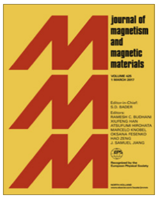
Journal of Magnetism and Magnetic Materials 452 (2018) 249–252

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm



Research articles

Large magnetoresistance in a directionally solidified $Ni_{44.5}Co_{5.1}Mn_{37.1}In_{13.3}$ magnetic shape memory alloy

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ARTICLE INFO

Article history:
Received 19 October 2017
Received in revised form 12 December 2017
Accepted 27 December 2017
Available online 27 December 2017

Keywords:
Shape memory materials
Magnetic materials
Texture
Magnetostructural transformation
Magnetoresistance

ABSTRACT

Polycrystalline $Ni_{44.5}Co_{5.1}Mn_{37.1}In_{13.3}$ alloy with coarse columnar-shaped grains and $\langle 001 \rangle_A$ preferred orientation was prepared by directional solidification. Due to the strong magnetostructural coupling, inverse martensitic transformation can be induced by the magnetic field, resulting in large negative magnetoresistance up to −58% under the field of 3 T. Such significant field controlled functional behaviors should be attributed to the coarse grains and strong preferred orientation in the directionally solidified alloy.

1. Introduction

Since a 3% magnetic-field-induced strain was reported in a $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ single crystal [1], Ni-Mn-In based alloys have attracted considerable attention. In these alloys, the martensitic transformation involves not only the structural changes but also the magnetization variations, *i.e.*, from ferromagnetic austenite to weak magnetic martensite. Accordingly, the martensitic transformation temperatures of these alloys can be greatly reduced by an external magnetic field, which enables the occurrence of field induced inverse martensitic transformation [1,2]. Associated with such a field induced transformation, some remarkable field controlled functional behaviors, such as magnetic shape memory effect [1,2], magnetocaloric effect (MCE) [3–6], and magnetoresistance (MR) [7–9], were developed, which is promising for the technical applications in novel magnetic actuation, refrigeration and sensoring.

Yu et al. firstly reported the MR in Ni-Mn-In alloys and a giant MR over −80% was achieved in a $Ni_{50}Mn_{34}In_{16}$ single crystal under the magnetic field of 5 T [8]. Although the single crystal alloys can exhibit superior field controlled functional behaviours, the relatively higher cost for the fabrication of single crystals becomes an unavoidable hindrance for practical applications. Alternatively, the preparation of polycrystalline alloys is much easier and of lower cost. Thus, more attention was paid to the polycrystalline alloys. It has been reported that large MR of −64% and −56% can be achieved under the field of 5 T in polycrystalline $Ni_{50}Mn_{34}In_{16}$ and $Ni_{50}Mn_{35}In_{15}$ alloy [9,10], respectively. In addition, the substitution elements were introduced in order to improve the MR in polycrystalline alloys. It is found that in Fe doped $Ni_{50}Mn_{37-x}Fe_xIn_{13}$ ($x = 2–4$) polycrystalline alloys, the MR increases with the increase of Fe content and the maximum MR reaches −57% for the field of 5 T [11]. In a $Ni_{48.4}Co_{1.9}Mn_{34.2}In_{13.8}Ga_{1.7}$ polycrystalline alloy, a large MR of −66% can be obtained with the application of the field of 7 T [12]. Generally speaking, the MR properties in polycrystalline alloys are relatively lower with respect to those of single crystals. This could be due to the deteriorated preferential crystallographic orientation as well as the introduction of large amounts of grain boundaries in polycrystalline alloys. Microstructure control through texturation could be a practicable strategy to realize property optimization in polycrystalline alloys.

