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A novel route for growing single-crystal and internal-stress-induced martensitic transformation of ferromagnetic shape memory alloys $Co_{50}Ni_{20}Ga_{30}$

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As a new single-crystal preparation method, undercooling directional solidification has been proposed for the case of the ferromagnetic shape memory $Co_{50}Ni_{20}Ga_{30}$ rod. The as-grown single crystal has strong [1 1 1] orientation and a very homogenous composition along the rod axis, which confirms that the undercooling directional solidification is a feasible and effective approach for preparing Co–Ni–Ga single crystals. Additionally, the drastically increased transformation temperatures upon undercooling was ascribed to the internal stress induced martensitic transformation.

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) have attracted much interest as promising in making magnetically controlled actuators and sensors since the first report came out on the magnetic-field-induced strain (MFIS) in Ni_2MnGa [1]. As a new member of FSMAs, Co–Ni–Ga has recently attracted a great deal of attention owing to its magnetic-controlled two-way shape memory effect [2], high martensitic transformation temperatures [3] and good ductility [4]. A large MFIS of about 2.3% can be achieved in Co–Ni–Ga single crystals due to large magnetic anisotropy energy [2]. However, preparation of single crystals is a time- and cost-consuming process, and there can be compositional changes along the axis of the crystal [5]. Therefore, directional solidification has been proposed to prepare highly textured polycrystals, by which the oriented Ni–Mn–Ga and Co–Ni–Al FMSAs were produced showing a large MFIS of about 1.5% and 0.013% respectively [6,7]. However, the compositional segregation as occurred in the conventional single-crystal growth cannot be avoided somehow. Meanwhile, melt-spinning as a rapid quenching method was also used to prepare textured Co–Ni–Ga ribbons, but possessing an even lower MFIS 0.011% due to the constraint of twin boundary motion in refined grains [8]. Thus directional and rapid solidification methods are effective ways to prepare oriented alloys, but have their intrinsic weaknesses. If these two solidification methods are to be combined, we can expect to develop their corresponding advantages. Thus, a rapid directional solidification method, here the undercooling-directional solidification, is proposed. This novel approach is based on the fact that under bulk undercooling conditions, once the undercooled melt is triggered, it solidifies very quickly around the core and forms an oriented single crystal [9,10].

Our previous studies found in undercooled Co–Ni–Ga alloys a high density of sub-grains, which were deemed to result from some redistributions of line defects introduced by internal stresses during rapid solidification [11,12]. Meanwhile, the reverse transformation temperature was greatly increased after undercooling treatment, which was also attributed to the huge internal stresses [12,13]. In comparison with the external stress ~20 MPa to induce martensitic transformation for $Co_{49}Ni_{22}Ga_{29}$ alloys at room temperature [14], martensitic transformation may be in situ induced at the post-stage of undercooling solidification. In this paper, a new method of undercooling directional solidification to prepare $Co_{50}Ni_{20}Ga_{30}$ single crystal is reported. The microstructure, martensitic transformation temperatures and orientation of the $Co_{50}Ni_{20}Ga_{30}$ single crystal were also investigated.

2. Experimental

$Co_{50}Ni_{20}Ga_{30}$ ingots were prepared by arc-melting under an argon atmosphere. They were melted four times in order to achieve the compositional homogenization. The ingots were cut into small pieces and treated by undercooling directional solidification experiment in a high frequency induction unit. The schematic diagram of undercooling directional solidification is shown in Fig. 1a. Glass fluxing combined with superheating cycling was used to achieve a reasonably large undercooling. The fluxed glass, consisting of 70 wt.% $Na_2B_4O_7$, 30 wt.% NaSiCa, was employed as the

