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Microstructure and martensitic transformation behavior of the $Ni_{50}Mn_{36}In_{14}$ melt-spun ribbons

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The microstructure and martensitic phase transformation behavior of the $Ni_{50}Mn_{36}In_{14}$ melt-spun ribbons were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The results show that fine crystal grains with preferential orientation have been obtained in the rapidly quenched ribbons, the martensitic transformation temperatures of the as-cast ribbon are low, and increased after heat treatments. The reason is clarified as the variation in degree of order and internal stress.

Keywords: Melt-spinning; Preferential orientation; Microstructure; Grain refining; Martensitic phase transformation

Ferromagnetic shape memory alloys (FSMAs) that can be driven by magnetic fields have attracted considerable attention as a type of magnetic actuator material. Large magnetic-field-induced strain of about 9.5% had been obtained in the Ni–Mn–Ga single crystal [1], which is quite hard to prepare and has composition segregation along the axial direction. Therefore, polycrystal is more valuable from the point of application. Because of the different orientation and the boundaries of the polycrystal grain, the magnetic-field-induced strain is small. Aiming at solving the problems above, Ni–Mn–Ga rapidly quenched ribbons have been investigated by many researchers [2–5], in which the grains distribute orientedly, and have obtained large magnetic-field-induced strain. Recently, some other kinds of ribbons such as Ni–Fe–Ga [6], Co–Ni–Ga [7] and Cu–Al–Ni [8] are prepared, the microstructures and magnetic performances are investigated in detail. The Ni–Mn–In alloy is a new kind of magnetic-field-induced shape memory alloy, and becomes another hot issue of research [9–12]. In 2006, Kainuma discovered magnetic-field-induced shape recovery by reverse martensitic transformation in the Ni–Co–Mn–In alloy [13], called "metamagnetic shape memory alloy", and the theoretical output stress is up to 108 MPa, which is 50 times higher than the Ni–Mn–Ga alloys, thus the Ni–Mn–In series are identified as the real magnetic-field-induced phase transformation materials, and have a great potential in practical applications, but as far as we know, there is no report on the ribbons of Ni–Mn–In alloys. Recently, our group prepared rapid quenched ribbons of $Ni_{50}Mn_{36}In_{14}$ polycrystal, obtained the orientedly distributed and fine crystal grains, which are in favor of the magnetization and improving the brittleness of the $Ni_{50}Mn_{36}In_{14}$ alloy. In this paper, the microstructure and martensitic phase transformation of the rapidly quenched $Ni_{50}Mn_{36}In_{14}$ ribbons have been investigated, in order to demonstrate the basic characteristics of this material.

The polycrystal with nominal composition of $Ni_{50}Mn_{36}In_{14}$ was prepared by arc melting an elemental mixture of Ni (99.95%), Mn (99.92%), In (99.95%) under argon atmosphere, and cast into rods of 6 mm in diameter. About 10 g of the alloys were inductively melted in a quarts tube and spun in a vacuum at a typical wheel rotation speed of 900 rad min^{-1}, and then the ribbons were separately annealed in vacuum quarts at 1073 K, 973 K, 873 K and in 1.2 T magnetic field at 873 K for 1 h and cooling in the furnace. The crystal structure was determined by X-ray diffraction (XRD, Riguku-D/max-γ B rotating anode X-ray diffractometer). The microstructures of the ribbons were observed through scanning electron microscopy (SEM, Hitachi S570). The phase transformation temperatures were measured by differential scanning calorimetry (DSC, Perkin Elmer) at a cooling and heating rate of 20 K min^{-1}.

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The XRD patterns of the $Ni_{50}Mn_{36}In_{14}$ bulk material and ribbon are shown in Figure 1. As shown in Figure 1, both the bulk material and ribbon consist of the martensite phase at room temperature, and has mixed modulated structures (the details of which will be reported later), which is consistent with the results of Sutou and co-workers [14–16]. The diffraction peaks marked with an asterisk correspond to a kind of modulated structures, while the peaks without the asterisk accord with another kind of modulated martensite, and the ribbon has the lattice constants of $a = 4.387$ Å, $b = 5.937$ Å, $c = 21.173$ Å, $\beta = 88.22°$, which are slightly larger than the bulk material. In addition, the intensities of $(1\,2\,\overline{1}\,\overline{1})$, $(3\,1\,\overline{1})$, $(1\,3\,3)^*$, $(1\,2\,\overline{1}\,\overline{4})^*$ and $(3\,1\,4)^*$ are relatively higher than those observed in the bulk material with the same composition, suggesting that the $Ni_{50}Mn_{36}In_{14}$ as-cast ribbon has some preferential orientation. A similar observation has been reported [4,17] in Ni–Mn–Ga series. This would be proved by the SEM BSE micrographs afterwards. The XRD patterns of ribbons after heat treatment (not shown in this paper) are almost the same as that of the as-cast ribbon, it indicates that the preferential orientation is not eliminated by heat treatment. The preferential orientation is in favor of getting large saturation magnetization difference (ΔM), and hope to decrease the driving magnetic field to some extent.

