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Structure and phase transformation of melt-spun $Gd_5Si_2Ge_2$

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Abstract

$Gd_5Si_2Ge_2$ materials were prepared by rapid solidification at different wheel speeds. The crystal phase and phase transformation of the rapidly solidified materials have been investigated by powder X-ray diffraction (XRD), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). The materials contained mainly a $Gd_5Si_2Ge_2$-type single phase at a wheel speed of 20 m/s; a Gd_5Si_4-type major phase and a $Gd_5Si_2Ge_2$-type minor phase at 30 m/s; a Gd_5Si_4-type single phase at 40 m/s; and Gd_5Si_4-type and $Gd_5Si_2Ge_2$-type double phase at 50 m/s. A first-order phase transformation occurred at approximately 273 K in the materials prepared at a wheel speed of 20 m/s whereas a second-order phase transformation appeared at approximately 290 K in the materials prepared at other wheel speeds. Furthermore, we observed some exothermic peaks located at ~250–300 °C in the DSC curves for all the melt-spun samples. These exothermic reactions can be attributed to the crystallization of a small amount of glassy phase. The presence of glassy phase has been confirmed by both the electron diffraction pattern observed in the TEM observation and the glass transition found in the DSC scan.

Keywords: Magnetocaloric materials; $Gd_5Si_2Ge_2$ alloy; X-ray powder diffraction; Differential scanning calorimetry

1. Introduction

Magnetic refrigeration based on the magnetocaloric effect (MCE) has attracted much attention because of its potential advantages over traditional vapor-compression refrigeration [1–5]. The recently discovered $Gd_5(Si_xGe_{1-x})_4$ alloys, which exhibit a giant magnetocaloric entropy change [2], triggered more research interests in the field of magnetocaloric effect. As one of the most important phases in the Gd_5Si_4–Gd_5Ge_4 system, $Gd_5Si_2Ge_2$ crystallizes in the monoclinic structure (space group $P112_1/a$) with lattice parameters of $a = 7.5808(5)$, $b = 14.802(1)$, $c = 7.7799(5)$ Å, and $\gamma = 93.190(4)^\circ$ [6]. The magnetic binary diagram of the pseudo-binary Gd_5Si_4–Gd_5Ge_4 system has been rebuilt by Pecharsky et al. based on X-ray powder diffraction, magnetic, and thermodynamic measurements [7]. The magnetic entropy change of $Gd_5Si_2Ge_2$ alloy based on high-purity Gd (99.99 wt.%) can be increased from −18.4 J/kg K to −36.4 J/kg K by heating treatment [8]. A higher temperature second-order phase transformation (at ~300 K) and a lower temperature first-order phase transformation (at ~273 K) have been detected in the Gd_5Si_4–Gd_5Ge_4 system and ascribed to the existence of a small amount of secondary Gd_5Si_4-type phase [7,8].

Fu et al. [9] have investigated the phases in $Gd_5(Si_xGe_{1-x})_4$ ($x \sim 0.5$) alloys prepared by using Gd of different purities. The results indicated that the alloys prepared from high-purity Gd contained a single phase whereas those prepared from low purity Gd contained multiple phases ($Gd_5Si_2Ge_2$-type, Gd_5Si_3-type, and GdGe-type). In addition, the non-stoichiometric $Gd_{5.2}Si_2Ge_2$ and $Gd_{5.3}Si_2Ge_2$ alloys synthesized using low purity Gd contained a Gd_5Si_4-type phase.

In this work, we prepared $Gd_5Si_2Ge_2$ ribbons by melt spinning at different wheel speeds. We found that the structure and phase transformations of our alloys strongly depend on the wheel speeds, which in turn determines the cooling rates. The ability of changing alloys' structure and phase transformation by varying solidification rates provides an alternative technique to design magnetocaloric alloys and optimize their magnetocaloric properties.

