Journal of Alloys and Compounds 433 (2007) 18–21

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

The phase formation and thermal hysteresis of $Gd_5Si_2Ge_2$ with the addition of transition elements (Mn, Fe, Co, Ni)

Tiebang Zhang, Yungui Chen *, Yongbai Tang, Huijun Du, Tong Ren, Mingjing Tu

School of Materials Science and Engineering, Sichuan University, Chengdu 610065, PR China

Received 22 May 2006; received in revised form 12 June 2006; accepted 13 June 2006
Available online 18 July 2006

Abstract

The $Gd_5Si_2Ge_2$ and $Gd_5Si_2Ge_{1.9}T_{0.1}$ (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_5Si_4-type and $Gd_5Si_2Ge_2$-type phase. Transition elements Mn and Ni result in the orthorhombic Gd_5Si_4-type phase formation in $Gd_5Si_2Ge_{1.9}T_{0.1}$ (T: Mn, Ni) alloys. Magnetic measurement shows that all the four experimental transition elements could reduce the thermal hysteresis of $Gd_5Si_2Ge_2$.

Keywords: Phase formation; Thermal hysteresis; Magnetocaloric effect

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 $Gd_5Si_2Ge_2$ [2], many researches have been carried out in the R_5T_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 $Gd_5(Si_xGe_{1-x})_4$ 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 $Gd_5Si_2Ge_2$ 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 $Gd_5(Si_xGe_{1-x})_4$ (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 $Gd_5Si_2Ge_2$ 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 $Gd_5(Si_xGe_{1-x})_4$ 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 $Gd_5Si_2Ge_2$ 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 $Gd_5Si_2Ge_2$ 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 $Gd_5Si_2Ge_2$ has been investigated. Correspondingly, the correlation between the thermal hysteresis and phase composi-

* Corresponding author. Tel.: +86 28 85405670; fax: +86 28 85407335.
E-mail addresses: scuztb@sohu.com (T. Zhang), ygchen60@yahoo.com.cn (Y. Chen).

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doi:10.1016/j.jallcom.2006.06.056

tion of $Gd_5Si_2Ge_{1.9}T_{0.1}$ (T: Mn, Fe, Co, Ni) is established in this work.

2. Experimental procedure

The $Gd_5Si_2Ge_2$ and $Gd_5Si_2Ge_{1.9}T_{0.1}$ (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° (2θ). 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 $(\partial M(T, H)/\partial T)_H$. 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 $Gd_5Si_2Ge_2$ 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 $Gd_5Si_2Ge_2$ at room temperature. From qualitative analysis, it is clear that the annealed $Gd_5Si_2Ge_2$ adopts in single phase and crystallizes in the monoclinic $Gd_5Si_2Ge_2$-type structure. The proper heat-treatment procedure could purify the phase of our experimental $Gd_5Si_2Ge_2$ 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 $Gd_5Si_2Ge_{1.9}T_{0.1}$ (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 $Gd_5Si_2Ge_2$. With the addition of Mn and Ni transition elements,

