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Thermostability of $Sm_2(FeGa)_{17}C_y$ prepared by gas-solid reaction (GSR)

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The gas-solid-reaction (GSR) was used to introduce interstitial carbon atoms into $Sm_2Fe_{17-x}Ga_x$ compounds with $x=0$, 0.5, 1, and 2. For this process, powders made from homogenized ingots were annealed at 500 °C under methane for different times. The thermostability increases for small amounts of Ga and the investigation shows that $Sm_2Fe_{16.5}Ga_{0.5}C_y$ is stable up to 750 °C. In the case of $Sm_2Fe_{15}Ga_2C_y$ carburized for 6 h ($y=2.0$) and 18 h ($y=2.2$), the x-ray diffraction patterns show the Th_2Zn_{17}-type structure only. After annealing at 800 °C for 20 min the 6 h carburized sample shows a small amount of α-Fe and other phases and there is a large Fe content after annealing at 850 °C. For an 18 h carburized sample, less Fe and no other phases have be seen after annealing at 800 °C, i.e., the material is nearly single phase. The result that longer carburization times stabilize the Th_2Zn_{17}-type structure could also be manifested by Kerr microscopy. A comparison with mechanically alloyed $Sm_2Fe_{15}Ga_2C_2$ powders prepared with Sm excess shows that those are very stable up to 900 °C. The density of fine-grained $Sm_2Fe_{17-x}Ga_xC_y$ could be increased by hot pressing, but the degree of compaction and the phase purity very sensitively depend on the Ga content. [S0021-8979(97)27508-0]

I. INTRODUCTION

In recent years there have been intensive efforts to use the good intrinsic properties of $Sm_2Fe_{17}N_y$ and $Sm_2Fe_{17}C_y$ compounds ($y>2$) for new permanent magnet materials. High values of coercivity could be obtained using different preparation methods as mechanical alloying,[1] melt spinning,[2] Zn bonding,[3] intense milling,[4] and hydrogenation disproportionation desorption recombination (HDDR).[5] However, high temperature procedures for making magnets with a high density cannot be applied because $Sm_2Fe_{17}(N,C)_y$ shows a weak thermal stability. It was found that a significant improvement in stabilization of $Sm_2Fe_{17}C_x$ could be achieved by the partial substitution of Fe by Al, Ga, or Si.[6,7] $Sm_2Fe_2Ga_2C_y$ powders produced by intense milling[8] or mechanical alloying[9] have been used successfully to make magnets with a high density by means of hot pressing. A higher Ga content gives a better thermostability, but simultaneously the saturation polarization decreases due to the dilution effect. Therefore, the optimization of the Ga content is a central point for achievement of a high thermostability and good permanent magnet parameters. In this context the influence of the Ga content was investigated in this article.

II. EXPERIMENT

$Sm_2Fe_{17-x}Ga_x$ alloys with $x=0$, 0.5, 1, and 2 were melted in an induction furnace and then homogenized at 1050 °C for one week. Powder from these alloys was produced by means of (i) ball milling up to 300 min and (ii) HDDR[5] at 720 °C to 750 °C. To introduce the interstitial carbon atoms the powder was annealed under methane at 450 °C (after HDDR) and at 500 °C (after milling) for times up to 18 h. For comparison powders were also prepared by mechanical alloying (cf. Ref. 1). Subsequent heat treatments were performed in purified argon gas. The phases were determined by x-ray diffraction (XRD) with Co $K\alpha$ radiation. Structural changes were also investigated by differential scanning calorimetry (DSC). The degree of carburization was visualized by Kerr microscopy. The carbon content was determined by the weight gain of annealed powder and by heat extraction using the combustion method. $Sm_2Fe_{17-x}Ga_xC_y$ powder was hot compacted in a die press at temperatures up to 900 °C at a pressure of about 300 MPa in argon or vacuum. Magnetic hysteresis curves were measured with a vibrating sample magnetometer (VSM) at fields up to 8 T.