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2. Experimental details

Master $Gd_5Si_2Ge_2$ alloys were prepared by arc-melting using 99.94 wt.% pure Gd and >99.999 wt.% pure Si and Ge. The alloy buttons were re-melted five times to ensure homogeneity. Pieces of ingots were then rapidly solidified by single-roller melt spinning at wheel speeds of 20, 30, 40, and 50 m/s. X-ray diffraction (XRD) analysis of the melt-spun alloys were carried out on a DX-1000 diffractometer, which uses Cu Kα radiation (wave length λ = 1.5406 Å). The operating voltage and current were 40 kV and 30 mA, respectively. The phase transformation behavior was measured using DSC (DSC131, Setaram company, France) with a scanning rate of 20 °C/min under a nitrogen atmosphere. The melt-spun ribbons prepared at a wheel speed of 50 m/s were grinded and dispersed by an ultrasonic method for transmission electron microscopy (TEM) observation.

3. Results and discussion

The powder XRD patterns of melt-spun $Gd_5Si_2Ge_2$ alloys prepared at different wheel speeds are shown in Fig. 1, where the upper part (red curve) shows the experimental scan and the lower part (blue and/or green curves) displays the scans simulated from PDF2 database using X'pert Highscore software. From these patterns, we can find that the melt-spun $Gd_5Si_2Ge_2$ alloy consists of a $Gd_5Si_2Ge_2$-type single phase at a wheel speed of 20 m/s; a Gd_5Si_4-type major phase and a $Gd_5Si_2Ge_2$-type minor phase at 30 m/s; a Gd_5Si_4-type single phase at 40 m/s; and Gd_5Si_4-type and $Gd_5Si_2Ge_2$-type double phase at 50 m/s. These results indicate that the solidification rates have strong effects on the type and content of crystal phases in the $Gd_5Si_2Ge_2$ alloy and higher solidification rate is in favor of the formation of Gd_5Si_4-type phase. This is understandable since the change in solidification rate alters the kinetics for phase transformation, leading to the formation of different crystal phases.

Fig. 2 shows the heating and cooling DSC scans of melt-spun $Gd_5Si_2Ge_2$ alloys. The peak temperatures of phase transformations are marked in the figure. For the alloys prepared at 20 m/s (Fig. 2(a)), there is an endothermic peak at 1 °C during heating and three continuous exothermic peaks in the ~250–300 °C temperature range. The phase transformation corresponding to the exothermic peak during heating is irreversible during the following cooling. For the alloys prepared at higher speeds of 30 m/s (Fig. 2(b)), 40 m/s (Fig. 2(c)), and 50 m/s (Fig. 2(d)), there is no big change in the higher temperature exothermic peaks during heating. However, the lower temperature endothermic peak shifts to ~26 °C. The phase transformation corresponding to this endothermic peak during heating is reversible during the following cooling.

Previous studies indicate [6–8] that $Gd_5Si_2Ge_2$ exhibits a first-order structural transition at ~276 K (=3 °C), where the low temperature orthorhombic phase (α-$Gd_5Si_2Ge_2$) transforms to the room temperature monoclinic phase (β-$Gd_5Si_2Ge_2$). In addition, there is a Curie transition at a temperature of above 295 K (=22 °C) for the orthorhombic Gd_5Si_4-type phase. The Curie transition temperature depends on the Si:Ge ratio in the alloy. Therefore, it is reasonable to believe that the endothermic