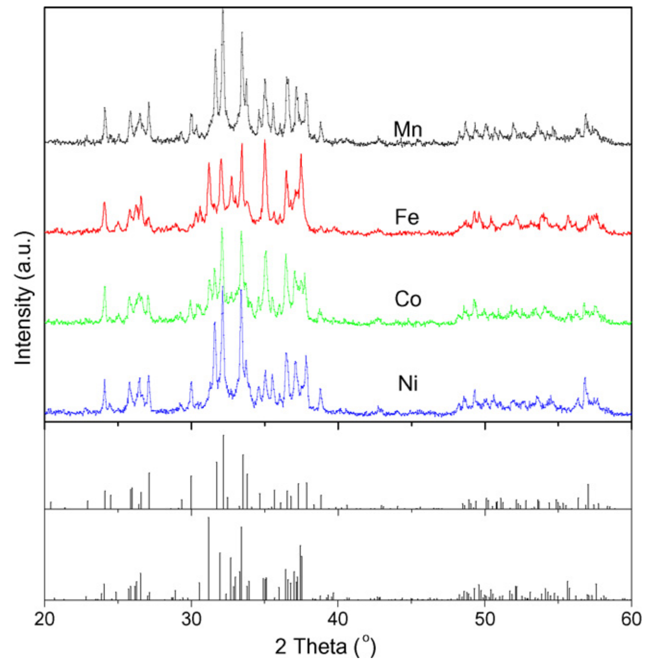

Fig. 2. Powder XRD patterns of the annealed $Gd_5Si_2Ge_{1.9}T_{0.1}$ (T: Mn, Fe, Co, Ni) alloys.

the Gd_5Si_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 $Gd_5Si_2Ge_2$-type and Gd_5Si_4-type mixture phases in the annealed state and the former is the major phase in $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ as observed in Ref [18]. From XRD examination, the monoclinic $Gd_5Si_2Ge_2$-type single phase in the $Gd_5Si_2Ge_2$ alloy has been destroyed with the addition of transition elements and the Gd_5Si_4-type phase is formed more or less. It should pointed out that only the Gd_5Si_4-type phase is observed in $Gd_5Si_2Ge_{1.9}T_{0.1}$ (T: Mn, Ni) alloys within the resolution of powder X-ray diffraction.

Fig. 3 shows the typical microstructure of $Gd_5Si_2Ge_2$ and the alloys with the addition of transition elements (Mn, Fe, Co, Ni). Metallographic observation shows that the annealed $Gd_5Si_2Ge_2$ 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 $Gd_5Si_2Ge_2$-type and Gd_5Si_4-type mixture phases or the Gd_5Si_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 $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ alloy has shown the Fe concentration in the grain boundary phase [18]. From the metallographs of $Gd_5Si_2Ge_{1.9}T_{0.1}$ 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 $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ are both 5:4. Since the concentration of transition elements, the grain boundary phase of each $Gd_5Si_2Ge_{1.9}T_{0.1}$ alloy is less stable than the matrix phase and is easy to be etched.

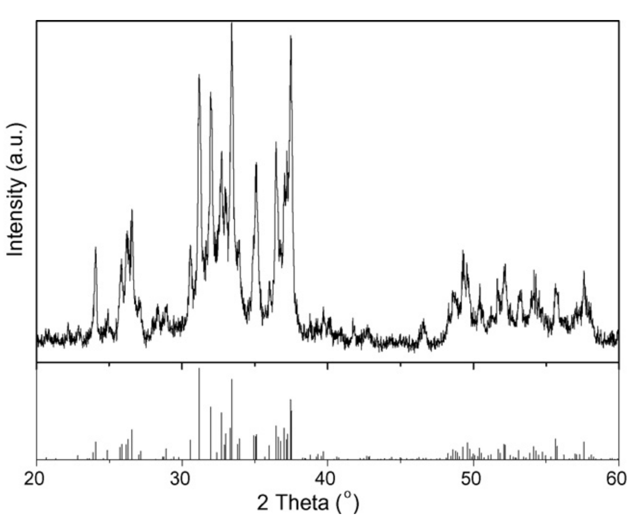

Fig. 1. Powder XRD pattern for the annealed $Gd_5Si_2Ge_2$ alloy.