Recent investigations have illustrated that the highly textured microstructure in Ni-Mn-based polycrystalline alloys contributes a lot to the improvement of field controlled performance [13–17]. Liu et al. obtained a 0.25% magnetostrain through field induced inverse martensitic transformation in a highly textured $Ni_{45.2}Mn_{36.7}In_{13}Co_{5.1}$ alloy [15]. Gaitzsch et al., reported a 1%

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https://doi.org/10.1016/j.jmmm.2017.12.093
0304-8853/

magnetostrain through field induced variant reorientation in a textured $Ni_{50}Mn_{29}Ga_{21}$ alloy prepared by directional solidification [16]. Mcleod et al., found that the magnetic entropy change (ΔS_M) can be increased by 84% in a $Ni_{54}Mn_{21}Ga_{25}$ alloy due to the strong texture induced by thermo-mechanical training [17]. Our recent investigations have shown that the adiabatic temperature variation (ΔT_{ad}) induced by magnetic field in directionally solidified Ni-Mn-Ga alloys can be significantly improved due to the formation of strong texture [13,14]. The enhanced field controlled performance in polycrystalline alloys with strong preferred orientation should be attributed to the optimization of crystallographic and magnetocrystalline anisotropy through texturation, which enables the polycrystalline alloys more close to the single crystal.

It is worth mentioning that the directional solidification is an efficient way to optimize the microstructure of polycrystalline alloys, by which the alloys usually form the coarse columnar grains with highly preferential orientation along the growth direction [13,14,18,19]. In this work, a polycrystalline $Ni_{44.5}Co_{5.1}Mn_{37.1}In_{13.3}$ alloy with $\langle 001 \rangle_A$ preferred orientation was prepared by directional solidification. Owing to the strong magnetostructural coupling, the field induced inverse martensitic transformation was evidenced, resulting in a large negative MR up to −58% under the field of 3 T.

2. Experimental

The master Ni-Co-Mn-In polycrystalline alloy was prepared by arc-melting under argon protection. To achieve a good composition homogeneity, the as-cast alloy was melted for four times. After that, the alloy was suctioned into a copper mould to obtain a cylindrical rod with the diameter of 10 mm for the subsequent directional solidification. The directional solidification was performed in a Bridgman type apparatus under argon atmosphere, where the cylindrical rod was enveloped in a high-purity corundum tube with the inner diameter of ~10.5 mm. A water-cooled cylinder containing liquid Ga-In-Sn metal is used to cool down the alloy. During the experiments, the alloy in the corundum crucible was melted by using resistance heating and then directionally solidified in the Bridgman apparatus by pulling the crucible into the liquid Ga-In-Sn metal cylinder at a growth rate of 50 μm/s. The as-solidified alloy was then homogenized at 1173 K for 24 h, followed by quenching into water. Parts of homogenized alloy were ground into powder and then sealed in a vacuum quartz tube, followed by annealing at 873 K for 5 h to remove the internal stress.

The composition verification was performed by energy dispersive spectrometry (EDS) and the actual composition was determined to be $Ni_{44.5}Co_{5.1}Mn_{37.1}In_{13.3}$ (at.%). The crystal structure was analyzed by powder X-ray diffraction (XRD) at room temperature in a PANalytical X'Pert Pro MPD diffractometer. The incomplete pole figures were measured by XRD in a Rigaku SmartLab diffractometer at room temperature on the transverse section of the directionally solidified alloy. The martensitic transformation temperatures were measured by differential scanning calorimetry (DSC) with a heating and cooling rate of 10 K/min. The thermal-magnetic (*M-T*) curves were measured using a vibrating sample magnetometer VersaLab system with a heating and cooling rate of 3 K/min. The martensitic transformation temperatures were determined by the conventional tangent extrapolation method in DSC and *M-T* curves. The electrical resistance (bar sample, 10 mm × 3 mm × 2 mm) under the field were measured by four probe method using VersaLab system [20], where the magnetic field was applied along the length direction (*i.e.*, directional solidification direction). The MR is calculated by $MR = [R(H) - R(0)]/R(0) \times 100\%$, where $R(H)$ and $R(0)$ are the electrical resistance measured with and without the magnetic field, respectively.