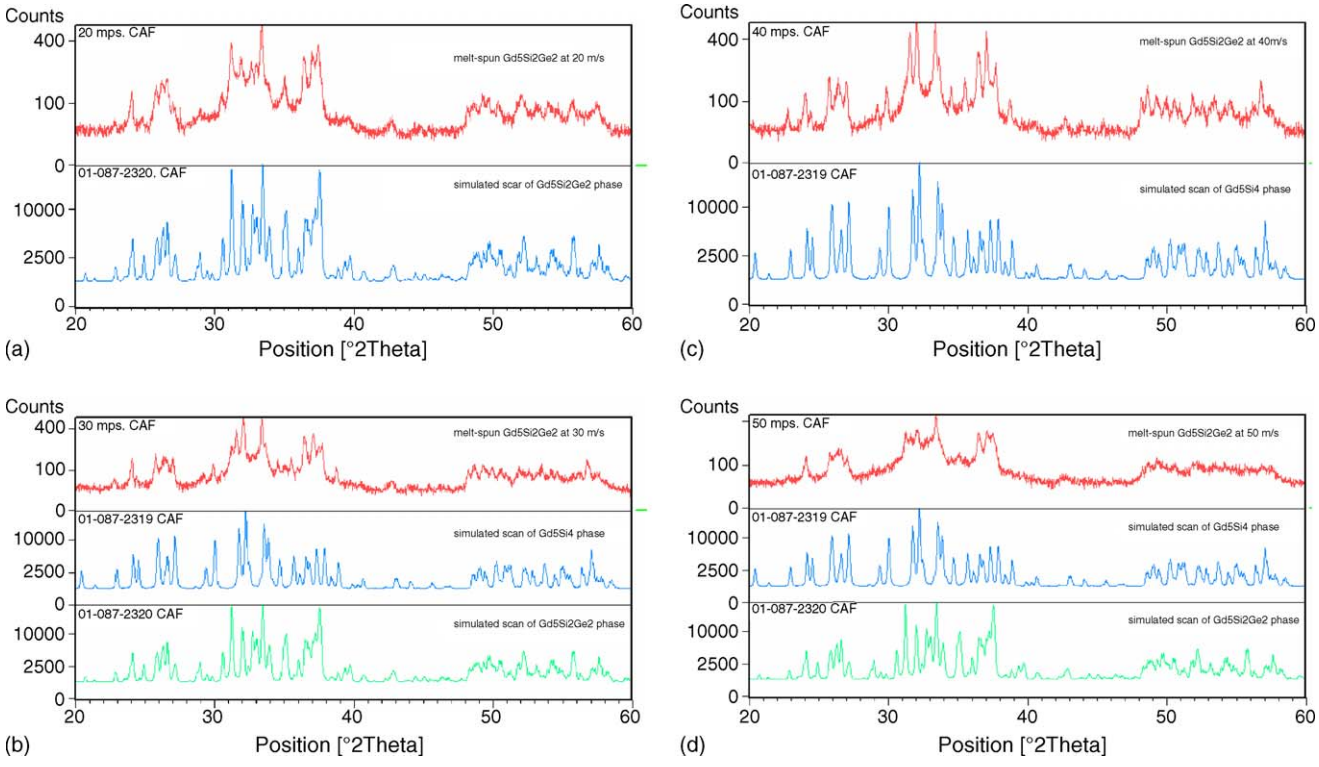

Fig. 1. Powder XRD patterns of melt-spun $Gd_5Si_2Ge_2$ alloys prepared at different wheel speeds: (a) 20 m/s, (b) 30 m/s, (c) 40 m/s, and (d) 50 m/s.

