Crystal structure and formation mechanism of the secondary phase in Heusler Ni-Mn-Sn-Co materials

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Abstract In the present work, crystal structure and formation mechanism of the secondary phase in Heusler Ni-Mn-Sn-Co materials were investigated using X-ray diffraction, scanning/transmission electron microscopy and selected-area electron diffraction techniques. Experimental results showed that the secondary phase presented in both $\text{Ni}_{44.1}\text{Mn}_{35.1}\text{Sn}_{10.8}\text{Co}_{10}$ as-cast bulk alloy and melt-spun ribbon, possessing a face-centered cubic (*fcc*) $\text{Ni}_{17}\text{Sn}_3$ -type structure. The secondary phase in the as-cast bulk alloy was resulted from a eutectic reaction after the formation of a primary dendritic β phase during cooling. However in the melt-spun rapidly solidified ribbon, the secondary phase was largely suppressed as nano-precipitates distributed along the grain boundaries, which was attributed to a divorced eutectic reaction. The secondary phase exhibited partial amorphous state due to high local cooling rate.

Keywords Heusler Ni-Mn-Sn-Co materials · Secondary phase · Melt spinning · Divorced eutectic reaction · Microstructure

1 Introduction

In the past decades, alternative solid-state refrigeration methods have increasingly received attentions which provide high efficiencies, and thus they can contribute to a more efficient use of resources and lower greenhouse gas emissions [1]. Heusler Ni-Mn-(Ga,In,Sn,Sb) with magnetocaloric effect represents a promising class of candidate materials based on two solid-state transitions including the first-order martensitic transformation and the second-order magnetic transition of austenite [2–5]. Nowadays a lot of efforts have been made on the doping of the fourth element since it has been considered as an effective way to improve the magnetic properties [6–10]. Meanwhile, it was found that the secondary phase would form with these additions and produce strong effects on the martensitic transformation and magnetic properties as well. Feng et al. observed that face-centered cubic (*fcc*) particles appeared both along the grain boundaries and inside the grains after doping 5 % Fe to Ni-Mn-In alloys, and enhanced mechanical properties were obtained with the precipitation of the secondary phase particles [8]. A $\text{Dy}(\text{Ni,Mn})_4\text{Ga}$ phase with a hexagonal CaCu_5 -type structure was identified by Gao et al. in $\text{Ni}_{50}\text{Mn}_{29}\text{Ga}_{21-x}\text{Dy}_x$ alloys. They found that the crystal structure of martensite evolved from five-layered to orthorhombic, and then to non-modulated structures. The martensitic transition temperatures also notably increased with increasing Dy content due to the presence of the $\text{Dy}(\text{Ni,Mn})_4\text{Ga}$ precipitates [9]. Very recently, a *fcc* γ phase in $\text{Ni}_{43}\text{Co}_{12}\text{Mn}_{41}\text{Sn}_9$ alloy was identified based on conventional X-ray diffraction technique, which could be fully suppressed under melt-spun condition, and thus the martensitic transformation shifted to higher temperature with positive effects on magnetic properties in the $\text{Ni}_{43}\text{Co}_{12}\text{Mn}_{41}\text{Sn}_9$ ribbon [10]. Additionally, melt-spinning

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technique could generate highly textured homogeneous polycrystalline ribbons [11, 12] with substantially improved magnetic properties [13], and it is being widely used for the fabrication of high-performance magnetocaloric materials [14–17]. Considering that Ni-Mn-Sn is highly potential for large-scale engineering applications among the Heusler Ni-Mn based family, and Co doping is effective to enhance the magnetocaloric effect through intensifying the magnetization discrepancy between the austenite and the martensite [18, 19], it is necessary to better understand the crystal structure and formation mechanism of the secondary phase in the Heusler Ni-Mn-Sn-Co materials. However, fewer reports on the secondary phase could be found in the literature. The main objective of the present work is to provide more information on this point based on $\text{Ni}_{44.1}\text{Mn}_{35.1}\text{Sn}_{10.8}\text{Co}_{10}$ alloy.

