The phase formation and thermal hysteresis of Gd$_{5}$Si$_2$Ge$_2$ with the addition of transition elements (Mn, Fe, Co, Ni)

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Abstract

The Gd$_5$Si$_2$Ge$_2$ and Gd$_5$Si$_2$Ge$_{1.9}T_{0.1}$ (T: Mn, Fe, Co, Ni) series alloys have been prepared by arc-melting method and annealed at 1300 °C for an hour. The phase formation and thermal hysteresis of the experimental alloys have been examined with the help of powder X-ray diffraction and optical metallographic combined with magnetic measurement. From XRD results, the alloy with the addition of Fe or Co is inclined to form the mixed Gd$_5$Si$_4$-type and Gd$_5$Si$_2$Ge$_2$-type phase. Transition elements Mn and Ni result in the orthorhombic Gd$_5$Si$_4$-type phase formation in Gd$_5$Si$_2$Ge$_{1.9}T_{0.1}$ (T: Mn, Ni) alloys. Magnetic measurement shows that all the four experimental transition elements could reduce the thermal hysteresis of Gd$_5$Si$_2$Ge$_2$.

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1. Introduction

Magnetocaloric effect is the phenomenon of emitting or absorption of heat by a magnetic material under the action of a magnetic field [1]. Since the discovery of the giant magnetocaloric effect (MCE) in Gd$_5$Si$_2$Ge$_2$ [2], many researches have been carried out in the R$_5$T$_4$ (where R is a rare-earth element and T is Si, Ge, or Sn) [3–8] considering its potential use in the near room temperature magnetic refrigeration. As the Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ with $x$ near 0.5 cooling through its Curie temperature ($T_C$), the room temperature monoclinic paramagnetic phase ($β$) transforms to the low temperature orthorhombic ferromagnetic phase ($α$) [4,9,10]. In the first order magnetic-crystallographic transition (FOMT), the covalent-like bonds between some of the Ge and/or Si atoms are broken and reformed on heating and cooling, respectively [4]. It is now well established that the mechanism behind the giant MCE in Gd$_5$Si$_2$Ge$_2$ is the coupled magnetic-structural first order transition under the influence of temperature, magnetic field or pressure [3,4,11,12]. According to the former works, the MCE property and phase composition of Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ ($x$ near 0.5) depend on the purity of Gd and heat treatment procedure [13–17]. The proper heat treatment is also needed even in the Gd$_5$Si$_2$Ge$_2$ prepared from 99.99 wt.% purity Gd [15].

In addition to the giant MCE, the large thermal and magnetic hysteresis are also observed in the Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ system [9,10,13,18]. The hysteresis nature of materials would inevitably result in energy losses in the magnetic refrigeration [18,19]. With the addition of about 1 at. % Fe [18], the magnetic hysteresis losses of Gd$_5$Si$_2$Ge$_2$ has been significantly reduced (~94%) without decreasing its refrigerant capacity (RC). Considering the practical application, the hysteresis losses of giant MCE materials, which make magnetic refrigeration less efficient, have attracted much attention especially in recent years.

In this contribution, the phase formation and thermal hysteresis of Gd$_5$Si$_2$Ge$_2$ with the addition of transition elements (Mn, Fe, Co, Ni) have been studied with the help of powder X-ray diffraction, optical metallography and magnetic measurements. The influence of the transition elements on the thermal hysteresis of Gd$_5$Si$_2$Ge$_2$ has been investigated. Correspondingly, the correlation between the thermal hysteresis and phase composi-
tion of Gd$_5$Si$_2$Ge$_{1.9}$T$_{0.1}$ (T: Mn, Fe, Co, Ni) is established in this work.

2. Experimental procedure

The Gd$_5$Si$_2$Ge$_2$ and Gd$_5$Si$_2$Ge$_{1.9}$T$_{0.1}$ (T: Mn, Fe, Co, Ni) series alloys, with 99.9 wt.% Gd and over purity higher 99.99 wt.% Si and Ge, were prepared in copper crucible by arc-melted method in an argon atmosphere. In the melting process, each button was re-melted five times to ensure homogeneity. All the as-cast alloys were annealed at 1300 °C for an hour in 5 × 10$^{-3}$ Pa vacuum. The phase composition of each sample was checked by X-ray diffraction and optical metallography. With the continuous scanning mode with 0.03° interval and 1.0 s counting time, the X-ray powder diffraction data were collected at room temperature on the DX2000 diffractometer using Cu Kα radiation between 20° and 60°. The voltage and anode current were 40 kV and 30 mA, respectively. Temperature dependence of magnetization for each alloy was performed on a vibrating sample magnetometer. The ferromagnetic ordering temperature ($T_C$) is determined from the minimum of (∂M(T, H)/∂T)$_H$. The difference between the $T_C$ in the increasing and decreasing procedure was used to evaluate the thermal hysteresis of the experimental alloys.

3. Results and discussion

3.1. Phase formation in Gd$_5$Si$_2$Ge$_2$ with the addition of transition elements

With the help of powder X-ray diffraction, we have evaluated the phase formation in the experimental alloys. Fig. 1 shows the XRD patterns of the homogeneous Gd$_5$Si$_2$Ge$_2$ at room temperature. From qualitative analysis, it is clear that the annealed Gd$_5$Si$_2$Ge$_2$ adopts in single phase and crystallizes in the monoclinic Gd$_5$Si$_2$Ge$_2$-type structure. The proper heat-treatment procedure could purify the phase of our experimental Gd$_5$Si$_2$Ge$_2$ alloy from XRD result, which is in good agreement with that reported in Refs. [15,20] for the same composition range.

