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Magnetocaloric effect of $Gd_5Si_2Ge_2$ alloys in low magnetic field

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Abstract. **The magnetocaloric effect of $Gd_5Si_2Ge_2$ alloys under heat treatment conditions are investigated in low magnetic fields. The magnetocaloric effect (MCE) is studied by measuring magnetic entropy change (ΔS_M) and adiabatic temperature change (ΔT_{ad}) in a magnetic field of 1·5 T using a vibrating sample magnetometer (VSM) and a home-made magnetocaloric effect measuring apparatus, respectively. The maximum ΔS_M of the alloys increases by 200% from 4·38 to 13·32 J kg^{-1} K^{-1}, the maximum ΔT_{ad} increases by 105% from 1·9 to 3·9 K when compared to the as-cast due to the homogeneous composition distribution and microstructure, while the magnetic ordering temperature is slightly reduced. These results indicate that the annealed $Gd_5Si_2Ge_2$ compounds are promising as high-performance magnetic refrigerants working room temperature in relatively low magnetic fields.**

Keywords. **Magnetic entropy change (ΔS_M); adiabatic temperature change (ΔT_{ad}); heat treatment; microstructure.**

1. Introduction

Recently, the giant magnetocaloric effect in the family of intermetallic compound $Gd_5(Si_xGe_{1-x})_4$ (Pecharsky and Gschneidner 1997; Provenzano *et al* 2004) has been developed and broadly investigated compared with other magnetic refrigerator materials around room temperature. The most important feature of $Gd_5(Si_xGe_{1-x})_4$ ($x \leq 0{\cdot}5$) serious alloys is that it undergoes a simultaneous first-order structural and magnetic-phase transition, which can lead to giant magnetic-entropy change at the order temperature. The typical alloy with the chemical composition of $Gd_5Si_2Ge_2$ possesses excellent giant magnetocaloric effect at the first-order temperature around 276 K, which closes to room temperature. So, the $Gd_5Si_2Ge_2$ alloy is regarded as an interesting candidate with a potential to be used as active magnetic refrigerants at room temperature. Consequently, considerable investigations for further developments have been conducted mainly on their chemical composition (Choe *et al* 2000), transformation theory (Morellon *et al* 2000), crystal structure (Gschneidner *et al* 2000) as well as their magnetic properties (Pecharsky *et al* 2003).

However, the researches about their magnetocaloric effect in low magnetic field are seldom reported. In the present work, we have synthesized the polycrystalline $Gd_5Si_2Ge_2$ alloy by arc-melting method, and investigated the magnetocaloric effects in low magnetic field, meanwhile the effect of heat treatment conditions on their structures and microstructures is also discussed.

2. Experimental

Metal Gd, Si and Ge with purity of 99·5 wt.%, 99·9 wt.%, and 99·9 wt.%, respectively, are used as the starting materials of $Gd_5Si_2Ge_2$ alloys. The $Gd_5Si_2Ge_2$ alloys are prepared using levitation melting in a water-cooled copper crucible under an argon atmosphere. During melting, the sample was homogenized by turning the buttons over and remelting six times to ensure homogeneity. The total weight loss of both the samples in this step was less than 0·8%. Then the homogenization treatments were conducted at 1473 K and 1573 K for 1 h. After the homogenization treatment, the $Gd_5Si_2Ge_2$ alloy crystallizes into a single phase with monoclinic structure, as indicated by powder X-ray diffraction analysis.

The microstructures and the chemical compositions of the alloys were investigated by means of scanning electron microscope (SEM) with the energy dispersive X-ray Detector (EDX). The magnetic properties of the as-cast and the annealed specimens were examined from 250 K to 300 K by using a vibrating sample magnetometer (VSM) in the magnetic field under 1·5 Tesla. Meanwhile, the magnetocaloric effect of the as-cast sample and the annealed samples was also studied by directly measuring the adiabatic temperature change (ΔT_{ad}) in the tempera-

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ture range of 253–313 K with a magnetic-field change of 1·5 T using a home-made magnetocaloric effect measuring apparatus. In this apparatus, sintered Nd–Fe–B permanent magnets were assembled to generate a static magnetic field, which work as the magnetic field source in the measurement (Huang *et al* 2005). Experimental errors for the direct measurement technique were estimated to be less than 10%.

