Journal of Alloys and Compounds 281 (1998) 60–63

Hydrogenation–disproportionation–desorption–recombination in $Sm_2Fe_{16}M$ (M=Al, Ga and Si) and magnetic properties of their carburized powders

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Abstract

The application of the hydrogenation–disproportionation–desorption–recombination (HDDR) process in $Sm_2Fe_{16}M$ (M=Al, Ga and Si) was investigated. The hydrogen absorption behaviour was studied by temperature–pressure analysis (TPA). In the temperature range between 500 and 800°C, $Sm_2Fe_{16}M$ samples with M=Ga and Si show a weaker hydrogen absorption than $Sm_2Fe_{16}Al$. This was confirmed by X-ray diffraction which showed a complete disproportionation of $Sm_2Fe_{16}Al$ into SmH_z ($1.9<z<2.8$) and α-(Fe,Al), while $Sm_2Fe_{16}Ga$ and $Sm_2Fe_{16}Si$ exhibit a fraction of undecomposed material with the Th_2Zn_{17}-type structure after the disproportionation procedure. These results point to a stabilization of $Sm_2Fe_{16}M$ against disproportionation by hydrogen for M=Ga and Si. The magnetization processes of carburized HDDR powders were studied by VSM measurements and Kerr microscopy. The demagnetization curve of our HDDR processed $Sm_2Fe_{16}AlC_y$ is well shaped, whereas those of $Sm_2Fe_{16}GaC_y$ and $Sm_2Fe_{16}SiC_y$ show a large decrease of the polarization at low fields. The favourable behaviour of $Sm_2Fe_{16}AlC_y$ is due to a homogeneous submicron grain structure. In $Sm_2Fe_{16}GaC_y$ and $Sm_2Fe_{16}SiC_y$ samples, an additional, magnetically soft phase with larger domains was observed which causes the low coercivity. As a consequence, HDDR was only favourable for the preparation of $Sm_2Fe_{16}MC_y$ hard magnets with M=Al but not for M=Ga and Si. Optimization of the HDDR process in $Sm_2Fe_{16}Al$ and subsequent nitrogenation or carburization led to coercivities of $\mu_0\,{}_jH_c=2.9$ and 2.5 T, respectively.

Keywords: HDDR; High coercivity; Hydrogen absorption; Sm_2Fe_{17}

1. Introduction

Rare earth–iron compounds with uniaxial crystal structure and high Fe content are candidates for permanent magnets due to their magnetocrystalline anisotropy and relatively low costs. The intrinsic magnetic properties of such materials with 1:12-, 2:17- or 3:29-type structure can be improved drastically by an interstitial modification with nitrogen or carbon [1–3]. A major drawback of these materials is their relatively low thermal stability. For $Sm_2Fe_{17}C_y$ it was shown that a partial substitution of Fe by Al [4], Ga [5] or Si [6] leads to an enhanced thermal stability, making possible the application of high temperature processing such as hot pressing (e.g., $Sm_2Fe_{15}Ga_2C_2$ [7]). Successful methods for preparing fine grained, highly coercive powders with this composition are rapid quenching [4–6], mechanical alloying [7] and intense ball milling [8]. Another, very effective method for magnetic hardening is the application of the hydrogenation–disproportionation–desorption–recombination (HDDR) process [9,10] prior to nitrogenation or carburization. A first study on $Sm_2Fe_{17-x}Ga_x$ compounds showed that the HDDR process converts the whole material into a fine grained material only for samples with a Ga content up to $x=0.5$ [11]. In this work the influence on the HDDR process of different substituents for Fe in $Sm_2Fe_{16}M$ (M=Al, Ga or Si) is investigated. Results of magnetic properties of nitrided or carburized HDDR powders will be presented.

2. Sample preparation and characterization

Elemental Fe, Sm and M (M=Al, Ga or Si) were arc melted to form Sm–Fe–M prealloys. These prealloys were melted together with additional Fe in an induction furnace. To reach the nominal composition $Sm_2Fe_{16}M$, a Sm excess of 30% was used in all cases to compensate for the high evaporation loss of Sm. The as-cast alloys were homogenized in Ar-filled quartz tubes at 1050°C for 72 h. Thereafter, the samples were crushed and milled into powders with average particle sizes between 5 and 10 μm.

