Materials Research, Vol. 7, No. 4, 535-538, 2004.

Giant Magnetocaloric Effect in $Gd_5(Si_2Ge_2)$ Alloy with Low Purity Gd

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Received: February 24, 2003; Revised: June 30, 2004

$Gd_5(Ge_{1-x}Si_x)$, $x \leq 4$ based alloys are potential candidates for magnetic refrigeration in the range ~20 – ~290 K. However, one of the greatest obstacles for the use of that technology in large scale is the utilization of high pure Gd metal (99.99 wt. (%)) to produce the GdGeSi alloys, since the impurity elements decrease the intensity of the magnetocaloric effect (EMC)[1]. In this work, we prove that annealing of the $Gd_5Ge_2Si_2$ can promote remarkable values for the EMC in comparison to those obtained for the alloy with high pure Gd. Also, the as cast alloy and the annealed alloy are not monophasic, but have at least two crystalline phases in their microstructure. Results for X-ray analysis, optical and electronic microscopy and magnetization measurements are reported.

Keywords: *magnetocaloric effect, magnetic materials, GdGeSi*

1. Introduction

The magnetocaloric effect (MCE) means the isothermal entropy change or the adiabatic temperature change by application/removal of a magnetic field. In other words it is the ability that some magnetic materials to heat up when they are magnetized, and cool down when removed from the magnetic field in a thermodynamic cycle.

That effect was originally discovered in iron by Warburg[2] in 1881. Recently a giant MCE (GMCE) was discovered in $Gd_5(Si_xGe_{1-x})$ alloys, where $x \leq 4$. This property makes these alloys potential candidates for magnetic refrigeration in the range of 20-276 K. The GMCE in these materials is associated with the strong first-order magnetic and structural transitions near the respective Curie temperature. The Curie temperature is strongly dependent on the alloy composition and its first order nature is preserved even in high magnetic fields ($H = 7T$)[1]. Therefore, the works on this matter are focused in materials that present first order transition, since they have intense entropy variation.

Just like the gas/liquid refrigerant in a conventional vapour-compression system, a solid magnetic refrigerant material is an essential part of the magnetic refrigerator, with the size reduction of the refrigerators, making them more efficient and more ecologically clean. Another advantage of magnetocaloric refrigerators is that the cooling power can be varied by scaling form miliwats to a few hundred watts as the cooling efficiency of magnetic refrigerators working with Gd reach values of 60% of the theoretical limit, comparated to only about 40% in the best gas-compression refrigerators[3].

Pecharsky and Gschneidner[1] have discovered that an as-cast $Gd_5Ge_2Si_2$ alloy, produced from high pure Gd (99.9 at.% with respect to all other elements), presents GMCE around 276 K. It is evident that this alloy and others of the $Gd_5(Si_xGe_{4-x})$ family are some of the most studied materials for use in magnetic refrigeration at room temperature. However, Pecharsky e Gschneidner reported that the GMEC is strongly dependent of the purity of the Gd. Furthermore, they asseverate that alloy melt congruently. In this work, it is showed a new alternative to the use of high pure Gd, with the use of suitable annealings on $Gd_5Ge_2Si_2$ alloy produced from commercially available Gd (99.8 at.%). The results show that the MCE to the annealed alloy is similar to that observed for that produced from high pure Gd. Furthermore, the as cast alloy presents a binary microstructure what is in disagreement with the congruent melting reported by those authors.

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Article presented at the XV CBECIMAT, Natal - RN, November/2002

2. Experimental

The alloys were prepared by arc melting of the pure constituents (Gd = 99.8 at.%, Si and Ge both > 99.99 at.%) in an argon atmosphere under normal pressure. Each ingot had the total weight of ~ 5 g and was arc melted 4 times, being the button (the form of the ingot) turned over each time to ensure sample homogeneity. All alloys were initially examined in the as-cast condition. The heat treatment of some alloys was carried out in an induction furnace in a pressure of 1 atm for 48 h at 1650 °C. After the heat treatment the alloy was cooled as quickly as possible by shutting down the power to the induction coil. Some authors[4] believe that heat treatment is appropriated to remove the C and O present in the commercial Gd. This can result in better magnetic properties for the heat treated alloys than that verified for the as-cast alloy.