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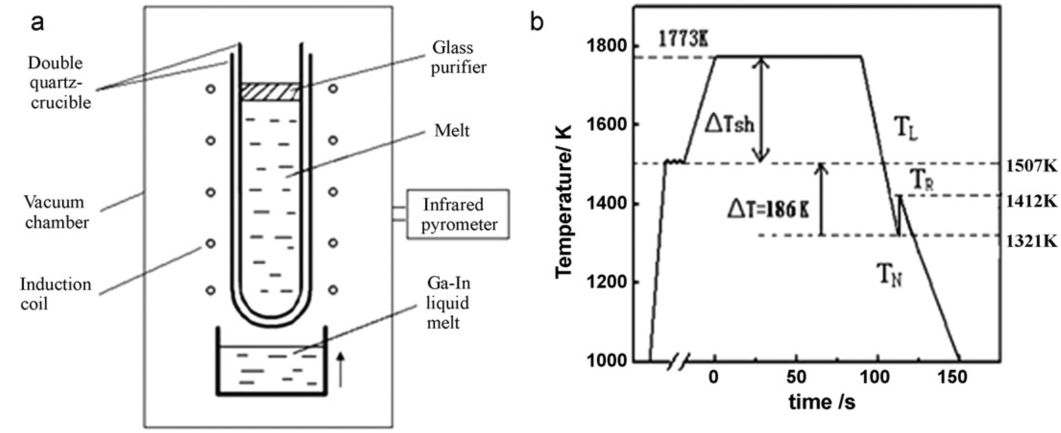

Fig. 1. Schematics diagram of undercooling directional solidification (a); and typical cooling curve of undercooled $Co_{50}Ni_{20}Ga_{30}$ alloys melts with $\Delta T = 186$ K (b). ΔT_{sh}-superheating temperature; T_L-liquidus temperature; T_R-recalescence temperature; T_N-nucleation temperature.

denucleating agent. The $Co_{50}Ni_{20}Ga_{30}$ sample was surrounded by the denucleating agent and put into a double-quartz crucible with a diameter of 7 mm and length of about 100 mm. In order to obtain a large undercooling, the sample was superheated to 1773 K for 1.5 min and then subjected to superheating-cooling cycle for several times. The heating–cooling curve is shown in Fig. 1b. The detail of denucleating technique was described in our previous paper [15]. Subsequently, the undercooled melt was triggered to solidify by the Ga–In liquid melt at the crucible bottom. The $Co_{50}Ni_{20}Ga_{30}$ melt rapidly solidified from the bottom and achieved the undercooling directional solidification rod. The cooling curve of the melt was measured by an infrared pyrometer, which was calibrated with a standard $PtRh_{30}$–$PtRh_6$ thermocouple, a relative accuracy of 5 K and a response time less than 1 ms. A part of the undercooled sample was annealed at 1073 K for 10 min followed by water quenching.

Microstructure was observed by a Neophot-1 optical microscope. The composition was determined by energy dispersion X-ray spectroscopy (EDS) in a scanning electron microscope (FEI SIRION 200). The crystal structure was analyzed by X-ray diffraction analysis (D/max 2550 V XRD) with Cu Kα radiation. Martensitic transformation temperatures were determined by a differential scanning calorimeter (Perkin-Elmer DSC) in the temperature range of −60 to 100 °C and the heating/cooling rate of 10 K/min.

3. Results and discussion

A $Co_{50}Ni_{20}Ga_{30}$ rod with a diameter of 6 mm and length of about 50 mm was obtained by undercooling directional solidification under the bulk triggering undercooling (ΔT) of 186 K. The macrostructure and chemical composition along the axis in the rod are demonstrated in Fig. 2. There is no grain boundary observed in the whole rod, which means the rod is likely to be a single crystal. Other evidences for the single crystal will be shown later on. Regarding the chemical composition along the axis, the average composition is very close to the nominal one. It shows that no

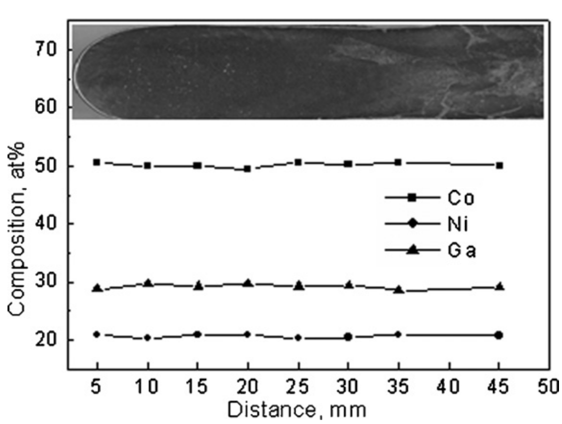

Fig. 2. Macrostructure of unidirectional $Co_{50}Ni_{20}Ga_{30}$ rods undercooled by 186 K and chemical composition along the axis.

chemical reaction occurred between the alloy melt and the denucleating glass, and there is no compositional segregation along the crystal growth direction. Because the melt composition is initially uniform under induction stirring, once nucleation occurred at the crucible bottom the undercooled melt will rapidly solidify along the axis without composition diffusion and grow up to an intact single crystal. Accordingly, the undercooling directional solidification can be considered as an excellent approach to prepare the homogenous Co–Ni–Ga single crystal.

