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Tuning of magnetocaloric effect and optimization of scaling factor for $Gd_{55}Ni_{10}Co_{35}$ amorphous microwires

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We have investigated the $Gd_{55}Ni_{10}Co_{35}$ amorphous microwires with a large supercooling temperature range of 132 K in terms of thermally induced microstructural evolution and their magnetocaloric effect (MCE). With the emerging and growth of the nanocrystals against the maintained amorphous matrix, there appears a threshold annealing temperature of 513 K where the Curie temperature (T_c) sees an abrupt increase from 192 K to 212 K as a result of competition between amorphous and crystalline phase. Another effect from these two phases is to conspire to a broadening of working temperature range. The scaling factor *n* as in $\Delta S_M \propto H^n$ is found to follow a Boltzmann type of dependency on the annealing temperature and can hence serve as an indicator for the desirable microstructure in favor of MCE. All these results demonstrate that the MCE performance of Gd-based amorphous microwires can be formulated via the fine control of microstructure.

1. Introduction

Magnetic refrigeration (MR) based on magnetocaloric effect (MCE) [1] emerges as a promising green refrigeration technology to replace the traditional vapor compression refrigeration, which meet the requirement of a sustainable society [2–4]. The MCE performance is evaluated by isothermal magnetic entropy change (ΔS_M) and refrigerant capacity (RC), defined as the integral of -ΔS_M from the cold and hot sinks [5,6]. Generally, magnetic materials that possess a large -ΔS_M over a broad temperature range is desirable for magnetic refrigeration application.

MCE materials can be categorized as first-order magnetic transition (FOMT) and second-order magnetic transition (SOMT) materials. FOMT materials, in spite of large scale of -ΔS_M [7–10], have rather narrow temperature range and large thermal and magnetic hysteresis which limit them for further practical application [11]. By contrast, SOMT materials are featured with a wide temperature extent and a larger RC due to a continuous phase transition [6,12]. A number of investigations [13–15] suggest that the metallic glass as a SOMT material is a decent candidate for MCE applications due to their negligible magnetic hysteresis and enhanced electrical resistivity [16], wide transition temperature range, and excellent mechanical properties [17,18]. In particular, metallic glasses with heavy rare-earth elements [14,19] often have large magnetic moment, which is conductive to a large ΔS_M. Among the reported metallic glasses, Gd-based microwires show a good MCE performance due to an ideal comprehensive cooling capacity [17,20]. Especially the amorphous microwires have larger value of ΔS_M than their bulk metallic glass (BMG) and ribbon counterparts contributed by a larger specific surface area and inter-wire interaction effects [17,21,22]. Most recently, it is demonstrated that modulating the microstructure of wires by inducing nanocrystalline phases into the amorphous structure can improve RC greatly [18,21,23]. However, due to the limitation of the amorphous structure stability of the studied wires, the scarcity of reported studies on relating a fine microstructural control of Gd-based wires to their MCE characteristics encourages us to explore further in the area.

In this context, following our previous work [24], we take a step further to target here on $Gd_{55}Ni_{10}Co_{35}$ microwires with broad supercooling region. With thermally controlled induction of nanocrystalline phases into the amorphous matrix by annealing at different temperatures, we aim to explore the detailed mechanism relating the microstructural evolution to the major MCE features and improvement of MCE of Gd-based amorphous microwires. The key findings are summarized as follows. Although the ΔS_M of the

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amorphous microwires is not outstanding with 2.51 J/Kg*K at 2 T, annealing can induce structural transition, which results in significant increase of working temperature range from 110 K to 146 K at 2 T [25]. When the content of nanocrystalline exceeds a certain limit, Curie temperature (T_c), has a significant increase. The scaling factor n as in $\Delta S_M \propto H^n$ presents a Boltzmann type of dependency on annealing temperature, which can be used as a probe to the homogeneity of the materials' microstructure in favor of MCE.

2. Experiment

The amorphous microwires with a nominal composition of $Gd_{55}Ni_{10}Co_{35}$ were manufactured by a melt-extraction method, which is described elsewhere [17,24]. For heat treatment, samples were enclosed in a vacuum glass tube before annealed at 373 K, 453 K, 493 K, 503 K, 513 K and 533 K for 12 h, respectively, with heating rate of 5 K/min. The samples were then in-furnace cooled down with a constant rate of 10 K/min. The annealing process was conducted in the protection argon gas to prevent microwires from oxidation. Thermal analysis was performed in a differential scanning calorimeter (DSC) at the heating rate of 20 K/min. The X-ray diffraction (XRD) patterns were obtained from MAXimaXRD-7000 using Cu-K_a radiation. The microstructure was observed by field emission scanning electron microscope (SU-70) and transmission electron microscope (Tecnai G2 F20 S-TWIN, 200 KV). The magnetic properties were measured utilizing a commercial Physical Property Measurement System (PPMS-9T) from Quantum Design in a temperature range of 10–300 K and with a magnetic field up to 5 T.