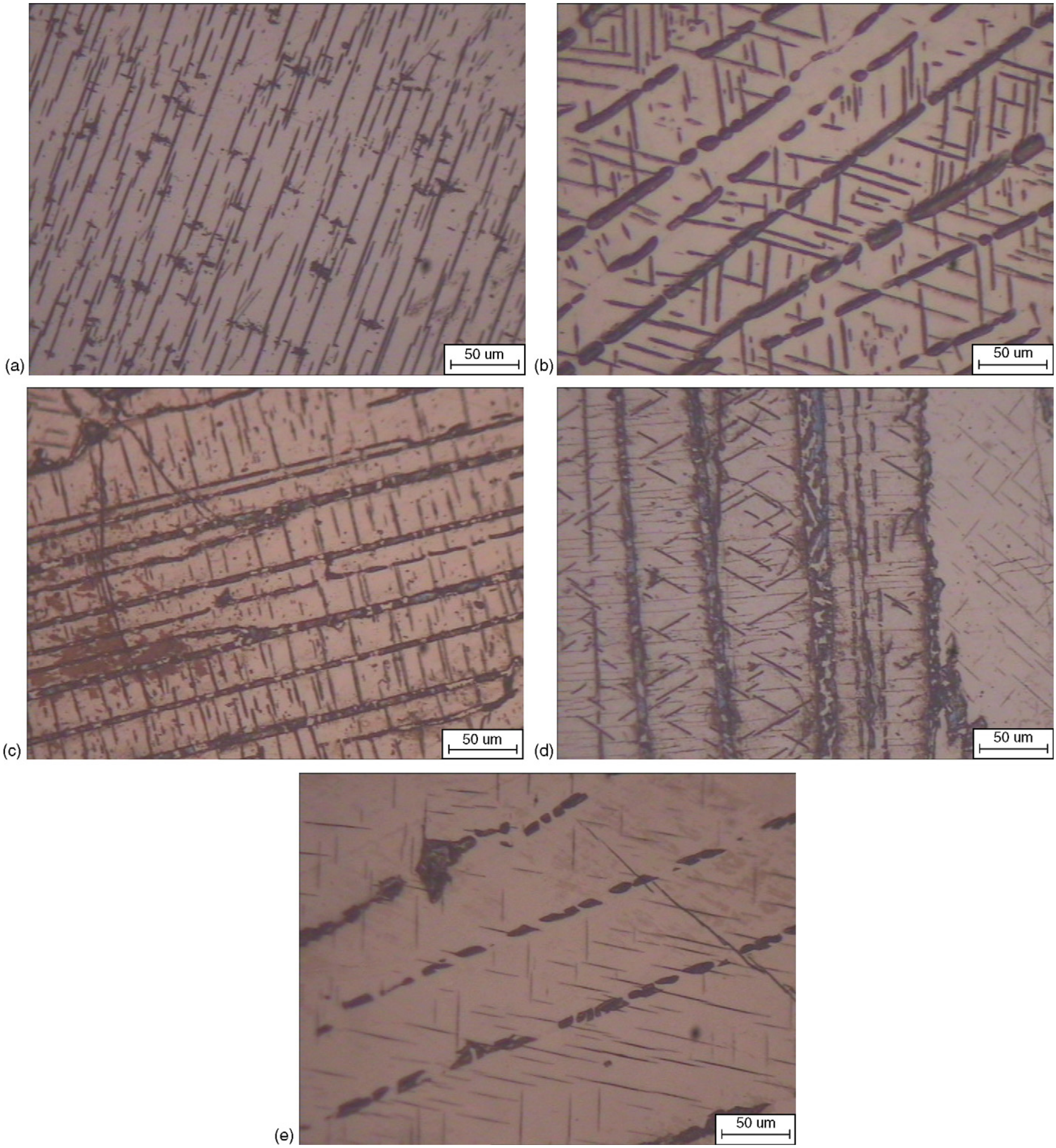

Fig. 3. The optical metallographs in the longitudinal section of the $Gd_5Si_2Ge_2$ and $Gd_5Si_2Ge_{1.9}T_{0.1}$ (Mn, Fe, Co, Ni) alloys in acid-etched condition: (a) $Gd_5Si_2Ge_2$; (b) $Gd_5Si_2Ge_{1.9}Mn_{0.1}$; (c) $Gd_5Si_2Ge_{1.9}Fe_{0.1}$; (d) $Gd_5Si_2Ge_{1.9}Co_{0.1}$; (e) $Gd_5Si_2Ge_{1.9}Ni_{0.1}$.