2 Experimental

As-cast $\text{Ni}_{44.1}\text{Mn}_{35.1}\text{Sn}_{10.8}\text{Co}_{10}$ ingot with mass about 80 g was arc melted from Ni, Mn, Sn, Co with purities of 99.99 % (mass fraction) in argon gas atmosphere. Additional $w(\text{Mn}) = 5\%$ was added to compensate for its evaporation loss. The ribbons were fabricated using melt spinning technique at a linear speed of 10 m/s and the resultant melt-spun ribbons were about 20 mm long, 4–6 mm wide and 30–35 μm thick.

X-ray diffraction (XRD, DLMAX-2200) was employed to detect the phases and crystal structures. Microstructural observations were conducted using a field-emission scanning electron microscopy (SEM, JSM-6700F). Transmission electron microscopy (TEM) analyses were performed in a JEOL JEM-2010F microscope equipped with an

energy dispersive spectrometer (EDS), operated at 200 kV using a double-tilt stage. High-temperature differential scanning calorimetric measurement (NETZSCH DSC 404C) was carried out at heating/cooling rates of 10 K/min.

3 Results and discussion

Figure 1 shows the XRD patterns of $\text{Ni}_{44.1}\text{Mn}_{35.1}\text{Sn}_{10.8}\text{Co}_{10}$ as-cast bulk alloy and melt-spun ribbon at room temperature. In case of the as-cast bulk alloy, besides the diffraction peaks from cubic $L2_1$ austenite (β phase), all the other peaks can be well indexed in reference to $\text{Ni}_{17}\text{Sn}_3$ phase, which is denoted as γ phase in Ref. [10]. For the melt-spun ribbon, $L2_1$ phase can be clearly distinguished, whereas the peaks of γ phase are rather weak. Based on the XRD data, the lattice parameters of $L2_1$ phase are calculated to be $a = 0.5998\text{ nm}$ for the bulk alloy and 0.5946 nm for the ribbon, respectively. The unit cell shrinks slightly, which can also be evidenced from the fact that the peaks from $L2_1$ phase of the melt-spun ribbon shift slightly towards higher angles in contrast to these peaks in the as-cast bulk alloy. The lattice parameter of the γ phase in the bulk alloy is about 0.3644 nm .

The microstructure of the as-cast bulk alloy was studied using SEM and TEM, as shown in Fig. 2. It can be observed that the sample consists of coarse dendritic β phase and lamellar ($\beta + \gamma$) eutectic microstructure, as shown in Fig. 2a. The eutectic microstructure is enlarged in Fig. 2b. The β phase would undergo an ordering transition from $B2$ structure to $L2_1$ structure upon subsequent cooling at around 1000 K [20]. Figure 2c is the TEM image of the as-cast bulk alloy. The selected-area electron diffraction pattern (SAEDP) inserted in Fig. 2c indicates that the γ phase

Fig. 1 XRD patterns of $\text{Ni}_{44.1}\text{Mn}_{35.1}\text{Sn}_{10.8}\text{Co}_{10}$ as-cast bulk alloy **a** and melt-spun ribbon **b** at room temperature

Fig. 2 **a** SEM backscattered electron micrograph of $\text{Ni}_{44.1}\text{Mn}_{35.1}\text{Sn}_{10.8}\text{Co}_{10}$ as-cast bulk alloy; **b** enlarged from **a**; **c** TEM image and the SAEDP taken from the area 2 highlighted with a white circle (The EDS chemical compositions from spots 1 and 2 are given in Table 1.)

has *fcc* structure. Furthermore, the EDS chemical compositions of spot 1 (matrix) and spot 2 (γ phase) are listed in Table 1. It is evident that the γ phase has much higher Co but much lower Sn contents than the matrix.

