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Improvement of mechanical property and large shape recovery of sintered $Ni_{45}Mn_{36.6}In_{13.4}Co_5$ alloy

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High mechanical properties $Ni_{45}Mn_{36.6}In_{13.4}Co_5$ magnetic shape memory alloy with preferred orientation were prepared by spark plasma sintering melt-spinning ribbons piled up orderly. Sintered at 1073 K, the orientation of grains becomes random. Sintered at 873 K, part of the grains grows inhomogeneously and some of the columnar grains are fractured under relatively large compressive pressure. Mechanical properties of Ni-Mn-In-Co alloy are improved significantly by spark plasma sintering the ribbons. The compressive fracture strength and strain of the $Ni_{45}Mn_{36.6}In_{13.4}Co_5$ bulks sintered at 873 K are 1200 MPa and 14%, which are approximately two times larger than that of ingots as-cast. The improvement of mechanical property can be attributed to the textured microstructure and relatively tiny grains in sintering ingots. It must be mentioned that the alloys sintered at 873 K show almost perfect shape memory effect, about 95% compressive strains (as high as 11.4%) was recoverable during heating, and shape recovery is achieved in reverse martensitic transformation process, which predicts a relatively high magnetic field induced strain recovery in polycrystalline.

1. Introduction

Since Kainuma *etal* [1].reported magnetic-field-induced strain (MFIS) generated by reverse phase transformation in $Ni_{45}Mn_{36.6}In_{13.4}Co_5$, the Heusler type Ni-Mn based compounds with compositions close to the stoichiometric Ni_2MnX(X = In,Sn,and Sb) have attracted considerable attention in recent years [2–7]. Attention has been dedicated to study magnetism, magnetic shape memory effect [8,9] and magnetic entropy change of these alloy [10–12].Unlike traditional Ni-Mn-Ga magnetic shape memory alloy in which shape memory effect originated from twin boundaries motion under magnetic field [13], a metamagnetic phase transformation occurs in some off-stoichiometric Heusler Ni_2MnX(X = In, Sn, and Sb) alloys [14]. As the fourth element Co is doped in order to increase the Curie temperature, both the magneto structural transformation and corresponding large MFIS can be obtained around room temperature in NiMnInCo [15]. NiMnIn Heusler alloys are therefore of significant prospective importance for applications in both magnetically driven actuators due to magnetic shape memory effect and as working substances in magnetic refrigeration technology [16–19]. Magnetic-field-induced strain and large theoretical output stress has been achieved in the off-stoichiometric single crystalline NiMnInCo [1]. However, the preparation of single crystals is a time and cost-consuming process, and there can be compositional changes along the axis of the crystal growth and segregations [20]. From a technological point of view, polycrystals are of great interest, they are much easier to be produced. Unfortunately, they usually exhibit lower strains than single crystal, because of the different orientations of the separate crystals and the presence of grain boundaries, which obstruct the strain generated from magnetostructural transformation. A possible approach to improve the smart property of polycrystalline magnetic shape memory alloy is to obtain a highly textured microstructure, which is similar as a single crystal [21]. Textured material can be obtained by plastic deformation and hot rolling [22], but the well-known brittleness of Ni-Mn-In makes it difficult [23]. Rapid quenching by melt spinning technology has two potential advantages: avoiding of the annealing to obtain a homogeneous single phase alloy and the synthesis of highly textured polycrystalline ribbons [24,25]. However, the brittleness of

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melt-spun ribbons also restricts its application in Ni-Mn-In alloy. Spark plasma sintering (SPS) is a kind of method of producing bulk materials by heating the sample with pulsed DC current under pressure. Due to its high sintering speed and the possibility to combine materials at relatively lower temperatures, thus, allowing the formation of bulk textured sample with high density and mechanical properties [26–28].

In this paper we attempt to obtain textured polycrystal $Ni_{45}Mn_{36.6}In_{13.4}Co_5$ with both excellent mechanical properties and large recoverable strain by spark plasma sintering the melt-spun ribbons piled up orderly. The structural information, phase transformation behavior, shape memory effect and texture as well as mechanical properties are demonstrated in detail, which provide a way to get high performance magnetic shape memory alloy.