The microstructures of $Co_{50}Ni_{20}Ga_{30}$ of as-arc melted and undercooled rods are shown in Fig. 3. A typical morphology of single phase of austenite was observed in the as-arc melted alloy with the grain size of a few hundred microns (Fig. 3a). For the $Co_{50}Ni_{20}Ga_{30}$ rod treated by undercooled directional solidification, it exhibits the absence of grain boundary in a large scale (Fig. 3b), which further testifies the undercooled alloy as a single crystal. However, a large amount of parallelogram lines appeared on the whole chemically etched surface (Fig. 3b). A higher magnification reveals that the lines are sharp cracks approximately perpendicular to each other and form quite regular parallelograms, whose widths are about 300 μm (Fig. 3c). Such a result was also previously found in $Co_{50}Ni_{20}FeGa_{29}$ single crystals [16]. As described above, the denucleated $Co_{50}Ni_{20}Ga_{30}$ melt would abruptly nucleate and rapidly solidify once it was triggered; also, the cavity collapse and the crystal lattice deformation of the undercooled alloy would result in a large number of vacancies, interstitials and dislocations, and thus generate an internal stress field [17]. The internal stress gradually increases with the sample cooling down and sequentially induces recovery, during which a small amount of dislocations climb and/or cross slip to annihilate, and those vacancies and interstitials would be annihilated by the diffusion of dislocations. The remaining free and random dislocations rearrange into dislocation walls [11,12], and eventually reorganize into deep cracks as the melt continues cooling down. Meanwhile, the heat of the $Co_{50}Ni_{20}Ga_{30}$ alloy is mostly eliminated in the axis direction, which leads to these cracks in parallelogram along the axis. In short, the undercooling directional solidification generates in the crystal a high-level internal stress, which is released by slight lattice deformation in a small region and condenses to form cracks at the region edge.

More interestingly, it can be clearly seen that a mass of martensitic variants appears in undercooled $Co_{50}Ni_{20}Ga_{30}$ alloys, as shown in Fig. 3c. As seen in Fig. 3a, the as-cast $Co_{50}Ni_{20}Ga_{30}$ alloy is in the austenitic state at room temperature. The appearance of martensitic plates indicates that the high internal stress, introduced by undercooling rapid solidification, may lead the $Co_{50}Ni_{20}Ga_{30}$ alloy to transform from austenite (A) to martensite (M). As we know, the martensitic transformation of FSMAs can be induced by tem-