The backscattered electron images of the $Ni_{50}Mn_{36}In_{14}$ ribbon side view are shown in Figure 2. From the full view on the side of the ribbon in Figure 2b, crystal grains which are perpendicular to the surface of the ribbon could be clearly observed: it is another evidence of the preferential orientation. In Figure 2c, the crystal boundaries are wide and etched off, and the martensitic stripes on the side of the ribbon are visible.

The SEM micrographs of the ribbons near the wheel side are shown in Figure 3. As the phase transformation temperatures are all above the room temperature whatever the heat treatment methods, the microstructures of the ribbons observed are all martensite at room temperature.

As shown in Figure 3, all the grain dimension decreases after the melt-spun process (the micrographs of the bulk material has not been shown in this paper), due to the rapidly cooling process which prevents the grains from growing to some extent. Figure 3a is the microstructure of the as-cast ribbon, large cooling speed during melt-spinning brings us the tiny tissue (refine the crystal grains), which improves the brittleness of the intermetallic material $Ni_{50}Mn_{36}In_{14}$ in favor of the practical application. Figures 3b–d are the microstructures of the ribbons annealed at different temperatures, the grain boundaries of the ribbons annealed in higher temperature are more clear than those in lower temperature. Obviously, the grains are columnar crystals after annealing at 873 K and 973 K, but equiaxed crystals after annealing at 1073 K; this is mainly because the recrystallization and the growth of grains while annealing at 1073 K. Figure 3e is the microstructure of the ribbon annealed in 1.2 T magnetic field at 873 K, the grains of this ribbon are much more clear and orderly than that of the ribbon just annealed at 873 K. Otherwise, the martensitic stripes being observed not only in the ribbons after heat treatment but also just as-cast are quite different from the phenomenon reported by Albertini in $Ni_{53}Mn_{23.5}Ga_{23.5}$ ribbon [17].

The DSC curves of the as-cast ribbon and ribbons after heat treatment are shown in Figure 4, where exothermic peak and endothermic peak associated with the martensitic and reverse transformations are observed in the cooling and heating processes respectively. The martensitic start (M_s), martensitic finish (M_f), austenitic start (A_s) and austenitic finish (A_f) transformation temperatures marked with tangential method are collected in Table 1.

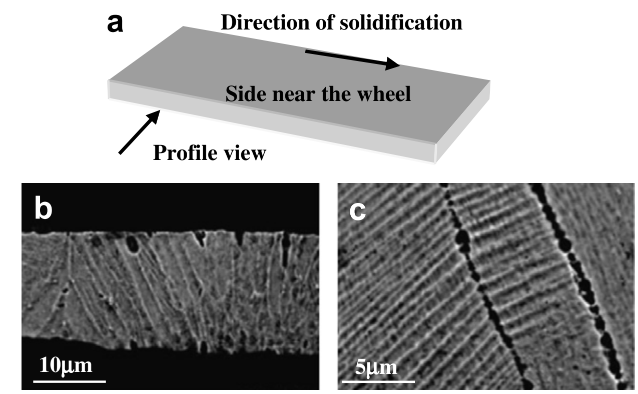

Figure 2. (a) Sketch map of the ribbon, (b) BSE micrographs of the $Ni_{50}Mn_{36}In_{14}$ ribbon profile view and (c) martensitic stripes on the profile of the ribbon.

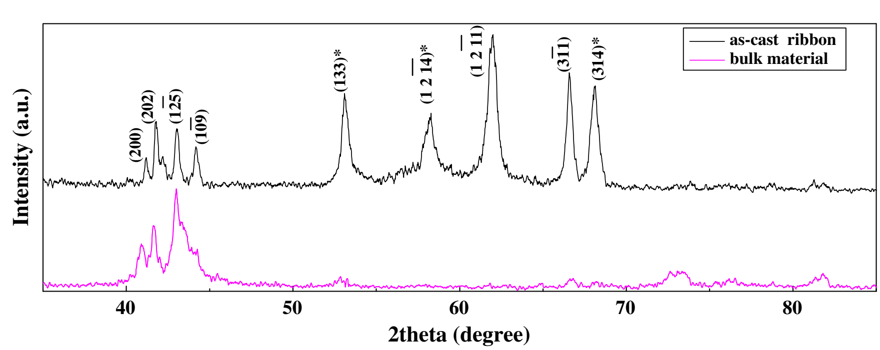

Figure 1. XRD of the $Ni_{50}Mn_{36}In_{14}$ bulk material and ribbon as-cast in room temperature.