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Low field induced large magnetic entropy change in the amorphousized $Tm_{60}Co_{20}Ni_{20}$ ribbon

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A B S T R A C T

The magnetic properties and magnetic entropy change of amorphousized $Tm_{60}Co_{20}Ni_{20}$ ribbon were systematically studied. The results indicate that the $Tm_{60}Co_{20}Ni_{20}$ amorphous ribbon reveals a second order magnetic transition (paramagnetic to ferromagnetic state) based on the Arrott plots and rescaled magnetic entropy change curves. A large magnetic entropy change is achieved around its Curie temperature of T_C ~6.7 K. Under the magnetic field change (ΔH) of 0–5 T, the maximum values of magnetic entropy change ($-\Delta S_M^{max}$) and relative cooling power (*RCP*) are 17.1 J/kg K and 273 J/kg, respectively. In particular, under a relative low ΔH of 0–2 T, a large magnetic entropy change of 11.8 J/kg K reaches, making it attractive in the field of low-temperature magnetic refrigeration.

1. Introduction

Magnetic refrigeration (MR) based on the magnetocaloric effect (MCE) has been considered as one of alternative techniques which can theoretically save about 30% energy compared to the conventional gas compression refrigeration technology and also can avoid using ozone-depleting gases [1–5]. With the increasing environment problems in recent years, to quickly develop MR technology to replace the conventional gas compression refrigeration technology is recognized as being of an active research topic. In this case, increasing attempts have been denoted to explore the magnetic materials with excellent MCE properties at various temperature ranges for commercial applications. During last several decades, a number of promising MCE materials have been developed, including $Gd_5(Si_2Ge_2)$ and related compounds, manganites (*RE*,*M*)MnO_3 (*RE* = lanthanide, *M* = Ca, Sr and Ba), MnAs based compounds, $La(Fe,Si)_{13}$ and related compounds, as well as some heavy rare earth (*RE*) based alloys, oxides and amorphous materials [6–21].

Amorphous materials are of the structure with no long-range ordering but short-range ordering, which makes them possess unique properties for magnetic refrigerants, such as high refrigerant efficiency, good electrical resistivity, excellent thermal stability, outstanding mechanical properties, and tailorable ordering temperature, *etc.* Many rare earth-rich ternary or quaternary amorphous materials have been prepared and systematically investigated with respect to the MCE properties, some of these materials exhibit large/giant reversible MCE [22–24]. Additionally, for practical applications, searching for a material that can achieve giant/large MCE under low magnetic field changes ($\Delta H \leq 2$ T) is of vital importance, since it is feasible to design a refrigeration cycle using a permanent magnet. Very recently, the magnetic properties and MCE in Tm-based intermetallic compounds have been studied and some of them possess large low field reversible MCE [25–28]. In this work, we reported the magnetic and MCE properties in Tm based $Tm_{60}Co_{20}Ni_{20}$ amorphous ribbon. A large reversible MCE, especially under a low magnetic field change of 0–2 T was observed in $Tm_{60}Co_{20}Ni_{20}$ amorphous ribbon.

2. Experimental

Firstly, a pre-alloy with nominal composition of $Tm_{60}Co_{20}Ni_{20}$ was prepared by arc melting the mixture of pure Tm, Co, and Ni