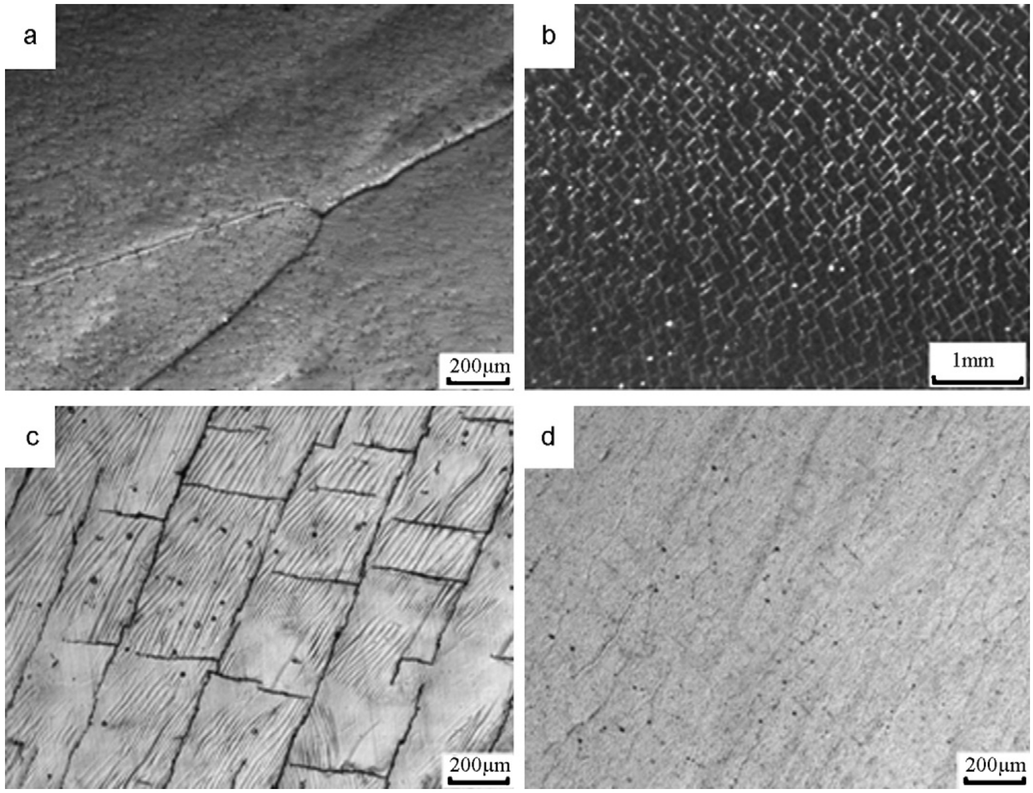

Fig. 3. Microstructures of $Co_{50}Ni_{20}Ga_{30}$ alloys of (a) as cast, (b) ΔT = 186 K, (c) higher magnification of (b), (d) annealed at 1073 K for 10 min of the undercooled alloy.

perature, external stress, magnetic field or integrated methods. For stress-induced martensitic transformation, the critical tensile stress for martensitic transformation is about 50 MPa at 40 °C and increases to 250 MPa at 300 °C with a rate of 0.78 MPa/°C in $Co_{49}Ni_{21}Ga_{30}$ single crystals [18]. It can be seen that the critical stress for martensitic transformation, especially at a high temperature, is quite large. Thus, the martenitic transformation, which is induced by undercooling directional solidification, takes place in the $Co_{50}Ni_{20}Ga_{30}$ austenitic alloy above room temperature and this indicates that the internal stress is also very large.

In order to prove whether the martensitic transformation of $Co_{50}Ni_{20}Ga_{30}$ single crystals is induced by the internal stress, parts of the undercooled sample went through annealing at 1073 K for only 10 min and then water quenched. The microstructure of the annealed $Co_{50}Ni_{20}Ga_{30}$ alloy exhibits the typical single austenite, as shown in Fig. 3d. It indicates that the internal stress was mostly released by annealing, even for such a short time. Meanwhile, those deep cracks in the martensitic state mostly disappeared and only a few indistinct sub-grain boundaries left, which were also due to the release of the internal stress during the recovery process [11,12].

In addition, the transformation temperatures of the $Co_{50}Ni_{20}Ga_{30}$ alloy were measured, as shown in Fig. 4a. It can be seen that the martensitic transformation start temperature (M_s), the martensitic transformation finish temperature (M_f), the austenitic transformation start temperature (A_s) and the austenitic transformation finish temperature (A_f) for as-cast $Co_{50}Ni_{20}Ga_{30}$ alloys are respectively −42.5 °C, −43.5 °C, −21.4 °C and −10.5 °C, respectively, which are in accordance with the observation of the austenite state for $Co_{50}Ni_{20}Ga_{30}$ alloys at room temperature (Fig. 3a). However, the transformation temperatures of the undercooled sample are greatly elevated and reach −13.5 °C, −21.5 °C, 22.7 °C for M_s, M_f and A_f respectively. It can be seen that the transformation temperatures increased by nearly 30 °C. As has been discussed, the critical tensile stress for martensitic transformation