III. RESULTS AND DISCUSSION

The substitution of Fe in Sm_2Fe_{17} by Ga results in a nearly linear increase of the Curie temperature T_c in $Sm_2Fe_{17-x}Ga_x$ up to $x=2$ as shown in Fig. 1. On the other hand, T_c of $Sm_2Fe_{17-x}Ga_xC_y$ powder ball-milled for 200 min and carburized at 500 °C for 6 h decreases with increasing Ga content x. This may be due to the decrease of the

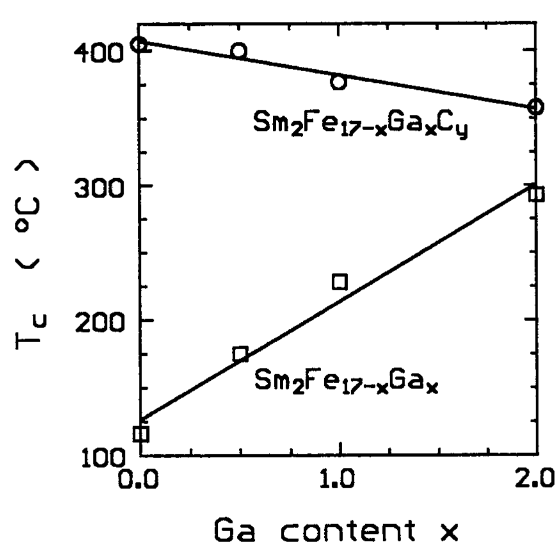

FIG. 1. Dependence of the Curie temperature T_c of $Sm_2Fe_{17-x}Ga_xC_y$ on the Ga content before and after carburization at 500 °C for 6 h.

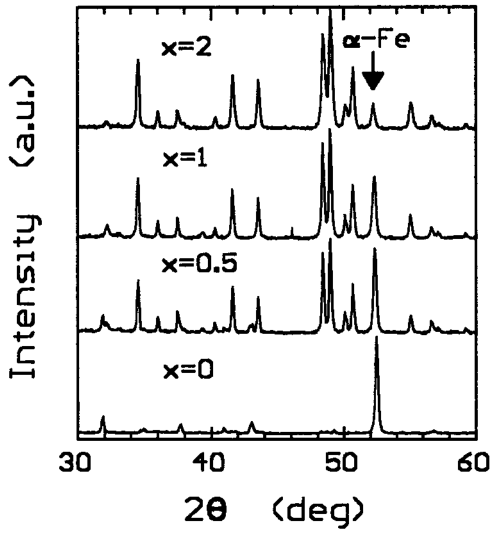

FIG. 2. Influence of the Ga content on the decomposition of $Sm_2Fe_{17-x}Ga_xC_y$ carburized at 500 °C for 6 h and annealed at 800 °C for 20 min.

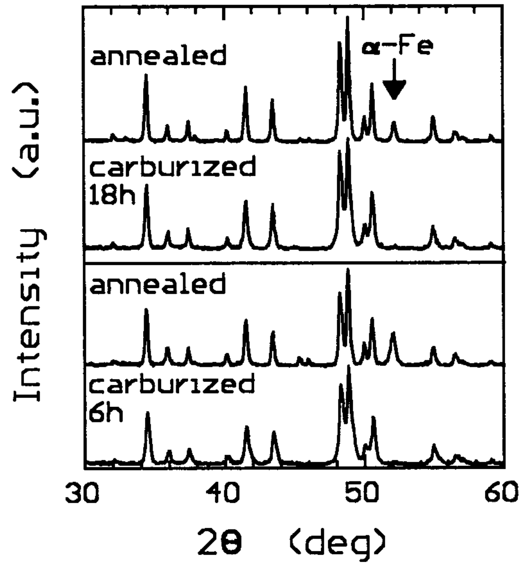

FIG. 3. Enhancement of the stability by carburization. The α-Fe content of annealed $Sm_2Fe_{15}Ga_2C_y$ powder (at 800 °C for 20 min) is larger after carburization at 500 °C for 6 h ($y=2.0$) than for 18 h ($y=2.2$).

carbon content in $Sm_2Fe_{17-x}Ga_xC_y$ from $y=3$ for $x=0$ to $y=2$ for $x=2$. This is probably caused by the slower diffusion rate of carbon atoms in the presence of Ga or an improved stability of the compounds with a higher Ga content. For melt spun $Sm_2Fe_{17-x}Ga_xC_{1.5}$ an increase of T_c from about 283 to 361 °C for an increasing Ga content from 0 to 2 was found for a fixed carbon content $y=1.5$.[10]