2. Experimental

As-cast ingots of nominal composition $Ni_{45}Mn_{36.6}In_{13.4}Co_5$ were prepared by arc melting of the pure metals under argon atmosphere and remelted four times to obtain homogenized bulks. The ingots were cut into small pieces by using a wire-electrode cutting. The precursor ingots pieces were induction melted in a quartz tube and then ejected with argon of 0.02 MPa onto water cooled copper wheel with rotating line velocity of 15 m/s. The prepared ribbons were of width about 5–7 mm and about 10–20 mm in length. They were stacked orderly in a graphite mold of $\Phi 15 \times 60$ mm and subjected to spark plasma sintering. The sintering parameters were shown in Table 1, and the as-sintered ingots after spark plasma sintering were about $\Phi 15 \times 3$ mm. The microstructure, composition and phase structure were studied by Scanning Electron Microscopy (SEM, Tescan MIRA3 XMU) equipped with Energy Dispersive Spectrum(EDS) and X-ray Diffraction (XRD, PANALYFICAL X'Pert PRO) using Cu $K\alpha$ radiation, respectively. The martensitic transformation temperatures were determined by Differential Scanning Calorimetry (DSC, METTLER TOLEDO) with heating and cooling rates of 10 K/min. Texture evolution was analyzed by using Electron Backscatter Diffraction (EBSD, Oxford HKL NORDLYS) equipment attached to the SEM. EBSD maps were collected with a scanning step size of 0.3 μm and1μm, depending on the grain size. The orientation and grain reconstruction were analyzed by using HKL CHANNEL5 package software. In EBSD maps the pixel color represents the unit cell orientation. The indexing rate, i.e. the fraction of pixels in EBSD maps, of which the unit cell orientation could be successfully indexed, depends on both the surface quality and matched degree of structure can be close to 100%. In our experiment results, the indexing grade of all the raw EBSD maps is high (above 90%). Stress-strain curves were obtained by testing with a mechanical testing machine (Shimatzu AGS-X) at room temperature, with an initial strain rate of $1 \times 10^{-3} s^{-1}$. Recoverable strains were measured by using Instron-5966 mechanical testing machine equipped with liquid nitrogen cooling unit, by measuring the sample height change. According to the martensitic transformation temperatures of the sintered samples, cylinder sample of 3 mm diameter was used for the shape memory effect measurement, the details of which were as follow: Firstly, the initial length of cylinders l_0 was measured at room temperature, and then compress at 193 K with a strain rate of 0.02 mm/min. The final compressive strain ε_0 is 8% for as-cast ingot and sample sintered at 1073 K, but 8% and 12% for sample sintered at 873 K, respectively, and then the samples were heated to 373 K for reverse martensitic transformation and strain recovery. Finally, the ultimate length l_2 was measured at room temperature, and the length of cylinders under the final compressive load is l_1. Thus the shape recoverable strain ε and recovery ratio η were calculated by equations (1) and (2), respectively:

$$\varepsilon = \frac{l_2 - l_1}{l_0} \tag{1}$$

$$\eta = \frac{l_2 - l_1}{l_0 - l_1} \tag{2}$$

3. Results and discussion

3.1. Microstructure and structure characteristics

The microstructure of ribbons and as-sintered samples were studied by SEM. Typical SEM images of fracture cross section of ribbons and surface of as-sintered sample are displayed in Fig. 1. As shown in the images, the ribbons are polycrystallines, and the columnar grains is around 2–6 μm which are perpendicular to the ribbons plane. It is suggested that the rapid solidification process induces a directional grain growth. The entire ribbon thickness is about 40 μm with two different sides: free side and wheel side. A layer of thin equiaxed crystals is formed in the wheel side where large under cooling has achieved as shown in Fig. 1(b). Due to the brittleness of the ribbon, several methods are tried to combine the ribbons together in order to improve the mechanical property. Spark plasma sintering is a compressing-sintering method which has many advantages. The characteristics of high sintering speed and the possibility to sinter at relatively lower temperatures are critical for keeping the grain size and orientation during sintering. Therefore, if appropriate sintering parameters are chosen, bulk samples with grains similar to the melt-spun ribbon can be obtained. As examined by DSC, the martensitic transformation and reverse martensitic transformation temperature M_s/A_s for melt-spun ribbon and bulk sintered at 1073 K are determined as 294 K, 306 K and 314 K, 329 K, respectively. Therefore, the microstructures observed in ambient temperature are parent phase without any martensitic stripes.

As shown in Fig. 2(d, c), the grain size of as-sintered samples is about 3–10 μm after spark plasma sintering at 873 K for 20 min, whereas the grain size is around 15–50 μm after sintering at 1073 K for 5 min. Thus sintering temperature has great effect on the grain size and morphology rather than the holding time. Melt spinning process is a rapid solidification process with high cooling rate, so the grains of melt-spun ribbon are small. During sintering process the tiny grains continue to grow, and temperature plays the most important role. So the size of grains become about several times larger than those of the melt-spun ribbon after holding at 1073 K for 5 min, whereas the tiny grains just grow slightly while holding at 873 K even for 20 min. The composition of ribbon and sintered

Table 1
Spark Plasma Sintering parameters.

	Compression stress(MPa)	Temperature(K)	Heating rate(K/min)	Holding time(min)
SPS 873 K	60	873	100	20
SPS 1073 K	40	1073	100	5