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Iron for nickel substitution effects on magnetic and magnetocaloric properties of melt-spun $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ alloys

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ABSTRACT

The melt quenched $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ alloys are found to exhibit a soft ferrimagnetic behavior in the whole concentration range ($0 \leq \times \leq 1$). Substitution of Fe for Ni in the $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ alloys results in a linear growth of the magnetic ordering temperature from 118 K to 244 K; although, an average value of the magnetic moment per transition metal atom, obtained from saturation magnetization measurements, does not change significantly with increasing Fe content. The variations of the Curie temperature and magnetization in $Gd_{75}M_{25}$-type amorphous alloys (M = Fe, Ni) are discussed bearing in mind a possible noncollinearity of magnetic moments of 3*d* metal atoms. The maximal values of the isothermal magnetic entropy change (ΔS_m) are observed to exhibit the Fe-poor $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ alloys. The change in the concentration of 3*d*-metal of different types in amorphous $Gd_{75}M_{25}$ alloys with a constant gadolinium content makes it possible to vary both the magnetocaloric effect and the operating temperature range.

1. Introduction

Amorphous magnetic materials have a remarkable set of properties (magnetic, electrical, corrosion resistive, mechanical) that make these materials attractive for use as working substances for magnetic cooling. In rare earth based amorphous alloys, the change in composition allows tuning the magnetic ordering temperature and magnetocaloric characteristics in wide ranges [1–4]. The magnetocaloric effect (MCE) is characterized by an adiabatic temperature change (ΔT) and a change in the isothermal magnetic entropy (ΔS_m) of the magnetic material with changes in the external magnetic field. As a rule, the amorphous magnetic alloys obtained the rapid quenching of the liquid melt exhibit a magnetic phase transition of the second-order and a relatively broad ΔS_m maximum. In some cases, the amorphization can modify substantially the magnetic state of a material. For instance, as was shown recently, the amorphous $Gd_{75}Ni_{25}$ alloy shows a magnetically soft ferrimagnetic behavior [5] while the crystalline compound Gd_3Ni with the Fe_3C-type structure and with the same composition exhibits an antiferromagnetic order and spin-flop-like phase transition at a critical field of about 40 kOe [6]. The change from antiferromagnetism to ferrimagnetism was also observed after amorphization of the Gd_3Co compound [7]. Besides, the structural disordering in Gd_3Ni and Gd_3Co is observed to result in the appearance of a magnetic moment on 3*d* metal atoms and in ~(20 − 30) % increase in the magnetic ordering temperature [8]. Enhancement of magnetism caused by structural disorder was reported earlier for the Y-Co amorphous alloys [9]. The amorphization of $Gd_{75}Ni_{25}$ is found to substantially improve the magnetocaloric properties (> 8 times increase in ΔS_m and about 20 times in relative cooling power) in a low field region in comparison with crystalline compound [5].

The present work aims to study how the substitution of iron for nickel in liquid-quenched $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ alloys will affect their magnetic and magnetocaloric properties. According to the gadolinium-iron binary phase diagram the Gd_3Fe ($Gd_{75}Fe_{25}$) compound does not exist [10]. The study of the crystalline Gd_3M compounds (M = Ni, Co Fe) with substitutions in the transition-metal sublattice has shown that the critical transition field from the antiferromagnetic to the forced ferromagnetic state decreases with decreasing number of 3*d* electrons, i.e. when going from Ni to Fe; however, the solubility of Fe atom is limited by 20 at. % [11]. Therefore, we, in the present work, prepared the liquid quenched $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ alloys in the whole concentration range keeping the constant Gd content and studied their properties for better understanding the role of 3*d* metal atoms in the formation of magnetothermal properties of rare-earth-rich amorphous alloys. The results obtained in the present work for $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ are discussed together with our recently published data for $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys [12].