The microstructural and magnetic properties of both as-cast and heat-treated alloys were established using the following experimental techniques: optical metallography, microprobe analysis by Wavelength Dispersive Spectroscopy (WDS) method, X-ray diffraction patterns and magnetic measurements (magnetization *vs.* temperature e magnetization *vs.* applied magnetic field). The X-ray powder diffraction analysis was carried out on a Philips diffractometer equipment, model PW 1830, using Cu-Kα radiation at room temperature. The X-ray diffraction patterns were collected between 20 and 60° (2 θ) with a step in data collection of 0.02°. The microprobe analysis of the metallographically polished samples was carried out in a LEO device, model 430 i. Magnetic measurements included dc magnetic susceptibility measured between 200 and 350 K (M × T), and the isothermal magnetization in the vicinity of the magnetic phase transitions in dc magnetic fields varying from 0 to 70 kOe (M × H). Magnetic measurements were carried out using a Quantum Design dc magnetometer model MPMS XL. The magnetocaloric property was calculated from the isothermal magnetization (ΔS_M) data.

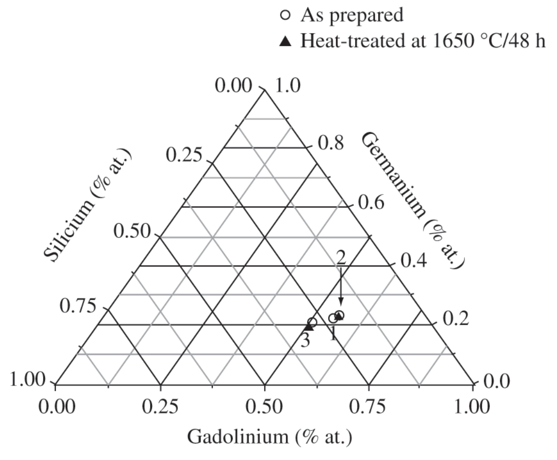


Figure 1. Ternary diagram representation of the composition of phases measured by microprobe analyses for the as-prepared alloy and heat-treated alloy, where (1) is the global composition of the alloys, (2) is the matrix phase and (3) represents the minority phase.

3. Results

The optical microscopy revealed that the as-cast and heat-treated alloys present two-phase microstructures. It is observed the existence of two clear differences between the microstructure of those alloys. First, the presence of some oxide of Gd in the as-cast alloy and second, the amount of minority phase into the heat-treated alloy is smaller than into the as-cast alloy. Moreover, the compositions of the majority phases are $Gd_5Ge_2Si_{1.84}$ (heat-treated) and $Gd_5Ge_{2.07}Si_{1.81}$ (as-cast). For the minority phase the compositions obtained are $Gd_5Ge_{1.89}Si_{2.91}$ (heat-treated) e $Gd_5Ge_{2.04}Si_{2.73}$ (as-cast). Those results are plotted in a ternary diagram showed in Fig. 1.

The composition of the matrix is next to the global composition of the alloy ($Gd_5Ge_2Si_2$) that confirms the production method was adequate. Furthermore, has been noted that the compositions of the phases into both alloys are similar to one another, but the magnetic properties are very different, as will be showed. Another important verification is the confirmation of the Si-rich phase (point 3 in Fig. 1) that was not reported before in literature.

Although electronic and optical metallography indicates the presence of 2 phases into the microstructure of the as-cast alloy, M × T measurements for that alloy showed only one ordered magnetic phase whose Curie temperature (T_C) is 300 K. This Tc is in good agreement with the Tc of the second order magnetic phase reported in literature[1]. After annealing, is observed a new magnetic transition around 275 K, which is the temperature of the first order magnetic transition of the $Gd_5Ge_2Si_2$ alloy. We observed that for longer heat treatments, the signal of the first order transition becomes

