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Phase separation and its effect on the magnetic entropy change profile in an amorphous $Gd_{48}Co_{50}Nb_2$ alloy

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ABSTRACT

In the present work, we studied the microstructure, thermal and magnetic properties of a $Gd_{48}Co_{50}Nb_2$ amorphous ribbon for the purpose of revealing the mechanism of the table-like magnetic entropy change ($-\Delta S_m$) profile of the ribbon. It was found that the amorphous ribbon was fully amorphous with only short-range orders. The two-step magnetic phase transitions indicate that there are two amorphous phases in the $Gd_{48}Co_{50}Nb_2$ amorphous ribbon. The table-like $-\Delta S_m$ profile of the $Gd_{48}Co_{50}Nb_2$ amorphous ribbon is supposed to be due to the superposition of two $-\Delta S_m$ peaks corresponding to two separated amorphous phases with different magnetic properties. The amorphous ribbon is expected to be a good candidate for magnetic refrigerant because of its high maximum $-\Delta S_m$ and high effective refrigeration capacity of the specific table-like $-\Delta S_m$ profile.

1. Introduction

In recent years, magnetic refrigeration (MR) based on the magnetocaloric effect (MCE) of magnetic materials has attracted intensive interest because MR can avoid ozone-depleting gases and is more compact, more efficient than the traditional vapor expansion-compression cycle [1–5]. Therefore, MCE materials have been extensively investigated and the number of available materials increases exponentially over the past few decades [6–15]. It is commonly accepted that a specific table-like magnetic entropy change ($-\Delta S_m$) profile provides optimal efficiency when utilizing a certain thermodynamic cycle (e.g., the Ericsson cycle) [4–11]. However, the table-like $-\Delta S_m$ profile cannot be achieved in the alloys undergoing a first-order magnetic phase transition because of their sharp but narrow $-\Delta S_m$ peak.

More recently, efforts have been spent on achieving table-like $-\Delta S_m$ profile around room temperature in some of the amorphous composites or alloys undergoing a second-order magnetic phase transition. Compared with the amorphous composites fabricated by combining different amorphous ribbons together, a single amorphous ribbon with flattened $-\Delta S_m$ profile is hard to be obtained and the mechanism for its table-like $-\Delta S_m$ curve has not been investigated [6–11]. In the present work, we obtained $Gd_{48}Co_{50}Nb_2$ as-spun ribbon by a single roller melt spinning method. The amorphous ribbon exhibits a table-like $-\Delta S_m$ profile. The microstructure, thermal and magnetic properties of the as-spun ribbon were investigated for the purpose of revealing the mechanism for the flattened $-\Delta S_m$ profile of the amorphous alloy.

2. Experimental procedure

$Gd_{48}Co_{50}Nb_2$ ingot was prepared by arc-melting of 99.9% (at.%) pure Gd, Co and Nb elements under a titanium-gettered argon atmosphere. As-spun ribbons were fabricated by spinning the $Gd_{48}Co_{50}Nb_2$ melts on a copper wheel with a surface speed of 20 m/s under an argon atmosphere. The average thickness of the ribbons is about 45 μm. The amorphous structure of ribbons was ascertained by X-ray diffraction (XRD) on a Rigaku D\max-2550 diffractometer using Cu K_α radiation. The amorphous ribbons checked by XRD were employed for microstructure observation and physical property measurements. Thermal properties of the amorphous ribbons were obtained from the differential scanning calorimetry (DSC) traces measured by a Perkin-Elmer DIAMOND DSC under a purified argon atmosphere at a heating rate of 20 K/min. The magnetic properties of the amorphous ribbons were measured by a Quantum Design Physical Properties Measurement System (PPMS 6000): the temperature dependence of the magnetization (*M-T*) curve was obtained under a field of 0.03 T in the cooling process; isothermal magnetization (*M-H*) curves were obtained at various temperatures under a field of 5 T. The microstructure of the as-spun ribbon was examined using a JEOL JEM-2010F high-resolution transmission electron microscope (HRTEM). The sample for HRTEM observations was prepared by ion-polishing under a pure argon atmosphere using a GATAN 691 precision ion polishing system.

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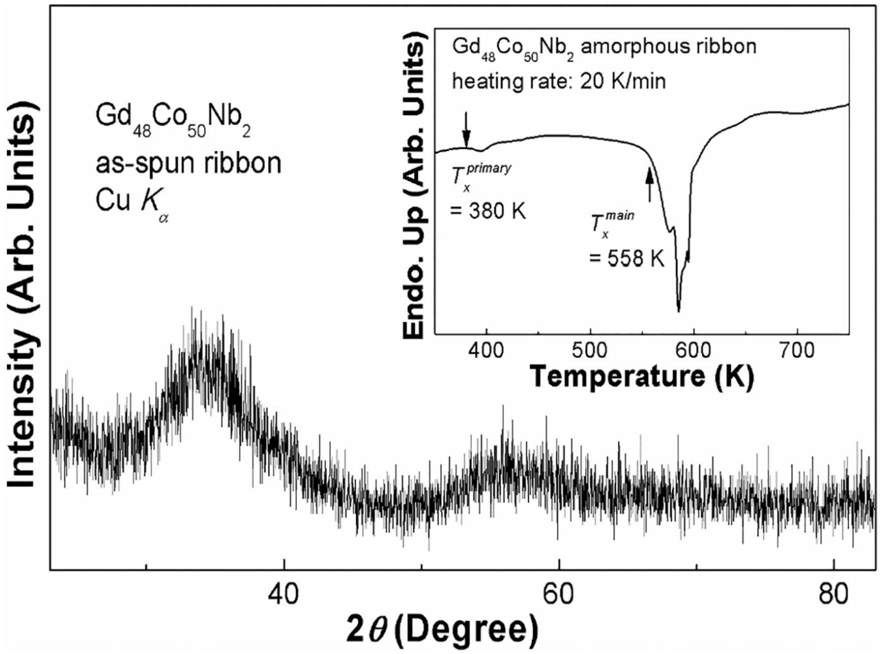

Fig. 1. XRD pattern of the $Gd_{48}Co_{50}Nb_2$ as-spun ribbon, the inset is the DSC trace of the amorphous ribbon obtained at a heating rate of 20 K/min.