The improvement of stability by Ga also follows from the results shown in Fig. 2. The XRD patterns show the influence of annealing at 800 °C for 20 min on the reflections of $Sm_2Fe_{17-x}Ga_xC_y$ carburized at 500 °C for 6 h. $Sm_2Fe_{17}C_y$ was completely destroyed and only the α-Fe reflex is clearly visible. Due to the increasing Ga content the intensity of the α-Fe peak diminishes and the Th_2Zn_{17}-type reflections are sharper as evidence for the increased thermostability. To better understand the structural changes in $Sm_2Fe_{17-x}Ga_xC_y$ an annealing procedure at 800 °C for 20 min under argon was performed. Figure 3 shows the results for ball-milled $Sm_2Fe_{17-x}Ga_xC_y$ powder carburized for 6 and 18 h. The XRD patterns only reveal the Th_2Zn_{17}-type structure for the as-prepared samples. A small enhancement of the C content from $y=2.0$ to 2.2 in these samples due to the longer carburization time can be recognized by the increased sharpness of the reflections. After annealing the 6 h-carburized sample already has a small amount of Fe and other phases. The Fe content increases further after annealing at 850 °C. For the 18 h-carburized sample less Fe and nearly no other phases can be seen after annealing at 800 °C, i.e., the higher carbon content stabilizes the Th_2Zn_{17}-type structure. The different influence of high-temperature annealing on the material after various carburization times could also be visualized by Kerr microscopy.

The domain pattern of a $Sm_2Fe_{15}Ga_2$ grain shown in Fig. 4(a) indicates a magnetically uniaxial anisotropy caused by the addition of Ga. The magnetically easy direction is nearly aligned perpendicular to the sample surface. Large grains are only partially carburized after annealing in methane at 500 °C for 6 h because of the slow diffusion, as can be seen on the inhomogeneous domain structure in Fig. 4(b). In the outer range of the grain the typical domain structure of magnetically highly anisotropic $Sm_2Fe_{15}Ga_2C_y$ is visible. Figure 4(c) shows the domain structure of a grain completely carburized at 500 °C for 18 h. Additionally the defocused picture of domains at the grain center [cf. Fig. 4(b)] reveals that the easy magnetization direction deviates from the c axis and rotates partially in plane because of the smaller anisotropy in comparison with the outer regions. This is evidence for the

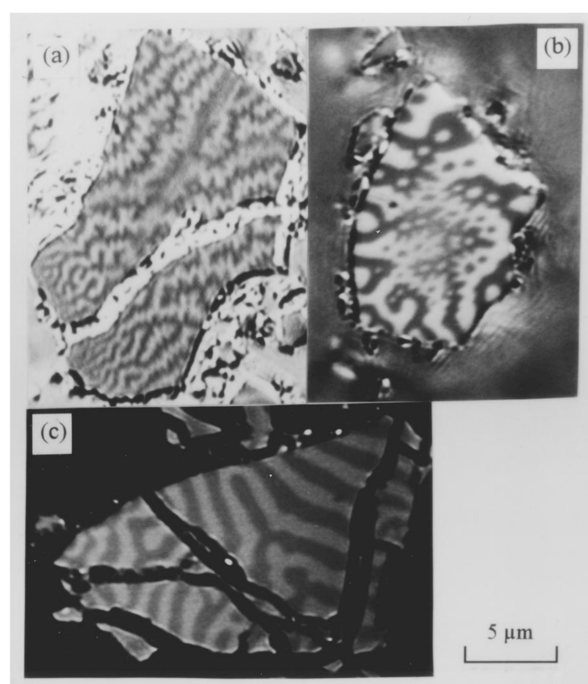

FIG. 4. Domain structure of $Sm_2Fe_{15}Ga_2C_y$ particles (a) before ($y=0$) and after carburization at 500 °C for (b) 6 h ($y=2.0$) and (c) 18 h ($y=2.2$).

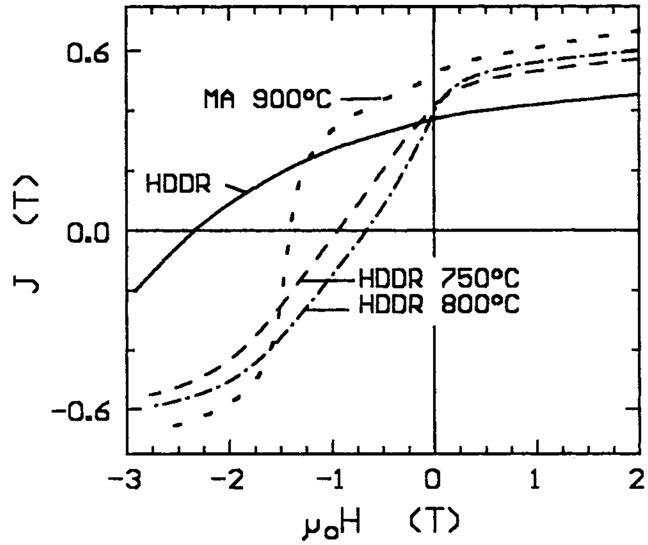

FIG. 5. Demagnetization curves (calculated with the real densities of the samples) of carburized HDDR $Sm_2Fe_{16.5}Ga_{0.5}C_y$ powder before and after hot pressing at 750 °C and 800 °C in comparison with the curve of a hot pressed $Sm_2Fe_{15}Ga_2C_2$ magnet (900 °C) made from mechanically alloyed powder.