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2. Experimental

The samples of $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ with x = 0, ¼, ½, ¾, 1.0 were prepared in two stages. At first, the crystalline compounds were synthesized by arc melting in a helium atmosphere. To obtain the uniform composition of samples, the ingots were turned over after each melting in the arc furnace and melted repeatedly. Then, the liquid quenched samples were prepared by a melt-spinning technique in an argon atmosphere onto a rotating copper wheel with a tangential velocity of about 50 m/s. The X-ray diffraction (XRD) patterns have been measured at room temperature using a diffractometer with monochromatic Cr Kα radiation. The magnetic measurements were performed using a SQUID magnetometer (Quantum Design MPMS-7XL, USA) in magnetic fields up to 50 kOe and in the temperature range from 2 K to 350 K. To obtain the data on magnetic part of the isothermal entropy change we used an indirect method based on the thermodynamic Maxwell relations [13]: $\Delta S_m = \int_0^{H_f} \left(\frac{\partial M}{\partial T}\right)_H dH$, where H_f is the maximum magnetic field. The magnetization was measured with a sufficiently high precision (< 1%). As for calculating the entropy changes, the error in determining ΔS_m can be estimated at about 5%.

3. Results and discussion

Fig. 1 shows XRD patterns for the melt-spun alloys $Gd_{75}Ni_{25}$ (x = 0) and $Gd_{75}Fe_{25}$ (x = 1) alloys. In our earlier work [5], it was shown that the amorphization of Gd_3Ni depends on the tangential speed of a rotating wheel. At a speed of 35 m/s the liquid quenched sample contains an amorphous matrix together with a small amount of crystalline phase Gd_3Ni and Gd_2O_3 oxide, while a growth of the speed up to 50 m/s allows obtaining a rapid quenched $Gd_{75}Ni_{25}$ sample mainly in an amorphous state with a negligible amount of the Gd_2O_3 oxide. Therefore, in the present study, all samples were obtained at a tangential speed of the wheel ~50 m/s. As was reported for the $Gd_{75}(Co_{1-x}Fe_x)_{25}$ system [12], the glass forming ability of alloys decreases with increasing iron content. Analogous tendency is observed for the $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ melt-spun alloys. As follows from Fig.1, in contrast to the Ni-containing alloy, the XRD pattern for the $Gd_{75}Fe_{25}$ sample together with broad maxima near $2\theta = 50^\circ$ and 90° shows a set of Bragg peaks associated with the persistence of about 20% gadolinium in the crystalline state after rapid solidification of the melt. Because of the existence of this crystalline phase, the amorphous phase is depleted by gadolinium; the amorphous phase in the sample with the nominal composition $Gd_{75}Fe_{25}$ is estimated to exhibit a composition of about $Gd_{70}Fe_{30}$. It seems that a higher cooling rate is needed to achieve fully amorphous state in this case.

Fig. 2 displays the variation of the Curie temperature in the melt-spun $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ alloys with the Fe concentration; the data for $Gd_{75}(Co_{1-x}Fe_x)_{25}$ are shown for comparison [12]. The Curie

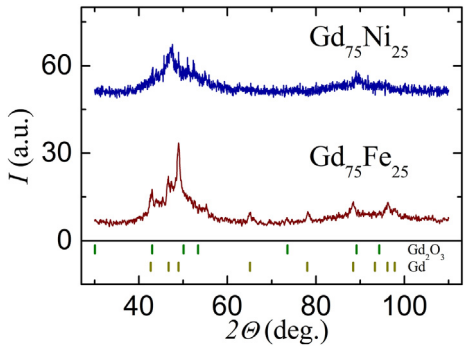

Fig. 1. X-ray diffraction patterns of the melt-spun $Gd_{75}Ni_{25}$ and $Gd_{75}Fe_{25}$ alloys. Vertical bars indicate the main Bragg peaks positions for the crystalline Gd_2O_3 (upper row) and Gd (lower row) phases.