3. Results and discussion

3.1 *Magnetic entropy change ($-\Delta S_M$) of $Gd_5Si_2Ge_2$ alloys*

The magnetization behaviours of the arc-melted, annealed $Gd_5Si_2Ge_2$ alloys measured between 250 K and 300 K in the magnetic field from 0 to 1·5 Tesla are shown in figure 1. From isothermal magnetization data, it can be concluded that the magnetization isotherms of both arc-melted and annealed alloys show the typical magnetic order transition from ferromagnet to paramagnet, which is characteristic of the first-order magnetic–crystallographic transition induced by the variation of temperature under the present magnetic field. Since the giant magnetocaloric effect in the family of intermetallic compound $Gd_5(Si_xGe_{1-x})_4$ is associated with the first-order magnetic–crystallographic transition, a conclusion can be drawn that the arc-melted and the annealed $Gd_5Si_2Ge_2$ alloys possess giant magnetocaloric effect. In addition, the magnetic properties of annealed sample have been remarkably improved comparing with those of the as-cast sample (figure 1), the magnetization rises from 95 emu/g of arc-melted alloy to 128 emu/g and 135 emu/g of the annealed $Gd_5Si_2Ge_2$ alloys for 1473 K/1 h and 1573 K/1h, respectively.

The temperature dependence of the magnetic entropy variation, $\Delta S_M(T)$, calculated from the magnetization curves displays a maximum negative value around the Curie temperature. The magnetic entropy change can be obtained by numerical integration using the magnetization data and the integrated Maxwell equation and the simplified numerical formula (as shown in formula (1) and (2))

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right) dH, \quad (1)$$

$$\Delta S_M\left(\frac{T_1+T_2}{2}\right) = \frac{1}{T_2-T_1}\int_0^H [M(T_2,H)-M(T_1,H)]dH, \quad (2)$$

where the symbols S, M, H, and T represent the magnetic entropy, magnetization of material, applied magnetic field and temperature of the system, respectively. This indirect method has been believed to be a reliable way to evaluate magnetic materials of magnetic refrigeration. Figure 2 shows the corresponding magnetic entropy change (ΔS_M) of $Gd_5Si_2Ge_2$ alloys as a function of temperature under field increase. A value of maximum (ΔS_M) = 4·38 J kg^{-1} K^{-1}, resulting from the rapid change of magnetization at the T_C, is obtained in the as-cast alloy at 268 K under 1·5 T. However, it is found from the figure that the maximum value of magnetic entropy change ($-\Delta S_M$) of the annealed $Gd_5Si_2Ge_2$ alloys for 1473 K/1 h and 1573 K/1 h are 6·34 and 13·32 J kg^{-1} K^{-1}, respectively, indicating that the heat treatment improves the