The XRD patterns of the annealed Gd$_5$Si$_2$Ge$_{1.9}$T$_{0.1}$ (T: Mn, Fe, Co, Ni) alloys are shown in Fig. 2. It is clear that the transition elements have significant effect on the phase composition of Gd$_5$Si$_2$Ge$_2$. With the addition of Mn and Ni transition elements, the Gd$_5$Si$_4$-type phase is easy to form in each experimental alloy unlike the alloy with a little Sn [21,22] and Bi [22] doping. In the alloys with Fe and Co, they both have the Gd$_5$Si$_2$Ge$_2$-type and Gd$_5$Si$_4$-type mixture phases in the annealed state and the former is the major phase in Gd$_5$Si$_2$Ge$_{1.9}$Fe$_{0.1}$ as observed in Ref [18]. From XRD examination, the monoclinic Gd$_5$Si$_2$Ge$_2$-type single phase in the Gd$_5$Si$_2$Ge$_2$ alloy has been destroyed with the addition of transition elements and the Gd$_5$Si$_4$-type phase is formed more or less. It should pointed out that only the Gd$_5$Si$_4$-type phase is observed in Gd$_5$Si$_2$Ge$_{1.9}$T$_{0.1}$ (T: Mn, Ni) alloys within the resolution of powder X-ray diffraction.

Fig. 3 shows the typical microstructure of Gd$_5$Si$_2$Ge$_2$ and the alloys with the addition of transition elements (Mn, Fe, Co, Ni). Metallographic observation shows that the annealed Gd$_5$Si$_2$Ge$_2$ alloy has no other second phase (Fig. 3a), which coincides with the XRD result and Ref [18]. The alloy with the addition of transition element has either the Gd$_5$Si$_2$Ge$_2$-type and Gd$_5$Si$_4$-type mixture phases or the Gd$_5$Si$_4$-type single phase from powder XRD results, the microstructure of which is observed to be a dominant matrix phase and a minor darker boundary phase is also found along the matrix (see Fig. 3b–d and Ref [18]). The EDS analysis conducted on the Gd$_5$Si$_2$Ge$_{1.9}$Fe$_{0.1}$ alloy has shown the Fe concentration in the grain boundary phase [18]. From the metallographs of Gd$_5$Si$_2$Ge$_{1.9}$T$_{0.1}$ in acid etched condition, it is found that all the experimental transition elements doped alloys include a grey phase and a black phase. Based on the aforementioned XRD experiments and the EDS analysis in Ref [18], the stoichiometric composition of the two phases in Gd$_5$Si$_2$Ge$_{1.9}$Fe$_{0.1}$ are both 5:4. Since the concentration of transition elements, the grain boundary phase of each Gd$_5$Si$_2$Ge$_{1.9}$T$_{0.1}$ alloy is less stable than the matrix phase and is easy to be etched.
3.2. Thermal hysteresis properties

Thermal magnetic curves of Gd$_5$Si$_2$Ge$_2$ and Gd$_5$Si$_2$Ge$_{1.9}$T$_{0.1}$ (T: Mn, Fe, Co, Ni) series alloys are shown in Fig. 4. The temperature of the annealed Gd$_5$Si$_2$Ge$_2$ is 4 K and this result coincides with that have been observed in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ alloy with the similar component [9]. The thermal hysteresis of each experimental alloy determined through the $T_C$ of decreasing and increasing temperature is shown in Fig. 4. With the addition of transition elements, the transition temperatures of Gd$_5$Si$_2$Ge$_{1.9}$T$_{0.1}$ alloys are all higher than that of Gd$_5$Si$_2$Ge$_2$. For Gd$_5$Si$_2$Ge$_{1.9}$Fe$_{0.1}$, the $M$–$T$ curves in measured with decreasing and increasing temperature are almost superposition and the thermal hysteresis is negligible. According to
the magnetic phase diagram of the Gd$_5$Si$_4$–Gd$_5$Ge$_4$ pseudo-binary system [3,20,23], the two phase transitions at the high and low temperature in Gd$_5$Si$_2$Ge$_{1.9}$Fe$_{0.1}$ should be attributed to the Gd$_5$Si$_4$-type and Gd$_5$Si$_2$Ge$_2$-type phase, respectively. From Fig. 4 and Table 1, it is easy to see that all the experimental transition elements addition could significantly reduce the thermal hysteresis comparing with that of Gd$_5$Si$_2$Ge$_2$. The magnetic hysteresis losses have been observed in Gd$_5$Si$_2$Ge$_1.9$Fe$_{0.1}$ [18], probably plays a pivotal role in the reduction of the thermal hysteresis in the experimental alloys.

4. Conclusions

In summary, we have investigated the thermal hysteresis and phase composition of the Gd$_5$Si$_2$Ge$_2$ and Gd$_5$Si$_2$Ge$_{1.9}$T$_{0.1}$ (T: Mn, Fe, Co, Ni) series alloys with the help of powder X-ray diffraction and magnetic measurements. With the addition of Fe and Co, the alloys have monoclinic Gd$_5$Si$_2$Ge$_2$-type and orthorhombic Gd$_5$Si$_4$-type diphase structure. However, Gd$_5$Si$_2$Ge$_{1.9}$T$_{0.1}$ (T: Mn, Ni) crystallize in the orthorhombic Gd$_5$Si$_4$-type structure and no other phases were observed within the resolution of X-ray powder diffraction. The grain boundary phase of each alloy is erodible for the concentration of transition element. With the addition of transition elements, the thermal hysteresis of Gd$_5$Si$_2$Ge$_2$ has been significantly reduced.

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