The HDDR process was performed to obtain a fine grained microstructure within the powder particles. The samples were heated in hydrogen up to 750°C and kept

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0925-8388/98/$ – see front matter
PII: S0925-8388(98)00772-5

there for 30–240 min to allow the hydrogenation and disproportionation of $Sm_2Fe_{16}M$ into SmH_z ($1.9<z<2.8$) and α-(Fe,M). The hydrogen gas was then pumped out and the samples were kept at temperatures between 720 and 800°C to start the hydrogen desorption and the recombination into fine grained $Sm_2Fe_{16}M$ with the 2:17 structure. Finally, the samples were carburized in CH_4 at 500°C for the rather long time of 16 h to guarantee complete carburization. Nitrogenation was carried out in N_2 at 500°C for 5 h.

In order to find the optimum conditions for the hydrogen absorption a TPA was carried out by heating the powder samples at a starting hydrogen pressure of 600 mbar from 200 to 900°C. The hydrogen absorption behaviour was thereby observed. The hydrogen content of the samples kept at 200°C in hydrogen for 30 min was determined by a hot extraction method.

Changes of the crystallographic structure of the samples were observed by X-ray diffraction (XRD) with Co Kα radiation. The magnetic microstructure was observed with a digitally enhanced Kerr microscope. Measurements of the hysteresis curve were carried out on epoxy resin bonded powders at room temperature with a vibrating sample magnetometer in an applied field up to 8 T.

3. Process characterization; structural and magnetic properties

3.1. Hydrogen absorption behaviour

TPA curves of as-milled samples are shown in Fig. 1. All curves are normalized according to their sample weights and starting pressures at 200°C. At the starting temperature, the interstitial phase $Sm_2Fe_{16}MH_y$ is formed. The amounts of interstitial hydrogen in the $Sm_2Fe_{16}M$ powders kept at 200°C in hydrogen for 30 min were determined by hot extraction. The measured values were 3.4, 3.7 and 3.9 hydrogen atoms per formula unit of the parent alloy, $Sm_2Fe_{16}M$, for M = Si, Ga and Al, respectively. The pressure increase in the TPA curves at lower temperatures from 200°C to approximately 500°C is caused mainly by the desorption of the interstitial hydrogen. The smaller pressure increase for $Sm_2Fe_{16}Si$ and $Sm_2Fe_{16}Ga$ compared to that of $Sm_2Fe_{16}Al$ points to a smaller interstitial hydrogen content in these samples. Although the accuracy of both TPA and hot extraction is limited due to the varying surface conditions influencing the interstitial absorption and desorption, the results show a similar tendency. At the maximum pressure between 500 and 600°C the interstitial hydrogen is almost completely removed. The rapid and large pressure drop for further increasing temperature for $Sm_2Fe_{16}Al$ indicates strong hydrogen absorption caused by the disproportionation reaction. For $Sm_2Fe_{16}Ga$ this pressure drop is less pronounced, for $Sm_2Fe_{16}Si$ it is the smallest. This indicates incomplete disproportionation of the Ga- and Si-containing samples. The temperature of the highest hydrogen absorption rate was derived from the maximum slope of the pressure vs. temperature curve. We found values of 640, 655 and 700°C for M = Al, Ga and Si, respectively. The ordering of these temperatures points also to an increasing stability against disproportionation by hydrogen, if one goes from Al over Ga to Si substitution. According to the TPA results, the $Sm_2Fe_{16}M$ samples were kept in a hydrogen atmosphere at 720°C for 60 min (M = Al), at 750°C for 145 min (M = Ga) and at 800°C for 160 min (M = Si) to perform hydrogenation and disproportionation.

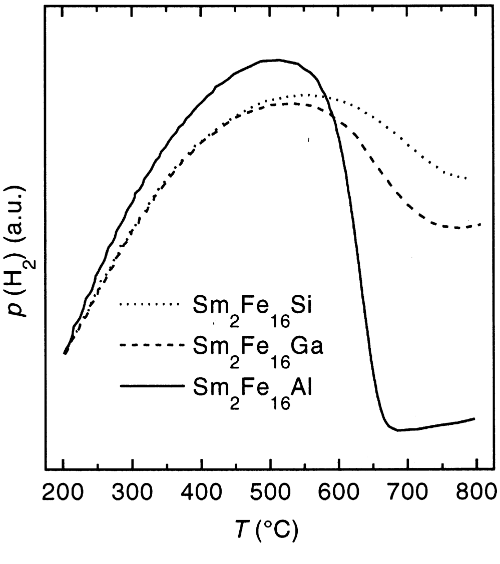

Fig. 1. Normalized TPA curves for $Sm_2Fe_{16}M$ (M = Al, Ga and Si) in hydrogen atmosphere for a heating rate of 6.4°C min^{-1}. The Ga- and Si-containing samples exhibit a much weaker hydrogen absorption than the Al-containing sample.