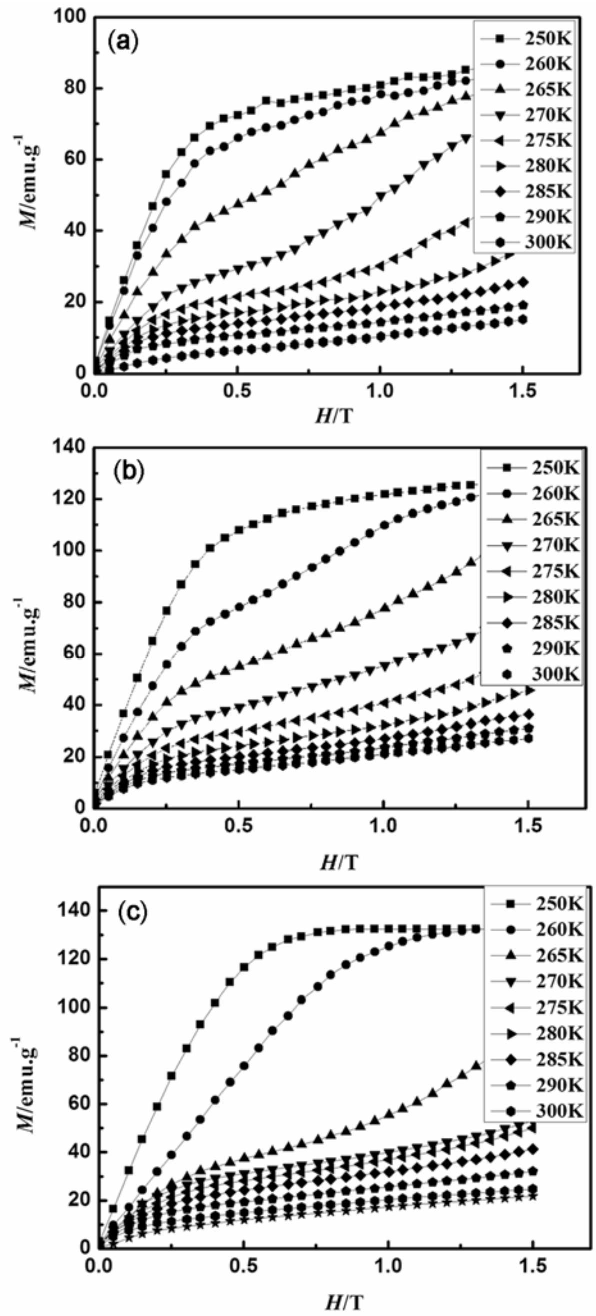

Figure 1. Magnetization isotherms of $Gd_5Si_2Ge_2$ alloys before and after heat treated: (**a**) as-cast, (**b**) 1473 K/1 h, (**c**) 1573 K/1 h.

ΔS_M of the alloys remarkably. Magnetic entropy change is related to the saturation magnetization. Because saturation magnetization of $Gd_5Si_2Ge_2$ alloys for 1573 K/1 h (135 emu/g) is larger than that of 1473 K/1 h (128 emu/g), the maximum magnetic entropy change for 1573 K/1 h is larger than that of 1473 K/1 h. Meanwhile, compared with that of as-cast sample, the Curie temperatures (T_C) of the annealed alloys for 1473 K/1 h and 1573 K/1 h decrease for about 5 K.

3.2 *Adiabatic temperature change (ΔT_{ad}) of $Gd_5Si_2Ge_2$ alloys*

The adiabatic temperature change (ΔT_{ad}) vs T curves of the as-cast, annealed $Gd_5Si_2Ge_2$ alloys measured between 253 and 313 K in the magnetic field from 0 to 1·5 Tesla are shown in figure 3. The as-cast $Gd_5Si_2Ge_2$ alloy possesses relatively low ΔT_{ad} (about 1·9 K) compared with the annealed alloys. It is well known that the MCE peaks at or close to the appropriate magnetic phase-transition temperature of the magnetic material. Namely, the maximum of the adiabatic temperature change (ΔT_{ad}) peaks at its Curie temperature (T_C) in the present work. It can be easily deduced that the magnetic ordering temperature (T_C) of the annealed alloy is slightly reduced, compared with that of the as-cast alloy. On the other hand, it should be noted that a deviation of T_C of the annealed samples compared to some previous report (Pecharsky *et al* 2003), which might result from the low purity of Gd used in our experiment and the evolution of the Curie temperature to be sensibly dependent on the experimental technique, has been found in our direct measurement.

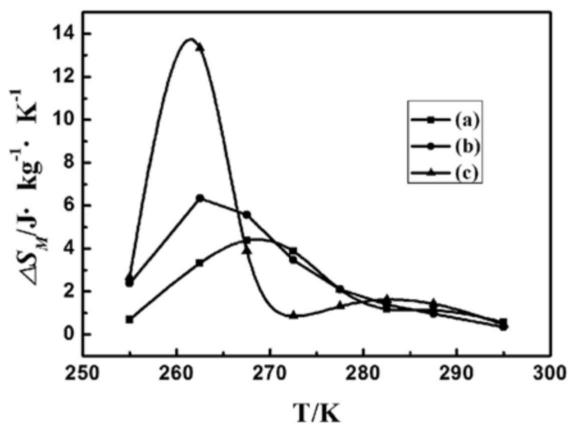

Figure 2. Magnetic entropy change (ΔS) of $Gd_5Si_2Ge_2$ alloys before and after heat treated: (**a**) as-cast, (**b**) 1473 K/1 h, (**c**) 1573 K/1 h.

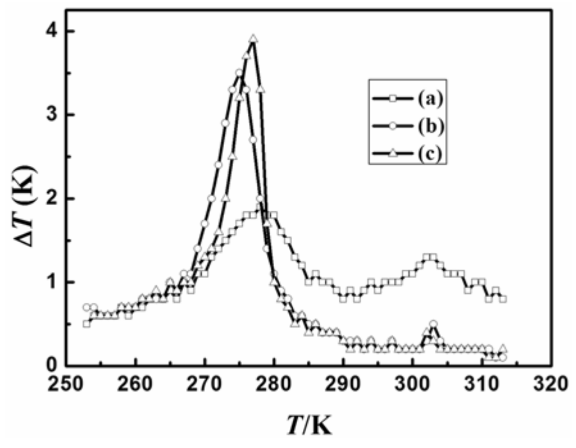

Figure 3. The adiabatic temperature change (ΔT_{ad}) of $Gd_5Si_2Ge_2$ alloys before and after heat treated: (**a**) as-cast, (**b**) 1473 K/1 h, (**c**) 1573 K/1 h.