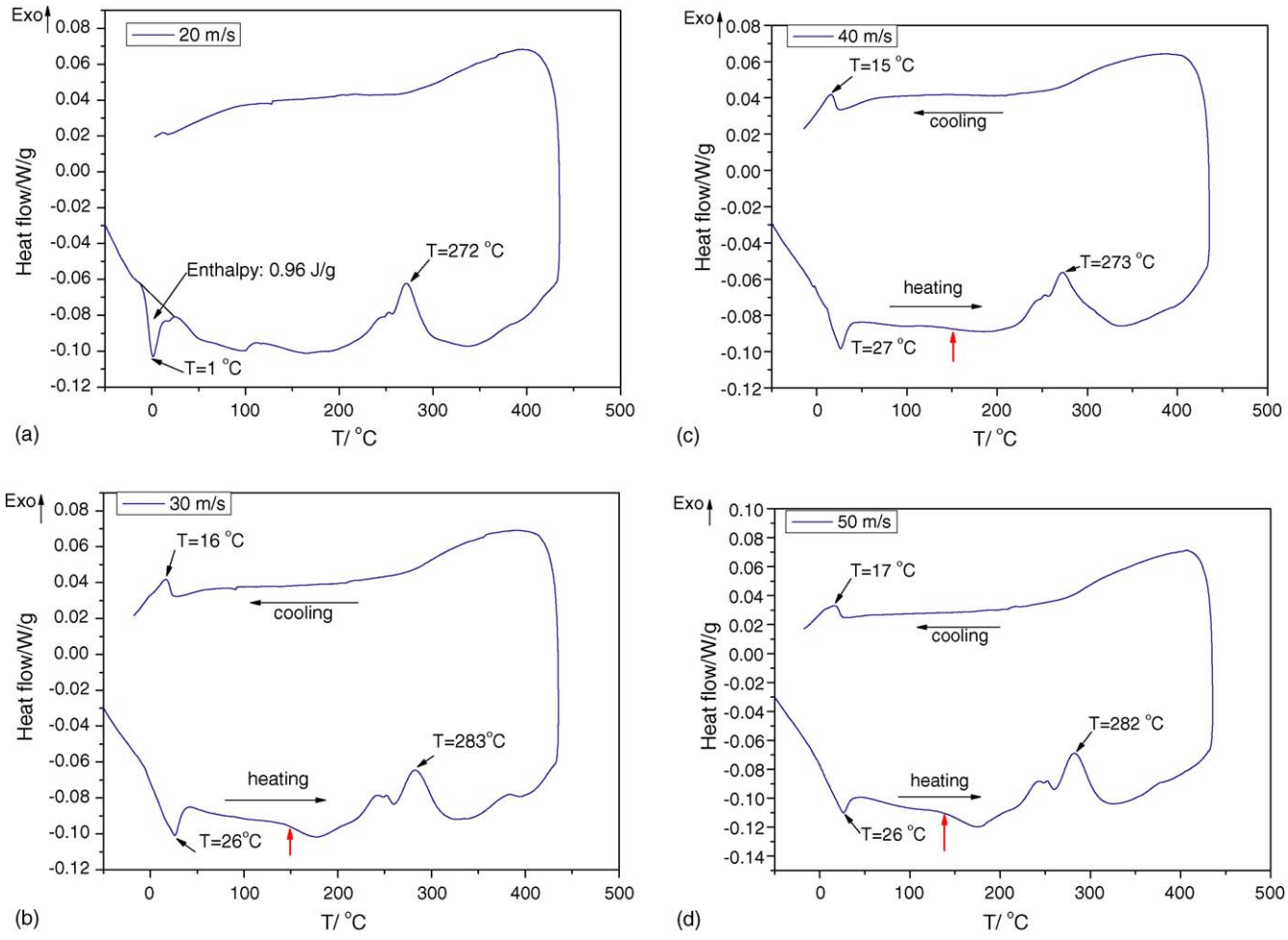

Fig. 2. DSC scans of melt-spun $Gd_5Si_2Ge_2$ alloys prepared at different wheel speeds: (a) 20 m/s, (b) 30 m/s, (c) 40 m/s, and (d) 50 m/s.

peak at 1 °C in Fig. 2(a) results from the first-order α–β transition of a $Gd_5Si_2Ge_2$ phase whereas the endothermic peaks at ∼26 °C in Fig. 2(b)–(d) correspond to the order–disorder magnetic phase transition of an orthorhombic Gd_5Si_4-type phase.