3. Results and discussions

Fig. 1 displays the powder XRD pattern for the directionally solidified alloy measured at room temperature. The pattern exhibits the characteristic of martensite and it is similar to that of six-layered modulated (6M) martensite in a $Ni_{50}Mn_{36}In_{14}$ alloy [21], suggesting that the present $Ni_{44.5}Co_{5.1}Mn_{37.1}In_{13.3}$ alloy may consist of 6M martensite at room temperature. Accordingly, the lattice parameters of 6M martensite were determined to be $a_M = 4.352$ Å, $b_M = 5.581$ Å, $c_M = 12.98$ Å and $\beta = 93.8°$, respectively. In addition, the $\{2\,2\,0\}_A$ diffraction of austenite was also identified in the powder XRD pattern, which may indicate that the martensitic transformation temperature is close to the room temperature.

Fig. 2a shows the macroscopic microstructure of the longitudinal section for the directionally solidified alloy. The initial austenite forms coarse columnar-shaped grains with several hundreds of microns in size along the solidification direction. Such microstructural feature should be attributed to the specific thermal gradient during the directional solidification process.

To analyze the preferential orientation of the directionally solidified alloy, $\{-1\,2\,3\}_M$, $\{1\,2\,3\}_M$ and $\{0\,4\,0\}_M$ incomplete pole figures of the 6M martensite were measured on the transverse section by XRD, as shown in Fig. 2b. Noted that $\{-1\,2\,3\}_M$ and $\{1\,2\,3\}_M$ poles are roughly located at the polar angle of ~40°, whereas $\{0\,4\,0\}_M$ poles are located at the centre of the pole figure. According to the lattice correspondence between austenite and 6 M martensite in Ni-Mn-In alloys, $\{-1\,2\,3\}_M$ and $\{1\,2\,3\}_M$ are originated from $\{2\,2\,0\}_A$ of austenite and $\{0\,4\,0\}_M$ from $\{4\,0\,0\}_A$ [21]. Thus, it can be inferred that the initial austenite possesses the strong preferred orientation with $\langle 0\,0\,1 \rangle_A$ parallel to the solidification direction, which is consistent with previous results obtained in directionally solidified alloys [18,19].

Fig. 3 presents the temperature dependence of magnetization (*M-T* curves) measured under the field of 0.1 T and 3 T. In the figure, the abrupt changes in magnetization should be attributed to the martensitic transformation from ferromagnetic austenite to weak magnetic martensite. Based on the low-field *M-T* curves (0.1 T), the martensitic transformation temperatures (M_s, M_f, A_s, A_f) were determined to 324 K, 303 K, 316 K, and 337 K, respectively, which is very close to those determined from DSC measurements (inset of Fig. 3), *i.e.*, $M_s = 325$ K, $M_f = 300$ K, $A_s = 318$ K, $A_f = 344$ K. Recently, it was reported that the martensitic transformation in directionally solidified $Ni_{40.6}Co_{8.5}Mn_{40.9}Sn_{10}$ and $Ni_{42}Co_8$-

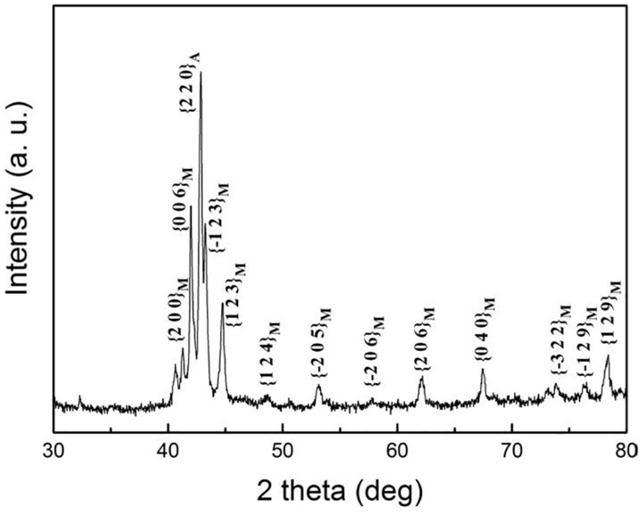

Fig. 1. Powder XRD pattern for the directionally solidified alloy measured at room temperature.