm0.2}$ as determined according to X-ray energy dispersive spectroscopy (EDS) analyser fitted to FEI E-SEM XL30 scanning electron microscope (SEM). Subsequently the crystal was oriented using the energy backscattered electron diffraction (EBSD) technique on high resolution field emission FEI Quanta 3D instrument equipped with an EBSD detector and then cut into a 4.16 mm × 2.74 mm × 1.72 mm rectangular prism by spark erosion along the {100} planes of the parent $L2_1$ cubic phase. Mechanical training was performed on an Instron testing machine at room temperature under a compressive stress of up to 250 MPa and at a strain rate of $10^{-3}\ s^{-1}$. The microstructure was studied using Tecnai G2 (200 kV) transmission electron microscope. Thin foils for TEM examination were prepared by first cutting a slice (circa 0.15 mm thick) from the bulk sample along the {001} type plane referred to the austenite phase with a precision wire saw, mechanically grinding it and finally electro polishing using TenuPol-5 double jet electropolisher and an electrolyte of nitric acid (1/3) and methanol (2/3) at 240 K. Crystal structure and lattice parameters of the martensite phase at room temperature were determined on the bulk single crystal by synchrotron high energy X-ray radiation (87.1 keV, $\lambda = 0.14236$ Å) at the beamline Petra P07B at Desy (Hamburg, Germany). High energy synchrotron radiation enables measurements in transmission geometry, which significantly improved the variant statistics of this sample. The DC mass magnetic susceptibility (and magnetization) was measured in the temperature range from 2 K up to 380 K and in the magnetic field of 5 mT (and 5 T) using Vibrating Sample Magnetometer (VSM) option of the Quantum Design Physical Property Measurement System (PPMS-9).

3. Experimental results and discussion

At room temperature the specimen shows a self-accommodated (SA) martensite microstructure with pairs of twin variants arranged into variant colonies (Fig. 1) [25]. The martensite structure is further confirmed by TEM. Fig. 2 (a) shows Bright Field (BF) image of two martensite plates separated by a twin boundary. The inset picture presents the corresponding Selected Area Diffraction Pattern (inset) taken from the single martensite variant. Three extra spots in between the main reflections suggest the modulated 4M structure [23]. Fig. 2(b) displays the diffraction pattern taken from two twinned variants (V1 and V2) with nearly orthogonal modulation direction. The modulation period determined by High Resolution TEM (HREM) appears to be $(3\bar{1})$ according to Zhdanov notation and it is indicated by the step like red and white line (Fig. 2(c)). The crystal structure and lattice parameters of the martensite phase for the $Ni_{49.5}Mn_{38.4}Sn_{12.2}$ specimen were further confirmed using high energy Synchrotron radiation. Fig. 3 shows the 2D diffraction pattern of martensite. It is explicit that martensite has a modulated structure in accordance with previous TEM analysis (Fig. 2). The crystal structure is determined to be 4-layered tetragonal structure with the following lattice parameters: $a_{4M} = 6.177$ Å and $c_{4M} = 5.669$ Å. From this the maximum twining strain given as $\epsilon_0 = (1 - c/a)$ can be deduced as amounting to 8.22%. It should be mentioned that the lattice parameters and the maximum strain for the 4M Ni-Mn-Sn structure is given with respect to the so-called "cubic coordinate system", which is related to the cubic axes of the parent $L2_1$ austenite.

In order to determine the magnetic ordering temperatures and study the behaviour of the MT the low field (5 mT) zero field cooled (ZFC), field cooled (FC) and field heated (FH) dc mass magnetic susceptibilities χ were measured as a function of temperature $(\chi)T$. Before ZFC the sample was cooled down from 380 K to 2 K at no applied magnetic field, then ZFC measurement was performed at 5 mT with temperature increasing up to 380 K. Subsequently FC and FH measurements were performed at the same field upon decreasing and increasing the temperature, respectively. All the measurements were performed in a step mode with stabilised temperature at each experimental point. The magnetic transformation temperatures corresponding to the Curie temperature of

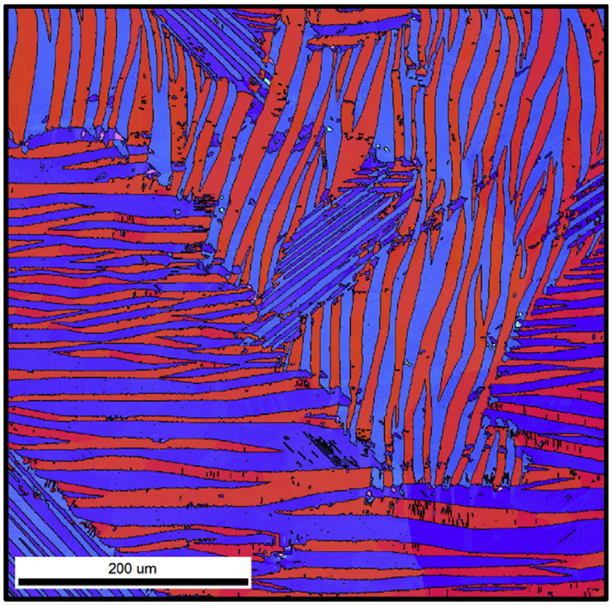

Fig. 1. EBSD map of the self-accommodated 4M martensite microstructure.