Pecharsky et al. [10] found that the monoclinic $Gd_5Si_2Ge_2$-type (β-$Gd_5Si_2Ge_2$) phase, after being heated to ∼500 K (227 °C), started to transform to a higher temperature orthorhombic Gd_5Si_4-type (γ-$Gd_5Si_2Ge_2$) phase. Furthermore, Mozharivskyj et al. [11] found that the elastic β–γ transformation occurs at 300–320 °C during heating and it is reversible during fast (600 °C/min) and slow (20 °C/min) heating and slow (20 °C/min) cooling but irreversible during rapid (840 °C/min) cooling. In view of the fact that the exothermic peaks in ∼250–300 °C temperature range shown in Fig. 2 are irreversible during slow heating and cooling, both at a rate of 20 °C/min, these exothermic peaks may not be attributed to the β–γ transformations mentioned above. Instead, they may result from the crystallization of amorphous phases in the melt-spun ribbons. Fig. 3 shows the TEM images of a particle obtained by grinding the melt-spun $Gd_5Si_2Ge_2$ alloy prepared at 50 m/s. The electron diffraction pattern indeed indicates that this particle is amorphous. The presence of a glassy phase can be further

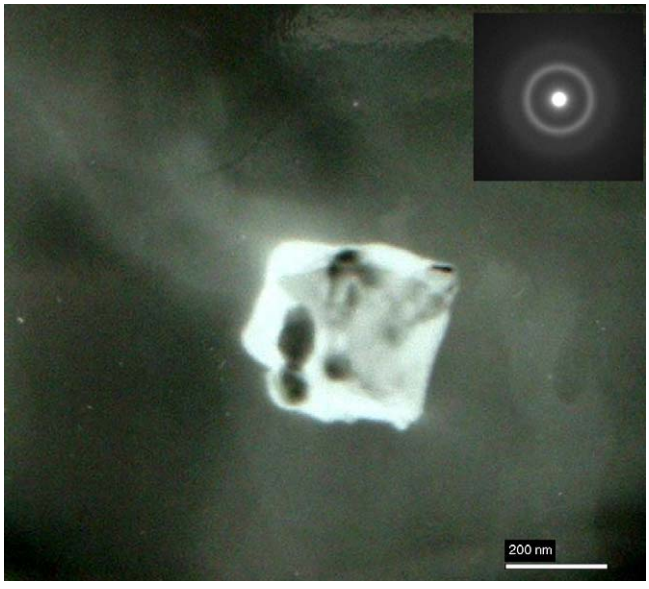

Fig. 3. TEM image of a glassy particle and the corresponding electron diffraction pattern for the $Gd_5Si_2Ge_2$ alloy prepared at 50 m/s.

confirmed by the DSC scans shown in Fig. 2, where each scan shows an endothermic peak at ∼150 °C (marked by the red arrow) during heating. The phase transformation corresponding to this endothermic peak can be ascribed to the glass transition, i.e., a transition from amorphous solid to supercooled liquid.

However, we also observed crystalline phases in some of the particles, as judged from their electron diffraction patterns. These results indicate that glassy phase and crystalline phase coexist in the melt-spun $Gd_5Si_2Ge_2$ alloy prepared at 50 m/s.

4. Conclusions

In summary, we have found that the type and content of phases in a $Gd_5Si_2Ge_2$ alloy depend strongly on the solidification rate. The alloy prepared at a wheel speed of 20 m/s was nearly a $Gd_5Si_2Ge_2$-type single phase. At 30 m/s, the alloy was consisted of a Gd_5Si_4-type major phase and a $Gd_5Si_2Ge_2$-type minor phase. At 40 m/s, the alloy contained a Gd_5Si_4-type single phase. At 50 m/s, the alloy was Gd_5Si_4-type and $Gd_5Si_2Ge_2$-type double phase. A first-order phase transformation was detected at approximately 273 K for the alloy prepared at 20 m/s whereas a second-order phase transformation was found at approximately 290 K for the alloys prepared at higher speeds of 30, 40, and 50 m/s. Exothermic reactions were observed in ∼250–300 °C range for the alloys heated in DSC at a rate of 20 °C/min. These reactions can be ascribed to the crystallization of a glassy phase, which was confirmed by both the electron diffraction pattern (in TEM observation) and the glass transition (in DSC scan).

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