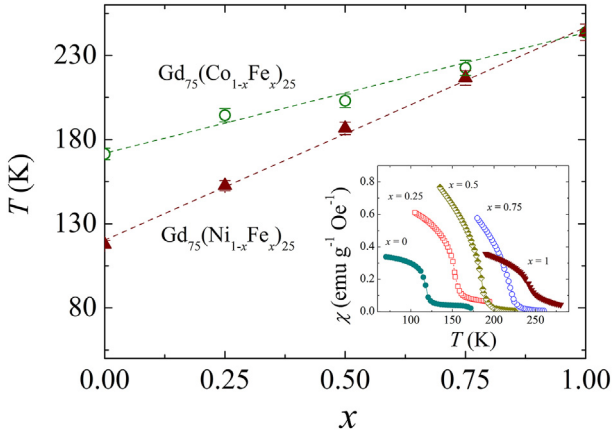

Fig. 2. Concentration dependences of the Curie temperature for the melt-spun $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ and $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys. The T_C values for the Co-containing alloys are taken from Ref. [1] The dashed lines are drawn as a guide to the eye. Inset shows temperature dependences of the dc susceptibility measured at H = 100 Oe.

temperatures were determined from the temperature dependences of susceptibility measured in the magnetic field H = 100 Oe (shown in the inset in Fig. 2). As can be seen, the Curie temperature increases linearly from 118 K for $Gd_{75}Ni_{25}$ to 244 K for $Gd_{75}Fe_{25}$ with the Fe for Ni substitution. Similar variation of T_C with increasing Fe content has been observed for the melt-spun $Gd_{75}(Co_{1-x}Fe_x)_{25}$ alloys [12]. As reported earlier [5], the magnetic critical temperature T_C ~118 K observed in the amorphous Gd_3Ni is higher than that observed in the crystalline Gd_3Ni counterpart having $T_N \approx 99$ K. Such a difference is ascribed to the appearance of a magnetic moment on Ni atoms and enhancement of exchange interactions. The amorphous $Gd_{75}Co_{25}$ also shows an increased value of T_C (~172 K [7, 8]) in comparison with the crystalline Gd_3Co ($T_N \approx 130$ K [14]). As to the $Gd_{75}Fe_{25}$ alloy, its Curie temperature ~ 244 K is lower than that observed for the amorphous Gd_yFe_{100-y} alloys with higher Fe concentrations [15–21]. An increase in T_C values observed for both the $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ and $Gd_{75}(Co_{1-x}Fe_x)_{25}$ systems (Fig. 2) indicates the enhancement of exchange interactions with increasing Fe content which can be associated with variations in the 5*d*-3*d* hybridization and with growth of magnetic moments in the 3*d* electron subsystem.

In order to reveal how the Fe for Ni substitution affects the magnetization behavior of alloys, the measurements of the field dependences of the magnetization were performed for the $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ samples with various Fe concentrations (shown in Fig. 3). As can be seen, the melt-spun alloys $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ show the $M(H)$ dependences characteristic for soft ferromagnetic or ferrimagnetic behaviors, unlike the polycrystalline Gd_3Ni sample which exhibits a field-induced first-order phase transition from the antiferromagnetic to ferromagnetic state [6, 22]. Magnetization curves for the substituted alloys are located between the $M(H)$ dependences for x = 0 and x = 1. To determine the saturation magnetization we used the law of approach to saturation [23]: $\mu = \mu_S(1 - A/H - B/H^2)$, where A and B are coefficients associated with the structural disorder, inhomogeneities, and magnetocrystalline anisotropy. For all the $Gd_{75}(Ni_{1-x}Fe_x)_{25}$ samples, values of the saturation magnetization per formula unit (from 19.4 μ_B/FU at x = 0 up to 19.9 μ_B/FU at x = 1) are found to be lower than an expected value of 21.0 μ_B/FU in suggestion that the Gd atoms only have a magnetic moment ($gJ\mu_B$ = 7.0 μ_B) and than the values 23.9 μ_B/FU obtained on the Gd_3Ni single crystals [6] and μ_S = 23.3 μ_B/FU on the polycrystalline samples [5]. Such a difference is suggested to originate in the appearance of magnetic moments on the Ni and Fe atoms after amorphization. As in other rare earth–3*d* transition metal systems, the Ni and Fe moments in our alloys are suggested to be oppositely directed in respect to the Gd moments. As follows from Fig. 3, the magnetization