smaller anisotropy in $Sm_2Fe_{15}Ga_2$. Furthermore, Fig. 4(c) reveals that completely carburized grains of larger dimension were destroyed into smaller parts because of volume increase due to the introduction of carbon atoms.

The ball milled $Sm_2Fe_{17-x}Ga_x$ powders carburized as described above have only small coercivities up to $\mu_{0J}H_c \approx 0.6$ T for all investigated Ga contents. This may be due to their grain size of about 3–10 μm. After the hot compaction of powders with $x=0.5$ and 1 at a pressure of 300 MPa and a temperature of 750 °C only small values of density ($\rho \approx 6.0$ g/cm^3) and coercivity ($\mu_{0J}H_c \approx 0.15$ T) were obtained due to a partial decomposition of material. To produce $Sm_2Fe_{17-x}Ga_xC_y$ magnets with a higher coercivity the HDDR process[5] was used for preparation of powders with Ga contents $x=0.5$, 1 and 2. These investigations have shown that the intensity of the hydrogenation disproportionation as the first part of HDDR is decreased with increasing Ga content. For $x=2$ a very large part of nondecomposed Th_2Zn_{17}-type structure was found in the material. A complete HDDR process could only be performed for Ga contents equal or less than 0.5. The gallium in $Sm_2(Fe,Ga)_{17}$ seems to stabilize the Th_2Zn_{17}-type structure with respect to the hydrogen assisted disproportionation as well as the introduction of carbon. Figure 5 shows demagnetization curves of different magnets prepared from this $Sm_2Fe_{16.5}Ga_{0.5}$ powder after a carburization at 500 °C for 6 h. The cold compacted magnet ($\rho=4.7$ g/cm^3) has a coercivity of 2.3 T. By means of hot pressing at 750 °C and 800 °C and a pressure of 300 MPa for 2 min the density could only be enhanced to about $\rho=5.5$ g/cm^3. Then the coercivity has decreased to 1 and 0.7 T, respectively, after these procedures. Magnets with higher densities up to 6.7 g/cm^3 could be made by hot pressing of HDDR powder with a low Ga content, but the coercivity is significantly reduced due to the decomposition of material. These results confirm the decrease in thermostability of material for a small Ga content. The values of coercivity and density obtained for this HDDR material are low in comparison with those obtained for mechanically alloyed $Sm_2Fe_{15}Ga_2C_2$ hot pressed immediately after milling at 900 °C and a pressure of 300 MPa for 5 min. The hot pressing resulted in a nearly full density of 7.77 g/cm^3 and a remanence of 0.55 T for this nontextured material. In addition a coercivity of 1.4 T was measured after this high-temperature treatment revealing the good thermostability of this compound. The magnetic properties of the carburized HDDR powder were destroyed due to decomposition of $Sm_2Fe_{16.5}Ga_{0.5}C_{2.9}$ during hot pressing. In the XRD patterns a higher Fe content was found for these materials in comparison with the state after carburization, possibly due to evaporation and oxidation of Sm. The mechanically alloyed $Sm_2Fe_{15}Ga_2C_2$ powder was prepared with a Sm excess of 30 wt % as a balance for Sm losses caused (i) by evaporation during milling and hot pressing and (ii) by oxidation. Against that the stoichiometric material used for HDDR is very sensitive to any additional heat treatment concerning Sm losses and decomposition.

In summary, the structural stability of $Sm_2Fe_{17-x}Ga_x$ increases with x as observed for carburization and HDDR experiments. $Sm_2Fe_{15}Ga_2C_2$ has a good thermostability allowing hot compaction. Hot pressed $Sm_2Fe_{15}Ga_2C_2$ magnets show high values of density and coercivity. HDDR was successfully applied to $Sm_2Fe_{16.5}Ga_{0.5}$. However, high values of density and coercivity could not be achieved for hot compacted $Sm_2Fe_{16.5}Ga_{0.5}C_y$ because of the decomposition of material.

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