3.2. Thermal hysteresis properties

Thermal magnetic curves of $Gd_5Si_2Ge_2$ and $Gd_5Si_2Ge_{1.9}T_{0.1}$ (T: Mn, Fe, Co, Ni) series alloys are shown in Fig. 4. The temperature of the annealed $Gd_5Si_2Ge_2$ is 4 K and this result coincides with that have been observed in $Gd_5(Si_xGe_{1-x})_4$ 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 $Gd_5Si_2Ge_{1.9}T_{0.1}$ alloys are all higher than that of $Gd_5Si_2Ge_2$. For $Gd_5Si_2Ge_{1.9}Fe_{0.1}$, the *M–T* curves in measured with decreasing and increasing temperature are almost superposition and the thermal hysteresis is negligible. According to

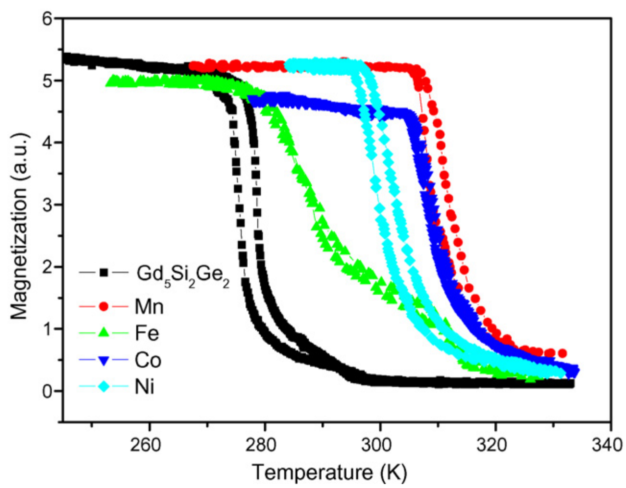

Fig. 4. Temperature-dependence of magnetization of the $Gd_5Si_2Ge_2$ and $Gd_5Si_2Ge_{1.9}T_{0.1}$ (T: Mn, Fe, Co, Ni) alloys annealed at 1300 °C for an hour.

Table 1
The thermal hysteresis of $Gd_5Si_2Ge_2$ and $Gd_5Si_2Ge_{1.9}T_{0.1}$ (T: Mn, Co, Ni) alloys

	$Gd_5Si_2Ge_2$	Mn	Co	Ni
Decreasing temperature, T_{des} (K)	274.8	310.6	308.7	303.2
Increasing temperature, T_{inc} (K)	278.8	308.2	308.4	300
Thermal hysteresis (K)	4	2.4	0.3	3.2

the magnetic phase diagram of the Gd_5Si_4–Gd_5Ge_4 pseudo-binary system [3,20,23], the two phase transitions at the high and low temperature in $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ should be attributed to the Gd_5Si_4-type and $Gd_5Si_2Ge_2$-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 $Gd_5Si_2Ge_2$. The little thermal hysteresis of $Gd_5Si_2Ge_{1.9}T_{0.1}$ (Mn, Ni) should be mainly attributed to the dominant Gd_5Si_4-type phase as it performs typical second-order phase transition at the corresponding T_C. But the case in $Gd_5Si_2Ge_{1.9}T_{0.1}$ (Fe, Co) is different and they both have mixed structures. In the alloy with Fe or Co doped, the thermal hysteresis corresponding to $Gd_5Si_2Ge_2$-type phase has been significantly reduced compared with that of $Gd_5Si_2Ge_2$. The transition elements concentration in the boundary phase, as the magnetic hysteresis losses have been observed in $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ [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 $Gd_5Si_2Ge_2$ and $Gd_5Si_2Ge_{1.9}T_{0.1}$ (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 $Gd_5Si_2Ge_2$-type and orthorhombic Gd_5Si_4-type diphase structure. However, $Gd_5Si_2Ge_{1.9}T_{0.1}$ (T: Mn, Ni) crystallize in the orthorhombic Gd_5Si_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 $Gd_5Si_2Ge_2$ has been significantly reduced.

Acknowledgements

This work was supported by the National High Technology Research and Development Program of China under contract No. 2002AA324010. Professor Shengji Gao at Sichuan University is gratefully acknowledged for his help in XRD measurements.

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