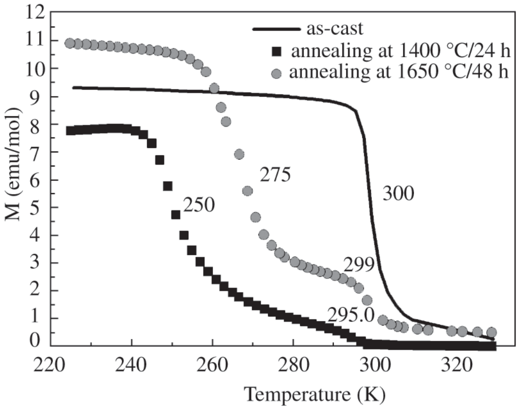


Figure 2. Comparison between the M *vs.* T curves at H = 200 for the as-cast and heat-treated alloys.

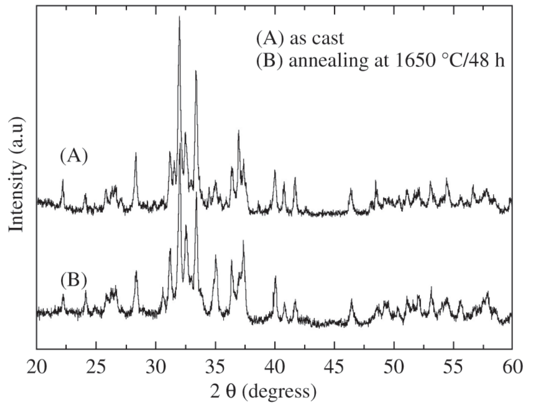


Figure 3. Comparison between the X-ray diffraction patterns for the as-cast and heat-treated alloy (45 kV, 30 mA, Cu-Kα).

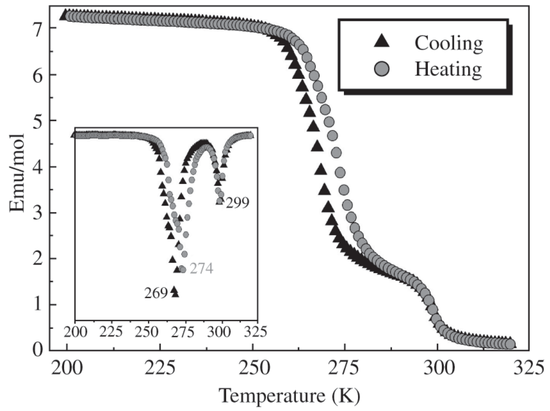
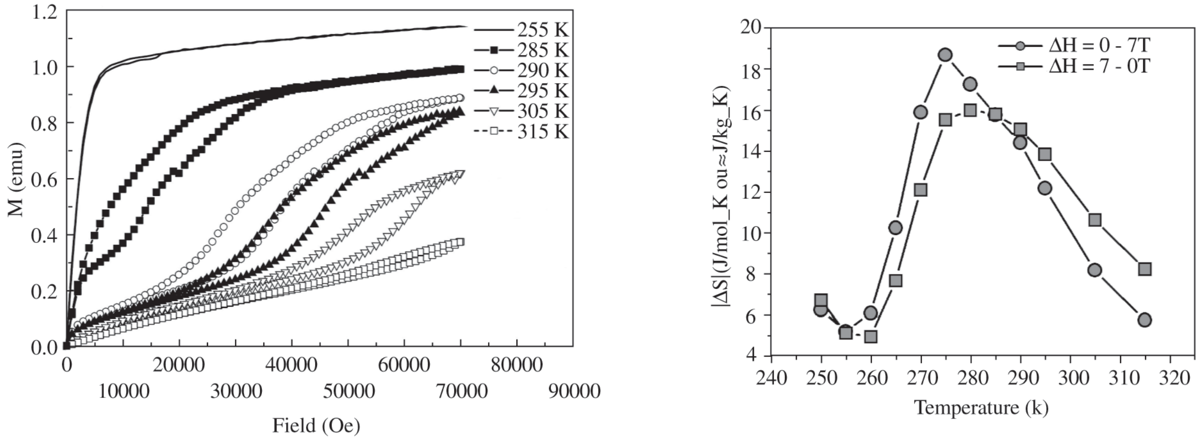


Figure 4. M *vs.* T measurement for the annealed $Gd_5Ge_2Si_2$ alloy.