3. Results and discussion

Fig. 1 shows the XRD pattern of the $Gd_{48}Co_{50}Nb_2$ as-spun ribbon. The typical broad diffraction maxima reveal the amorphous structure of the as-spun ribbon. The DSC trace of the as-spun ribbon is shown in the inset of Fig. 1. A weak exothermic peak at about 380 K corresponding to a primary crystallization and two sharp exothermic reactions due to the main crystallizations at the temperature above 558 K were found, as clearly marked on the DSC trace. The DSC trace of the $Gd_{48}Co_{50}Nb_2$ as-spun ribbon was similar to those of the $Nd_{60}Al_{10}Fe_{20}Co_{10}$ amorphous alloys: the fully amorphous ribbons show a weak primary crystallization peak, which is far from several main crystallization peaks; while the partially nano-crystalline bulk samples only exhibit the main crystallization peaks [16,17]. The primary crystallization in DSC trace is supposed to be due to the phase separation, which has been studied extensively in amorphous alloys and is very difficult to be distinguished from the XRD pattern.

The amorphous microstructure of the $Gd_{48}Co_{50}Nb_2$ as-spun ribbon was ascertained by the HRTEM observation. The morphology of the polished sample, as shown in Fig. 2(a), indicates that the specimen is homogeneous. Fig. 2(b) shows the HRTEM image of the as-spun ribbon. The specimen exhibits a typical disordered microstructure with only short-range orders. The select area electron diffraction (SAED) pattern of this region, as shown in Fig. 2(c), also indicates the fully glassy nature of the as-spun ribbon. However, no obvious phase separation can be distinguished from the HRTEM image.

Fig. 3 shows the *M-T* curve of the $Gd_{48}Co_{50}Nb_2$ amorphous ribbon measured within a temperature range of 100 K to 325 K under an applied field of 0.03 T. Two sharp drops at 264 K and 220 K, as marked on the derivative of the *M-T* curve in the inset of Fig. 2, indicate that there are two Curie temperatures (T_{c1} and T_{c2}) in the amorphous sample. Considering the fully amorphous microstructure of the as-spun ribbon, most likely there are two amorphous phases in the $Gd_{48}Co_{50}Nb_2$ amorphous ribbon corresponding to the two Curie temperature.

The formation of amorphous phase separation is considered to be sensitive to the cooling rate [18] and closely related to the atomic activity upon vitrification [19,20]. According to our previous results, the cooling rate required for the fabrication of the Nb free $Gd_{48}Co_{52}$ amorphous ribbon, which can be vitrified only when the wheel surface is larger than 36.7 m/s [15], is much higher than that of the $Gd_{48}Co_{50}Nb_2$ amorphous ribbon. And the *M-T* curve of the amorphous $Gd_{48}Co_{47}Nb_5$ ribbon prepared at a wheel surface speed of 20 m/s exhibits only one Curie temperature (not shown in the present work), indicating the full amorphous structure without any phase separations in the $Gd_{48}Co_{47}Nb_5$ amorphous ribbon. In the present work, as the situation in several Fe-based amorphous alloys, the addition of Nb may enhance the thermal stability due to the small diffusivity of Nb, i.e. increase the difficulty of movement of atoms and reduce the nucleation rate of the amorphous alloy. As such, 2% (at.%) addition of Nb leads to the amorphous phase separation as an intermediate stage before crystallization, and 5% (at.%) addition of Nb further improves the stability of supercooled liquid and lead to an enhanced glass forming ability of the alloy [19,20]. The radius of the diffraction ring or the distance between the nearest neighbor atoms for the two separated amorphous phases in the $Gd_{48}Co_{50}Nb_2$ amorphous ribbon may be so close to each other that the diffraction rings of the two phases stacked together, which make it difficult to distinguish the two amorphous phases from the diffraction halo.

The amorphous phase separation in the $Gd_{48}Co_{50}Nb_2$ as-spun ribbon makes it possible to obtain a flattened $-\Delta S_m$ peak because table-like $-\Delta S_m$ profiles are usually obtained in the amorphous composites constructed by several amorphous ribbons with different T_c [7–10]. Derived from the *M-H* curves of the $Gd_{48}Co_{50}Nb_2$ amorphous ribbons measured at different temperatures, we can obtain the temperature dependence of the magnetic entropy change ($(-\Delta S_m)$-*T*) curves according to the thermodynamic Maxwell equation. Fig. 4 shows the $(-\Delta S_m)$-*T* curves of the $Gd_{48}Co_{50}Nb_2$ amorphous ribbon under the fields of 2 T and 5 T. Just as expected, the $Gd_{48}Co_{50}Nb_2$ dual phase amorphous ribbon shows a table-like $-\Delta S_m$ shape within a temperature range of 220–265 K. The average maximum $-\Delta S_m$ of the $Gd_{48}Co_{50}Nb_2$