BONDED INTERMETALLIC POWDERS FOR THE APPLICATION IN MAGNETIC REFRIGERATION.

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Introduction.

Magnetocalorics (MC) are materials that show a magnetocaloric effect (MCE), which is defined as the heating or cooling of a magnetic material in response to the application of a magnetic field. Most magnetic materials exhibit a large MCE only at low temperatures, making them unsuitable for practical use in everyday life. But with the discovery of the giant MCE in $Gd_5Si_2Ge_2$ in 1997 by Pecharsky and Gschneidner[1], magnetic refrigeration (MR) became a viable and promising technology, which could become competetive with vapor cycle refrigeration. $Gd_5Si_2Ge_2$ is a ferromagnetic material with a spontaneous ordering temperature of 276 K.

In recent years, much research has been carried out to find new materials with higher MCEs around room temperature, with the goal of making the first magnetic refrigerator. Because such an apparatus must be small, energetically favorable and economically justified, we need MC materials that are not too expensive, are easy to produce and have a high MCE so that they can be operated using permanent magnets in the room-temperature region. However, $Gd_5Si_2Ge_2$ magnetocaloric material as such cannot be used for practical application due to the high hysteresis losses.

In 2004 Provencano[2] reported a reduction of hysteresis losses in $Gd_5Ge_2Si_2$ by adding a small amount of iron to the alloy, forming $Gd_5Ge_{1.9}Si_2Fe_{0.1}$. The peak magnetic entropy change of the new material shifted from 275 K to 305 K, broadening its width, but reducing its value drastically. The purpose of our investigation was to find a compromise of both properties with a systematic study.

Experimental.

We have investigated a wide range of Fe substitutions of the $Gd_5Si_2Ge_2$ magnetocaloric alloy with the aim to quantitatively clarify the effect of iron with respect to the reduction in entropy and hysteresis losses. Our activity was focused on substituting both elements (Si and Ge) with Fe ($Gd_5Si_{2-Z/2}Ge_{2-Z/2}Fe_Z$). We were looking for a possible explanation for the interesting magnetic properties of the newly formed $Gd_5(Si,Ge)_3$ phase. All three systems X for the Si, Y for the Ge and Z for the Si/Ge substitutions were compared in a systematic approach. The same starting materials were used and the same processing method. After arc melting the samples were heat treated at 1300 °C for 1h in an Ar atmosphere and characterized. The microstructures were observed by optical microscopy and analyzed by scanning electron microscopy (FEG SEM) equipped by EDS. The XRD patterns for the low-temperature measurements were collected with an X-ray diffractometer using Mo-K radiation with a nitrogen cold finger attached. The XRD patterns at room temperature were collected with an X-ray diffractometer using Co-K radiation[3, 4]. The magnetic properties were measured on a Physical Properties Measuring System (PPMS), with a vibrating-sample magnetometer attachment. To determine the MCE and the hysteresis losses, the magnetization was measured at discrete magnetic field values between 0 and 2 Tesla at constant temperature. This procedure was then repeated at different temperatures above and below the Curie point of each sample. From the magnetic measurements, the ΔS_M was calculated using Maxwell's relation.

Results and Discussion.

We found that Fe has defferent effects on the T_C, depending on whether it substitutes for Ge or Si. We also found that it produces a $Gd_5(Ge,Si,Fe)_3$-type phase with a T_C at approximately 110K. Substituting Ge with Fe was found to reduce the hysteresis losses almost to zero; substituting Si with Fe was somewhat less effective, because it tended to maintain the first-order transition. Our TEM studies revealed the presence of features not reported previously, such as amorphous regions, dislocations, planar faults and crystallographically related grains (Fig. 1). The results of our studies suggest that there is much more to discover about magnetocaloric materials, and that some of the problems associated with first-order transitions and hysteresis losses in Gd-Ge-Si materials can be overcome with small compositional modifications involving the substitution of Si with Fe and, to a greater extent, for Ge[3].