It can be seen from figure 3 that the maximum value of ΔT_{ad} for the as-cast $Gd_5Si_2Ge_2$ alloy, except a larger ΔT_{ad} peak at the 278 K, a relatively low ΔT_{ad} peak in the adiabatic temperature change curves at about 303 K is also observed clearly, indicating the presence of a second orthorhombic phase in the as-cast $Gd_5Si_2Ge_2$. As a result, the as-cast $Gd_5Si_2Ge_2$ sample exhibits the reduction of the MCE value compared to the annealed samples, which is due to the impurity in the as-cast sample. However, the ΔT_{ad} peak in the as-cast sample manifests a broader shape than in the annealed. At the same time, the absence of a second phase in the annealed alloy is confirmed by the disappearance of the corresponding anomaly at about 303 K in the adiabatic temperature change curves of the annealed $Gd_5Si_2Ge_2$ alloys compared to that of the as-cast, which is clearly evident in the later SEM observations (figure 4(a)). In addition, it is found from the figure that the maximum values of adiabatic temperature change (ΔT_{ad}) of the annealed $Gd_5Si_2Ge_2$ alloys for 1473 K/1 h and 1573 K/1 h are 3·5 K and 3·9 K, respectively, indicating that the heat treatment improves the MCE of the alloys remarkably, in excellent agreement with the previous magnetic entropy change (ΔS_M). The maximum value of ΔT_{ad} increases, maybe due to the occurrence of the fully homogenized microstructure and the transition of the orthorhombic $Gd_5Si_2Ge_2$ phase with the Gd_5Si_4-type structure into the monoclinic $Gd_5Si_2Ge_2$ phase with the $Gd_5Si_2Ge_2$-type structure in the alloys. On the other hand, the heat-treated alloy orders ferromagnetically at a slightly lower temperature (275 K for the 1473 K/1 h and 276 K for 1573 K/1 h) than the as-cast sample (278 K) but the ΔT_{ad} peak or the phase transition is much sharper, which is indicative of the field induced by the first-order phase transition in $Gd_5Si_2Ge_2$ under the present applied magnetic field. A high value of ΔT_{ad} for the annealed $Gd_5Si_2Ge_2$ in a low magnetic field change is advantageous to practical applications in a magnetic refrigeration system with a permanent magnet.

3.3 *Microstructure analysis*

In order to clarify the evident effects of heat treatment on the magnetocaloric effect of $Gd_5Si_2Ge_2$ alloys, the SEM micrographs (back scattered mode) of $Gd_5Si_2Ge_2$ alloys for the as-cast and the annealed at 1573 K are observed, the results are shown in figure 4. Meanwhile, the chemical compositions of the two specimens are also listed in table 1. EDX analysis shows the concentration of Si in the two phases is different. It is found from the figure that there are two phases in the microstructure of the as-cast: the miner phase (A) is regarded as orthorhombic $Gd_5Si_2Ge_2$ phase, while the matrix phase (B) is monoclinic $Gd_5Si_2Ge_2$ phase. After the heat treatment, the miner phase (A) containing more Si diminishes into the matrix phase (B), which the ratio of the elements of Gd, Si and Ge closes to 5 : 2 : 2. This result is very well corresponding to the former adiabatic temperature change research about the disappearance of the corresponding anomaly at 303 K in the ΔT_{ad} curves of $Gd_5Si_2Ge_2$ alloys annealed at 1573 K due to the absence of a second phase in the annealed alloys (figure 3). Considering the fact that the monoclinic $Gd_5Si_2Ge_2$ phase with the $Gd_5Si_2Ge_2$-type structure bears better magneto-thermal properties than the Gd_5Si_4-type structure; it is suggested that the annealing heat treatment can improve the transition of orthorhombic $Gd_5Si_2Ge_2$ phase with the Gd_5Si_4-type structure into the monoclinic $Gd_5Si_2Ge_2$ phase with the $Gd_5Si_2Ge_2$-type structure remarkably. Considering the fact that annealed alloys of $Gd_5Si_2Ge_2$ possess more homogeneous composition distribution and microstructure than the arc-melted one. Thus the annealed $Gd_5Si_2Ge_2$ alloy possesses much better magneto-thermal properties than the arc-melted one as described above.

Table 1. Chemical composition of $Gd_5Si_2Ge_2$ alloys before and after heat treatment.