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metals (2% excess Tm was included in the starting material) with purities above 99.9 at. % in a Ti-gettered argon atmosphere. The total mass of the pre-alloy was around 5 g. For reaching good chemical homogeneity, the pre-alloy was turned over and melted for four times under an argon atmosphere. The weighted loss during the overall melting process was less than 0.2 wt % for pre-alloy $Tm_{60}Co_{20}Ni_{20}$. Then, the ribbon of ~2 mm in width and 20–30 μm in thickness was prepared from the pre-alloy using a single copper wheel with a surface linear speed of about 30 m/s under Ar pressure. The compositions of the $Tm_{60}Co_{20}Ni_{20}$ ribbon were characterized by using the energy dispersive spectroscopy (EDS) attached a scanning electron microscope (SEM), and to be 58.8 (3) at.%, 20.6 (4) at.%, and 20.6 (3) at.% for Tm, Co and Ni, respectively. The amorphous structure of ribbon was ascertained via X-ray diffraction (XRD), (Bruker D8 Advance) in the angular range $20° \le 2\theta \le 80°$ using the Cu K_α radiation. The calorimetric signals of phase transformations occurring during heating (glass transition, crystallization and melting temperatures) were monitored by use of a differential heat-flow calorimeter (Netzsch STA 449C) at the heating rate of 20 K/min under a continuous argon gas flow. The temperature and magnetic field dependencies of magnetization were measured by using a commercial vibrating sample magnetometer (VSM), model PPMS-9 (Quantum Design).

3. Results and discussion

The XRD pattern at room temperature and DSC trace during heating processing of the $Tm_{60}Co_{20}Ni_{20}$ melt-spun ribbon are shown in Fig. 1 (a) and (b), respectively. A broad halo pattern at maximum around $2\theta = 35°$ with no appreciable crystalline peaks, which is expected for the amorphous state of this alloy. A very weak peak in the DSC curve can be observed which is probably related to the glass transition temperature (T_g). The T_g is determined by the point of obvious change in the slope of DSC curve [see inset of Fig. 1 (b)]. The values of T_g, the crystallization temperature (T_x) and the melting temperature (T_m) can be determined to be 622 K, 650 K and 1097 K for the $Tm_{60}Co_{20}Ni_{20}$ alloy, respectively. Accordingly, the temperature interval of undercooled liquid taken as the difference between T_g and T_x, $\Delta T = T_x - T_g$, is 28 K, which is a quite important factor in evaluating the glass forming ability.

The magnetization M (left scale) and the reciprocal susceptibility $1/\chi$ (right scale) for $Tm_{60}Co_{20}Ni_{20}$ amorphous ribbon as a function of temperature under the magnetic field H = 1 T are illustrated in Fig. 2. It is clear that a linear T-dependence at high temperature region above 30 K in the reciprocal susceptibility ($1/\chi$) can be observed for $Tm_{60}Co_{20}Ni_{20}$ amorphous ribbon, which obeys a typical Curie-Weiss law. In the inset of Fig. 2 present the magnetization M (right scale) measured by zero field cooled (ZFC) and field cooled (FC) modes as a function of temperature under $H = 0.2$ T for $Tm_{60}Co_{20}Ni_{20}$ amorphous ribbon. There is no splitting at low temperatures and no obvious hysteresis in the whole measurement temperatures of 2 K–50 K for both measured fields (ZFC and FC) which is beneficial to the magnetic refrigeration (MR). Moreover, together with the observation of saturation behaviour for magnetic isotherm at 3 K (as shown in Fig. 3), we can conclude that the magnetic transition for $Tm_{60}Co_{20}Ni_{20}$ amorphous ribbon is paramagnetic (PM) to ferromagnetic (FM). And the Curie temperature T_C is determined to be ~6.7 K which is taken as the inflection point of the dM/dT-T curve (see the inset of Fig. 2, left scale). The effective magnetic moment (μ_{eff}) is 7.40 μ_B/Tm for $Tm_{60}Co_{20}Ni_{20}$, which is close to the free ion value of Tm^{3+} (7.56 μ_B).