TEM observations were performed to characterize the crystal structure of the secondary phase in the ribbon. Figure 3a presents a TEM bright-field image where novel precipitates, with an average width less than 100 nm, appear along grain boundaries. It can be noticed that the grain boundaries indeed consist of two distinct phases with high contrast. The SAEDP taken from the area 1 confirms the $L2_1$ austenitic matrix (see Fig. 3b). However, the SAEDPs taken from the area 2 after tilting to three different zone axes [001], [011] and $[\bar{1}12]$, as shown in Figs. 3c, d and e, respectively, reveal the dark phase as the $\text{Ni}_{17}\text{Sn}_3$ -type *fcc* structure with the lattice parameter $a = 0.351$ nm and the space group of $F_m\bar{3}m$. Therefore it is concluded that the dark phase along the boundaries is the same γ phase in the as-cast bulk alloy. The EDS results in Table 1 show that the composition of the dark phase is about $\text{Ni}_{44.2}\text{Mn}_{35.5}\text{Sn}_{2.3}\text{Co}_{18.0}$. It is interesting that the SAEDP taken from the area 3 (the bright phase) shows typical amorphous ring (see Fig. 3f) and the corresponding HRTEM image demonstrates a highly disorder feature (see Fig. 3g). As compared with the dark γ phase, the bright phase contains slightly higher Sn content (see Table 1). Since a significant part of the γ phase with high Co and low Sn contents is dissolved in the ribbon, the matrix composition of the ribbon shows higher Co (atom radius, $r = 0.126$ nm) and lower Sn ($r = 0.163$ nm) in contrast to

the as-cast bulk alloy [21]. This explains well why the lattice constant slightly decreased. It should be mentioned that the black/white contrast of the precipitates originates from the diffraction contrast. The central beam selected for bright-field imaging has lower intensity since the crystalline γ phase diffracts electron beams, and thus it appears as darker. In fact, thickness fringes are visible, which also indicate their crystalline nature. However, the bright amorphous phase does not diffract electron beams and its contrast does not change even during tilting.

DSC result of the as-cast bulk alloy presents two exothermic peaks at 1 296 K and at 1 288 K upon cooling, corresponding to the formation of the primary β phase and ($\beta + \gamma$) eutectic microstructure, respectively (see Fig. 4). That is, the as-cast bulk alloy firstly forms dendritic β matrix ($L \rightarrow \beta$), and then a eutectic reaction ($L \rightarrow \beta + \gamma$) happens. In case of melt-spun ribbon, no lamellar eutectic microstructure is observed in Fig. 3. It seems to be reasonable to attribute that the dark γ phase originates from a divorced eutectic reaction in limited residual liquid phase after the formation of a large amount of primary β phase. While for the bright amorphous phase, it might form due to high local cooling rate. Such an explanation is in agreement with the EDS compositional results.

4 Conclusions

In summary, X-ray diffraction, SEM/TEM and SAEDP were employed to investigate the secondary phase in

Fig. 3 **a** TEM image of $\text{Ni}_{44.1}\text{Mn}_{35.1}\text{Sn}_{10.8}\text{Co}_{10}$ melt-spun ribbon; **b** SAEDP taken from area 1 in **a**; **c–e** SAEDPs from area 2 in **a** with different zone axes by tilting; **f** SAEDP from area 3 in **a**; **g** HRTEM image taken from area 3 in **a** showing amorphous feature (The EDS chemical compositions from spots 1, 2 and 3 are given in Table 1.)

Table 1 Composition results of spots marked in Figs. 2c and 3a, respectively (atomic fraction)

	Spot	Ni	Mn	Sn	Co
Fig. 2c	1 (matrix)	43.0	34.7	15.9	6.4
	2 (γ phase)	42.6	38.2	1.6	17.6
Fig. 3a	1 (matrix)	43.0	34.7	13.4	8.9
	2 (dark)	44.2	35.5	2.3	18.0
	3 (bright)	40.5	36.4	5.8	17.3

Heusler Ni-Mn-Sn-Co materials. The following conclusions were obtained.

- (i) The secondary phase is identified as *fcc* $\text{Ni}_{17}\text{Sn}_3$ -type structure. The as-cast bulk alloy firstly forms dendritic β matrix, and then undergoes a eutectic reaction during cooling. While in case of melt-spun rapid solidification, the secondary phase is resulted from a divorced eutectic reaction in limited residual

Fig. 4 DSC curve of $\text{Ni}_{44.1}\text{Mn}_{35.1}\text{Sn}_{10.8}\text{Co}_{10}$ as-cast bulk alloy at the heating/cooling rate of 10 K/min

liquid phase after the formation of a large amount of primary β phase.

- (ii) The secondary phase formed in melt-spun ribbons was largely suppressed as nano-precipitates, which distributed along the grain boundaries compared with the as-cast bulk alloy and meanwhile the secondary phase exhibited partial amorphous state due to high local cooling rate.

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