The XRD patterns of the samples after hydrogenation and disproportionation are shown in Fig. 2. In agreement with the TPA measurements, only $Sm_2Fe_{16}Al$ shows a complete disproportionation into SmH_z and α-Fe, whereas $Sm_2Fe_{16}Ga$ and $Sm_2Fe_{16}Si$ show remains of the Th_2Zn_{17}-type structure peaks. Therefore, the hydrogen absorption properties as well as the crystallographic data show that Si and Ga tend to stabilize the 2:17-type phase against disproportionation by hydrogen, while Al has the least inhibiting effect on this reaction.

3.2. Magnetic properties

A HDDR process was carried out for all samples. XRD patterns of subsequently carburized HDDR samples show no significant differences in the crystal structure, but the demagnetization curves (Fig. 3) exhibit different shapes. The demagnetization curve of $Sm_2Fe_{16}AlC_y$ is relatively well shaped and exhibits a high coercivity $\mu_0\,{}_jH_c$ of 2.4 T. The curves of $Sm_2Fe_{16}MC_y$ with M = Ga and Si, on the other hand, show the typical behaviour of a two-phase

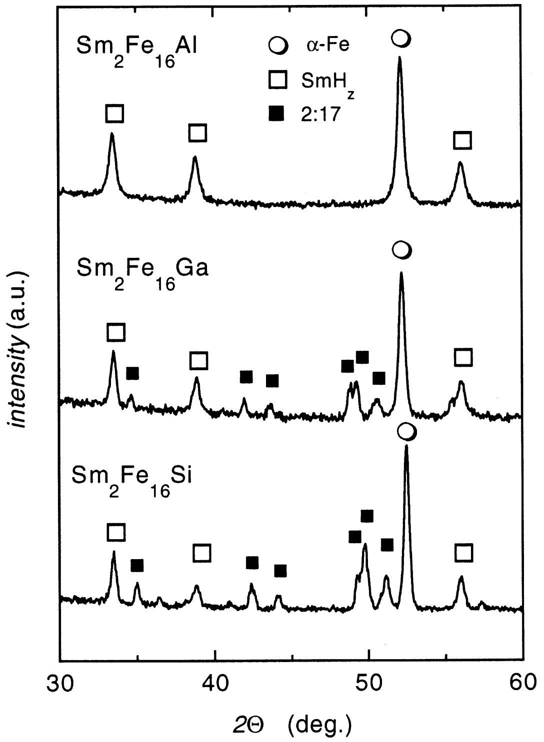

Fig. 2. X-ray diffraction patterns of the HD treated materials. While the Al-substituted material is disproportionated completely into α-Fe and SmH_z, the Ga- and Si-containing materials also show peaks due to the 2:17 phase.

material containing a magnetically softer phase leading to a rapid decay of the magnetization at low fields $H \leq 0.5$ T, and a harder phase leading to a slow saturation at high fields. For comparison, a demagnetization curve of non-HDDR treated $Sm_2Fe_{16}GaC_y$ is also shown. The curves for the Al and Si material in this state are quite similar.

The magnetization processes responsible for these different curve shapes were investigated by Kerr microscopy. Fig. 4a shows a difference image of different magnetization states of $Sm_2Fe_{16}AlC_y$ powder particles at zero field and -1 T (the maximum available field). Due to the fine grained microstructure, caused by the HDDR process, this material shows only very few and small regions with changed magnetization (white or black spots, visible in the magnification of a typical particle in Fig. 4b). The grain boundaries suppress long and easily moveable walls. In this way a high coercivity is achieved. The difference image of $Sm_2Fe_{16}GaC_y$ powder particles in Fig. 4c exhibits, in several particles, larger regions where the magnetization can be reversed at low fields. These regions are probably related to coarse grained regions in the interior of the powder particles, which were not disproportionated during the HDDR treatment (compare Fig. 2). The demagnetization of this magnetically softer volume fraction is responsible for the fast decrease of the magnetic polarization at lower fields ≤ 0.5 T (see Fig. 3). The magnetically harder phase of the fine grained volume fraction of the particles causes the slow saturation in the demagnetization curve. The difference image of $Sm_2Fe_{16}SiC_y$ powder particles in Fig. 4d shows particles with classical domain patterns characteristic for a magnetically uniaxial material. Depending on the relative orientation of the easy axis with respect to the surface, everything between maze and stripe domains can be found. No fine grained regions were seen in these particles, because of a more incomplete disproportionation during the HDDR procedure. Correspondingly, the demagnetization curve of