	Chemical compositions (%)		
Processing conditions	Gd	Si	Ge
As-cast (A)	52·42	28·73	18·85
As-cast (B)	55·98	23·01	21·01
Annealed at 1573 K/1 h	55·46	21·36	23·17

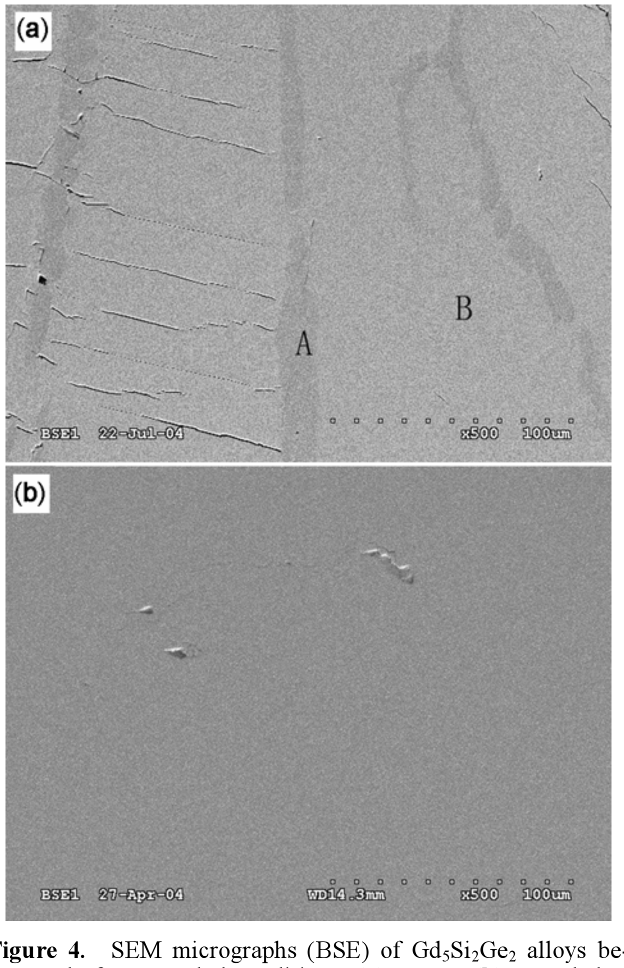

Figure 4. SEM micrographs (BSE) of $Gd_5Si_2Ge_2$ alloys before and after annealed conditions: (**a**) as-cast (**b**) annealed at 1573 K.

3. Conclusions

The magnetocaloric effects of $Gd_5Si_2Ge_2$ alloys under heat treatment conditions have been investigated in relatively low magnetic fields by measuring magnetic entropy change ($-\Delta S_M$) and adiabatic temperature change (ΔT_{ad}), respectively. Microstructure analysis reveals that the microstructure of the alloys could be fully homogenized and the impurities in the alloys could be remarkably removed via appropriate heat treatment. The maximum ΔS_M of the alloys increases by 200% from 4·38 to 13·32 J kg^{-1} K^{-1}, the maximum ΔT_{ad} increases by 105% from 1·9 to 3·9 K for a magnetic field change from 0 to 15 kOe when compared to the as-cast, while the magnetic ordering temperature slightly reduced. These results indicate that the annealed $Gd_5Si_2Ge_2$ compounds are promising as high-performance magnetic refrigerants working in wide temperature ranges covering room temperature in relatively low magnetic fields.

References

Choe W, Pecharsky V K, Young V G, Pecharsky A O, Gschneidner K A and Miller G J 2000 *Phys. Rev. Lett.* **84** 4617

Giguère A, Foldeaki M, Gopal B R, Chahine R, Bose T K, Frydman A and Barclay J A 1999 *Phys. Rev. Lett.* **83** 2262

Gschneidner K A, Pecharsky V K, Pecharsky A O, Ivtchenko V V and Levin E M 2000 *J. Alloys Compd.* **303–304** 214

Huang J H, Qiu J F, Liu J R, Jin P Y, Xu L Z and Zhang J X 2005 *First international conference on magnetic refrigeration at room temperature*, Switzerland, 179

Morellon L, Blasco J, Algarabel P A and Ibarra M R 2000 *Phys. Rev.* **B62** 1022

Pecharsky A O, Pecharsky V K and Gschneidner K A 2003 *J. Appl. Phys.* **93** 4722

Pecharsky V K and Gschneidner K A 1997 *Phys. Rev. Lett.* **78** 4494

Provenzano V, Shapiro A J and Shull R D 2004 *Nature* **429** 853