3. Results and discussion

Fig. 1 summarizes the basic structure and morphology characterization. As displayed in DSC trace, the glass transition temperature (T_g) and crystallization onset temperature (T_x) are identified at 458 K and 590 K, respectively. Supercooled liquid region ($\Delta T_x = T_x$-T_g) is 132 K, indicating a strong glass forming ability (GFA) and a good stability of amorphous phase. The morphology of the amorphous microwires displayed in the SEM graph reveals the diameter of the wires is around 50 μm determined by the processing parameters [26]. No grooves and fragments is observed on the sample surface, suggesting the fabrication parameters are adequately adopted to avoid such defects [18]. The XRD patterns reveal the transition of structure with the increase of annealing temperature. The as-cast microwire is fully amorphous with no visible crystalline peaks, as shown in (Fig. 1). Obvious crystalline peaks are generated and grow sharper with annealing temperature. Particularly when the annealing temperature reaches 503 K, crystal phases manifest themselves significantly, which are mainly Co_3Gd_4, $CoGd_3$ and (α-Co, Ni) solid solutions, suggesting that the structure relaxation and atomic diffusion become intense. Such microstructural evolution is further evidenced by TEM images and selected area electron diffraction (SAED) patterns (Fig. 2). As the annealing temperature is relatively low (373 K), the size of the nanocrystal is less than 5 nm (Fig. 2a). As the annealing temperature rises to 453 K, the crystal grain grows larger, ranging from 8 to 15 nm (Fig. 2b). Unlike the SAED patterns of Fig. 2a and b exhibiting a halo, the SAED pattern of Fig. 2c has obvious diffraction spots, suggesting a significant structural transition evidenced by the forming of nanocrystalline clusters. As shown in Fig. 2d, a touch of variation is observed in chemical composition between amorphous and nanocrystalline areas, indicating atomic diffusion accompanied therein. The ratio of Gd atoms in nanocrystalline region is less than that in amorphous region, suggesting that Gd is more likely to possess a larger coordination number in the nanocrystals.

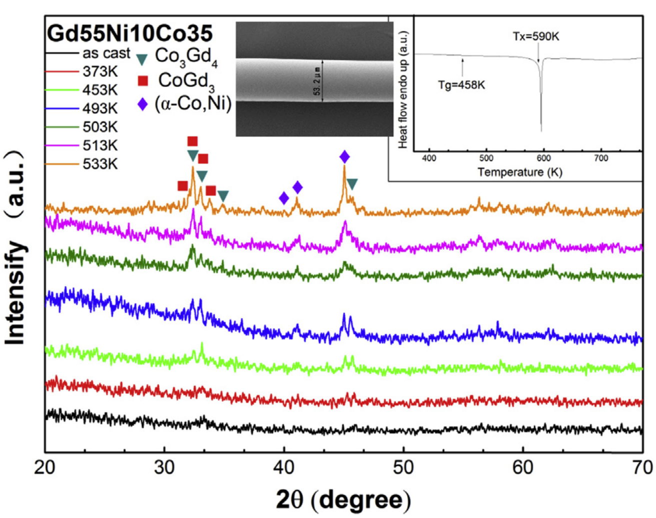

Fig. 1. XRD patterns of the as-cast and annealed microwires at different temperatures (373 K, 453 K, 493 K, 503 K, 513 K and 533 K). The insets show the side-view SEM image(*left*) and DSC trace of the as-cast microwire (*right*).

With reference to the DSC profiles shown in the inset of Fig. 1, the stability of amorphous phase with broad supercooled liquid region allows that the material can be annealed in a wide temperature range accordingly without changing the general amorphous structure, which will contribute to the observation of a delicate evolution of the microstructure (Fig. 2). The reasons for the stability are impediments of the microstructure (primary phase, Fig. 2c) of amorphous alloy in supercooled liquid region to the process of nucleation and growth of crystal [27] and the atomic rearrangement on a long-range scale [26]. The atomic rearrangement comes from the exchange of atoms at the boundaries of the old and new phases with the new phase growing up, which leads to the content variation in the two phases (Fig. 2d). In order to characterize the process of nanocrystalline phase growth qualitatively, a dynamic equation is applied, i.e. $K_T = K_0 exp\left(-\frac{\Delta H}{kT}\right)$, where K_T is reaction rate, K_0 is kinetic constant, ΔH is atomic activation energy, k is the Boltzmann constant and T is the temperature. When the annealing temperature is small (373 and 453 K, Fig. 2a and b), the rate of nanocrystalline phase formation is rather slow. And when a critical temperature is reached, a huge promotion will occur to the nanocrystalline formation process. The separation of the nanocrystalline phase from the amorphous phase has a profound effect on the magnetic properties of the material, which will be discussed later.

With an adequate knowledge of microstructure evolution, we now discuss the magnetic properties of wires. Fig. 3a shows the temperature dependence of magnetization for the as-cast and annealed microwires at different temperatures measured under the magnetic field of 0.2 T. The samples show a broad FM-PM transition around the Curie temperature (T_c). With gradual increase of the annealing temperature, the slope of the M-T curve decreases, near T_c as confirmed in the inset of dM/dT-T curve. It is worth noting that the absolute value of the slope of the M-T curve in samples annealed under low temperatures (373K and 453 K) is higher than that of the as-cast samples. By contrast, when annealing is performed under high temperatures (513 K and 533 K), a marked increase in T_c is observed from 192 K to 212 K. Fig. 3b shows the M-H curves of the as-prepared and annealed samples measured at 10 K. It is observed that similar to the trend of M-T curves varying with the heat treatment, saturation magnetization (M_s) of the low-