The magnetic isothermal $M(H)$ for a series of selected temperatures in the vicinity of transition temperature (T_C) for $Tm_{60}Co_{20}Ni_{20}$ was measured as a function of the magnetic field (H). Herein a temperature step of 1 K was adopted near the T_C

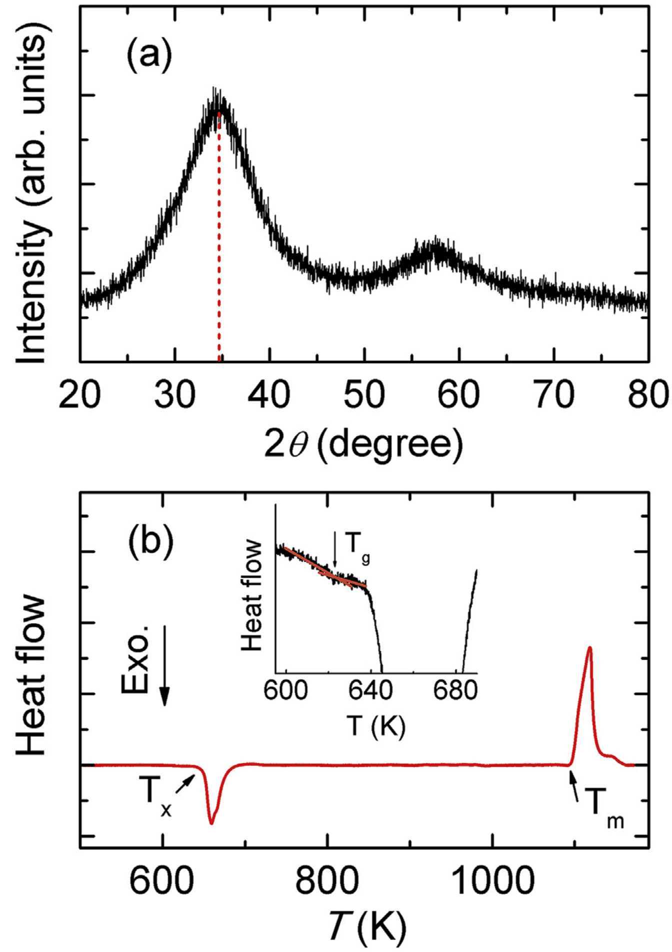

Fig. 1. (a) XRD pattern and (b) DSC trace measured at a rate of 20 K/min of the $Tm_{60}Co_{20}Ni_{20}$ amorphous ribbon. The inset of (b) shows an enlargement of the DSC trace from 580 K to 690 K.

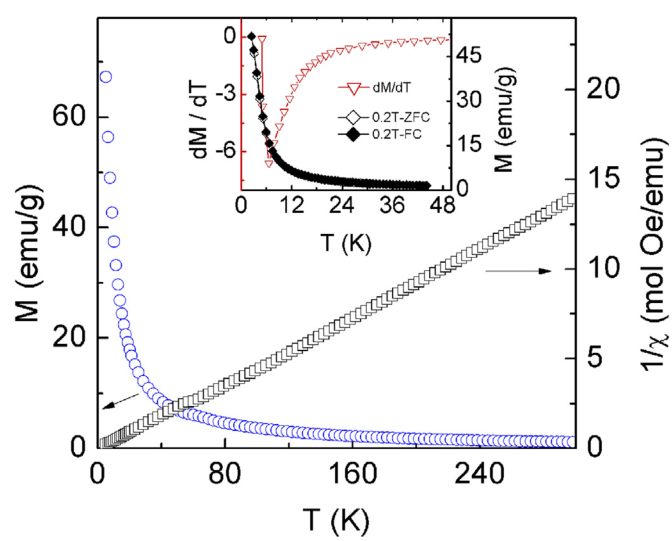

Fig. 2. The magnetization (M, left scale) and the reciprocal susceptibility ($1/\chi$, left scale) as a function of temperature under the magnetic field H = 1 T for $Tm_{60}Co_{20}Ni_{20}$ amorphous ribbon. Inset show the temperature dependence dM_{FC}/dT (left scale) and temperature dependence zero-field cooling (ZFC) and field cooling (FC) magnetization (M) under the magnetic field of 0.2 T (right scale) for $Tm_{60}Co_{20}Ni_{20}$ amorphous ribbon.