(a) (b)

Figure 5. M *vs.* H curves a) and the calculated MCE b) for the heat-treated alloy, produced from commercial Gd (99.9% at.).

sharper. We had treated samples at 1400 °C for 24 h and 1650 °C for 48 h. The results are showed in Fig. 2. From now on, our discussion will be centred in heat-treated alloy at 1650°/48 h.

Small deviations between the X-ray diffraction patterns of the as-cast and heat-treated alloys were observed, but both of them present very similar patterns to that of the $Gd_5Ge_2Si_2$ phase (Fig. 3). It is noticed in the X-ray powder diffraction pattern of the as-cast alloy extra Bragg peaks at 31.6, 34.5 and 37.0 degrees (2 θ). Those peaks are observed only for the as-cast alloy, although peaks at 30.6, 35.0 and 37.4 degrees (2 θ) are observed for the heat-treated alloy. The presence of those extra peaks must be related to the other phases into the microstructure of those alloys.

Measurements of the magnetic properties of both as-cast and heat-treated alloys indicated that both are ferromagnetic below 300 K. Figure 4 shows the M × T curves with an applied magnetic field of 200 Oe, for the heat-treated alloy. It's observed a first order magnetic transition at 275 K. The inset graphics present the dM/dT curves and it is used to determinate the magnetic transition temperature with good accuracy.

It's verified two transitions, at 299 K and 274 K. That of higher temperature is a second order transition since it is not verified thermal hysteresis for it. On other hand, the low temperature transition presents a hysteresis of 5 K between the heating and the cooling curve, which confirms it is a first order transition.

In Fig. 5a, it is showed that the magnetic hysteresis and the magnetic moment are higher in the vicinity of the first order transition temperature (275 K). Furthermore, the MCE ΔS_M (isothermal magnetic entropy change) value of the higher peak, 19 J/kg-K (Fig. 5b), is similar to that reported by Peacharsky and Gschneidner[5] for the alloy produced from high pure Gd, 23 J/kg-K, for ΔH = 0-7 T.

4. Conclusions

The as-cast $Gd_5Ge_2Si_2$ alloy, produced from commercial Gd (99.9 at.%), presents a two-phase microstructure that is in disagreement with the reported results for this material. Furthermore, the matrix has a composition near of the global concentration of alloy and no first order magnetic transition, also in disagreement with data reported in literature. The heat-treatment at 1650 °C for 48 h yields a two-phase microstructure with the matrix composition similar to that of the as-cast alloy, but now it is verified a very intense first order magnetic transition at 275 K. This fact proves that the annealing yield a microstructure change with a very important influence on the magnetic properties of that material. Besides that, the MCE value for the heat-treated alloy with commercial Gd is very similar to that for the as-prepared alloy with high pure Gd. These results indicate that an appropriate annealing on the $Gd_5(Ge_{4-x}Si_x)$, based alloys can be an excellent alternative to the use of high pure Gd to obtain GMCE in those materials.

Acknowledgments

The authors are grateful to Fundação Araucária (process number 3108) and to Fapesp (process number 00/13776-7) by the financial support. We are still grateful to Mrs. Cleusa Barnabé, by preparating of the metallographic samples.

References

1. Pecharsky, V.K.; Gschneidner Jr., K.A. *Phys. Rev. Lett.,* v. 78, n. 23, p. 4494-4497, 1997.
2. Warburg E. *Ann. Phys.*, v. 13, p. 141-146, 1881.
3. Gschneidner, Jr., K.A.; Pecharsky, K.A. *J. Appl. Phys.*, v. 85, n. 8, p. 5365-5368, 1999.
4. Pecharsky, A.O.; Gschneidner, K.A.; Pecharsky, V.K.; Schindler, C.E. *personal communication,* 2001.
5. Spichkin, Y.I.; Pecharsky, V.K.; Gschneidner, Jr., K.A. *J. Appl. Phys.*, C. 89, n. 3, p. 1738-1745, 2001