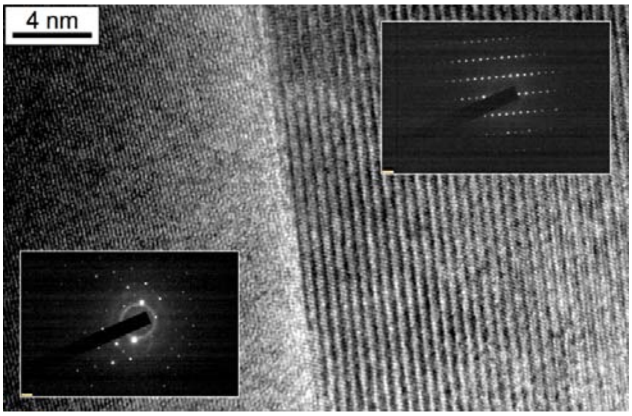

Fig.1. High-resolution TEM micrograph of a grain-boundary region from the sample $Gd_5Ge_2Si_{2-y}Fe0_y$ (Y = 0.25) and the corresponding electron-diffraction patterns.

The final results, which are collected in the diagram of Fig. 2 show that the refrigeration capacity (RC) was optimized with 0.125 % of Fe addition and partial substitution of both Ge and Si. GS alloy can be used at room temperature. The hysteresis losses are drastically decreased with small decrease of net refrigeration capacity (NRC).

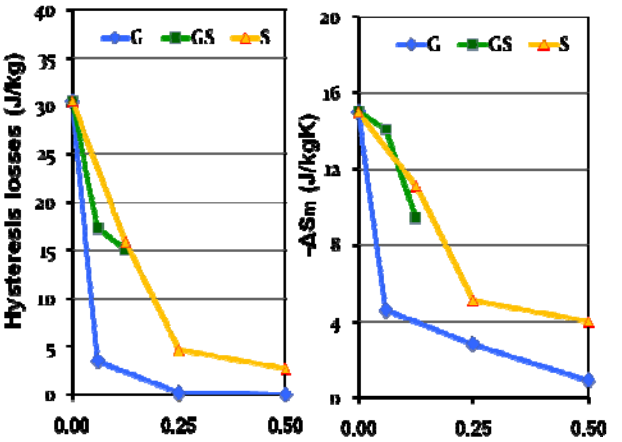

Fig.2. Dependence of the hysteresis losses and entropy change of the amount of Fe addition and the mechanism of substitution.

The final product should not be in the powder form due to the fact that the cooling liquid should pass through the powder and the flow would be too low. The idea is to use the discs, which will rotate in the applied magnetic field. The discs should be mechanically hard, but the amount of the bonding material should be as low as possible to prevent the dilution of the active magnetocaloric material. We used magneto caloric material (MCM) with the best properties achieved and various bonding materials. With the systematic experimental work we wanted to find out which composition gives us the highest density with simultaneously good mechanical strength. The metal particles were mixed from two different fractions: 1/3 of the powders with average particle size of 25 µm and 2/3 with the average particle size of 280 µm. The mixture was homogenized together with the bonding materials. The best results were achieved with the resin RT6000.

Fig. 3. Bonded discs of MCM.

Conclusions.

With the addition of very small amounts of iron and substituting both Ge and Si atoms in basic alloy a ***very high magnetocaloric effect was achieved, comparable to the one reported in previous papers, and with much lower hysteresis losses***. This material could be used in practical application as a bench material for construction of magnetic refrigerators. The goal was to fabricate the material in the shape of bonded sheets and/or discs. The critical problems to overcome are related to achieving the maximum packing density of the effective material and optimising the heat-transfer properties by the correct selection of bonding/binding material, and the dimensions of the sheets or discs. By selecting between various bonding materials the RT6000 resin was found to perform the right properties to fabricate 20 mm/2 mm discs so far (Fig. 3). The final goal is to produce functional magnetocaloric sheets or discs with losses below 1%.

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References:

[1] V. K. Pecharsky and K. A. Gschneidner, Jr. *Phys. Rev. Lett.* **78**, 4494 (1997).
[2] V. Provenzano, A. J. Shapiro, R. D. Shull, Nature 429 (2004), p. 853-857.
[3] B. Podmiljšak, P.J. McGuiness, N. Mattern, H. Ehrenberg, S. Kobe, IEEE Trans. Mag. **45**, 10, (2009) 4364-4367
[4] B. Podmiljšak at al., *J. appl. phys*., 2009, **105**, no. 7, pp. 07A941-1-07A941-3.