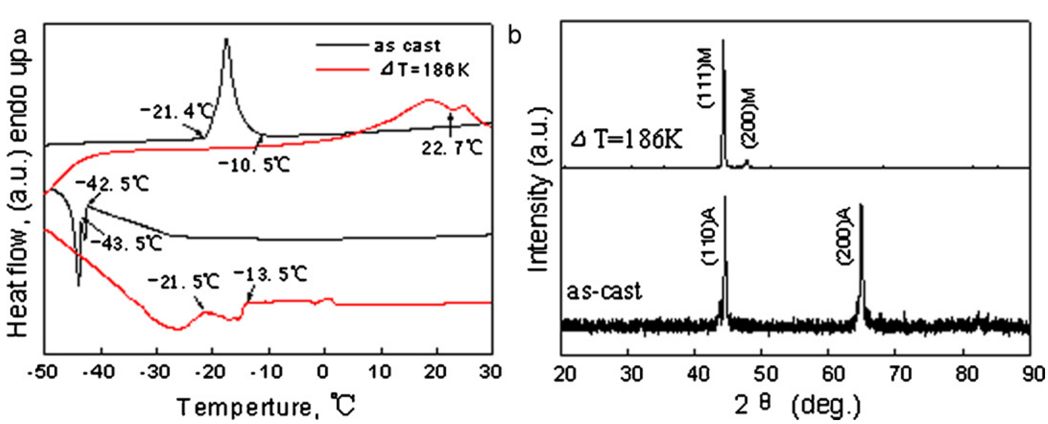

Fig. 4. DSC curves (a) and XRD patterns (b) of $Co_{50}Ni_{20}Ga_{30}$ alloys.

increases with a rate of 0.78 MPa/°C for $Co_{49}Ni_{21}Ga_{30}$ single crystals [18]. According to this result, the internal stress would increase by at least 23.4 MPa for the undercooled $Co_{50}Ni_{20}Ga_{30}$ alloy, which is enough for the critical stress to induce martensitic transformation at room temperature [14]. For the reverse transformation, it starts at above 0 °C and undergoes a long period due to the release of the large internal stress, which agrees with the observation of martensitic morphology for the undercooled sample. Thus, it is clear that the effect of high undercooling on the transformation temperatures is considerable. Similar results were found in undercooled $Co_{45}Ni_{25}Ga_{30}$ and $Co_{46}Ni_{27}Ga_{27}$ alloys [12,13], which implied that A_s temperature increases with the undercooling, i.e. a higher undercooling induces larger internal stress and thus leads to a higher A_s. It confirms that the high undercooling evidently raises transformation temperatures. Following the mechanism of elastic strain energy [19], the variant self-accommodation effect was damaged and the elastic strain energy stored in variants was released by the residual internal stress, thus the chemical energy drove the reverse transformation temperatures to increase. On the contrary, the internal stress assisted the austenite to transform into martensite during the cooling process, which would result in the increase of martensite transformation temperatures.

The orientation and phase structure can be confirmed by X-ray diffraction. Fig. 4b shows the XRD patterns of $Co_{50}Ni_{20}Ga_{30}$ alloys before and after undercooling. For as-cast $Co_{50}Ni_{20}Ga_{30}$ alloys, there are two peaks of (1 1 0)A and (2 0 0)A at the positions of 44° and 65° respectively. The optical observation in Fig. 3a shows the as-cast $Co_{50}Ni_{20}Ga_{30}$ alloy has non-preferred orientation and is austenite at room temperature. While for the undercooling directional solidification $Co_{50}Ni_{20}Ga_{30}$ alloy, the XRD patterns exhibit strong (1 1 1)M and weak (2 0 0)M peaks, which exhibits two facts: (1) a strong [1 1 1] preferred orientation; (2) a martensitic structure. The results imply that the undercooled $Co_{50}Ni_{20}Ga_{30}$ rod has an oriented martensitic phase, which is in good agreement with the optical observation (Fig. 3b and c). Therefore, the martensitic transformation can be induced during the undercooling solidification process, and the approach of undercooling directional solidification is feasible and effective enough to prepare single crystals.

4. Conclusion

In summary, in the current research a new preparation method of single crystals, i.e. undercooling directional solidification, was proposed, and a ferromagnetic $Co_{50}Ni_{20}Ga_{30}$ single crystal was prepared by it. The composition of the alloy is very close to the nominal composition, and the microstructure and XRD patterns exhibit a perfect single crystal with [1 1 1] preferred orientation along the rod, which shows that the undercooling directional solidification is a feasible and effective approach of preparing single crystals. Meanwhile, the typical change in morphology from austenite to martensite and high elevated transformation temperatures imply that an internal-stress-induced martensitic transformation took place at the post stage of undercooling directional solidification.

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