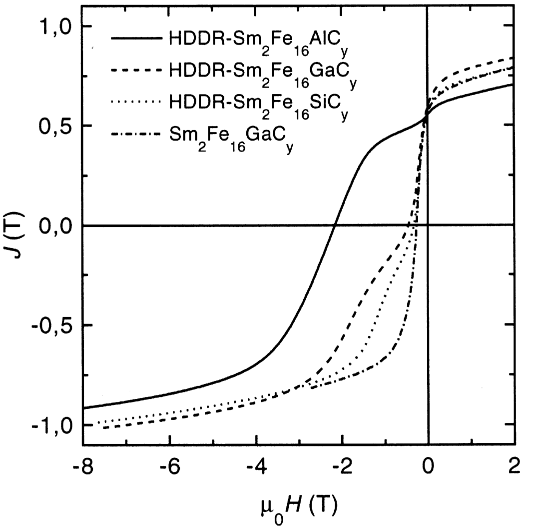

Fig. 3. Demagnetization curves (DMC) of the investigated materials. The Al-substituted material has a well shaped DMC and a high coercivity. In the Ga- and Si-containing samples a fraction of some soft magnetic phase causes a rapid drop of the polarization at low fields.

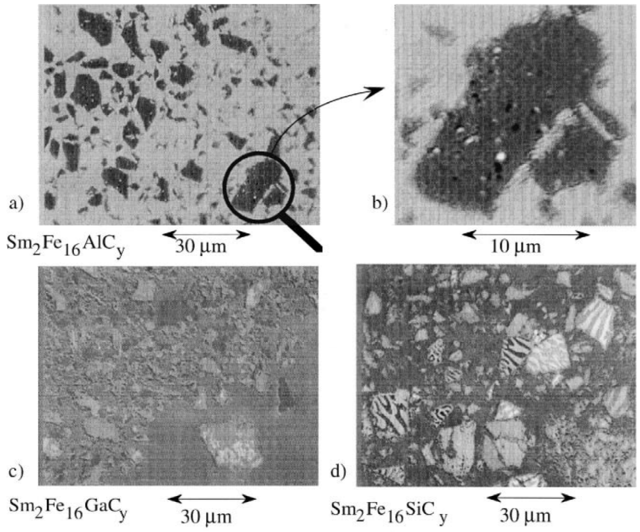

Fig. 4. Kerr observations on $Sm_2Fe_{16}Al$ confirm the nanocrystalline grain structure leading to high coercivity. In $Sm_2Fe_{16}Ga$ and $Sm_2Fe_{16}Si$ larger particles show wide domains which can be magnetized and demagnetized in fields below 1 T.

the Si material has a lower coercivity than that of the Ga-substituted material and the approach to saturation is more rapid (Fig. 3).

Thus, highly coercive material prepared by means of HDDR was only obtained from $Sm_2Fe_{16}AlC_y$. The stabilization of $Sm_2Fe_{16}M$ for M=Ga and Si against the disproportionation by hydrogen excludes the use of these substituents for the standard HDDR process. Optimization of the HDDR process for $Sm_2Fe_{16}Al$ with subsequent nitrogenation or carburization led to the preparation of single-phase magnets with coercivities $\mu_0\, {}_jH_c = 2.9$ T for nitrogenated and $\mu_0\, {}_jH_c = 2.4$ T for carburized samples. Further improvements should be possible by optimization of the milling procedure prior to the HDDR process.

4. Conclusions

In summary, the standard HDDR process is applicable for the preparation of single-phase $Sm_2Fe_{16}MC_y$ hard magnets, with M=Al but not for M=Ga or Si. Coercivities $\mu_0\, {}_jH_c = 2.9$ T for $Sm_2Fe_{16}AlN_y$ and 2.4 T for $Sm_2Fe_{16}AlC_y$ were obtained. The high coercivity of the carburized sample is promising for the preparation of thermally stable $Sm_2Fe_{17-x}Al_xC_y$ powders ($x \geq 1$) by the HDDR process which could be used for the production of fully dense permanent magnets by hot pressing.

Acknowledgements

The first author is grateful for support from the Sächsische Ministerium für Wissenschaft und Kunst. L.C. would like to thank the Alexander von Humboldt Foundation for financial support.

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