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Anisotropic $Sm_2Fe_{17}N_3$ powders prepared by special nitro-hydrogenation

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$Sm_2Fe_{17}N_3$-based powders used for permanent magnets need to contain a minimal amount of secondary phases (SmN and α-Fe). These are the products of the thermal decomposition of the metastable $Sm_2Fe_{17}N_3$ phase and of the reactions between $SmFe_3$ or $SmFe_2$ (if present in the initial alloy) with N_2. It is desirable to produce "clean" $Sm_2Fe_{17}N_3$ single-grain powders to be used for the production of anisotropic magnets. Such $Sm_2Fe_{17}N_3$ powders were prepared by Interstitial Hydrogen Absorption Desorption (IHAD) and subsequent special nitro-hydrogenation and dehydrogenation processes. Sm_2Fe_{17}-based alloys are subjected to cycled IHAD leading to final decrepitation into sub-single grain powders. Nitro-hydrogenation (N_2+H_2) at 400-475 °C produces a $Sm_2Fe_{17}N_3$-hydride which is subjected to preferential dehydrogenation in order to produce the $Sm_2Fe_{17}N_3$. Additional milling causes magnetic hardening with ${}_iH_c$>8 kOe and $(BH)_{max}$ of 36 MGOe, assuming full density.

1. INTRODUCTION

Coey, Hong Sun and Otani [1] were the first to show that the Sm_2Fe_{17}-nitride exhibits good intrinsic magnetic properties and could be used for permanent magnets. Since then, Sm_2Fe_{17}-nitride-based permanent magnets have been produced by several methods such as mechanical alloying [2], rapid solidification [3-5], HDDR [5-6] and powder metallurgy [5]. Basic studies on the reactions between Sm, $SmFe_2$, $SmFe_3$, Sm_2Fe_{17} and H_2 or N_2 gases can be found in the refs. 7 through 14. The present study deals with the $Sm_2Fe_{17}N_3$ anisotropic powders produced by employing special hydrogen and nitrogen treatments and a final milling process.

2. EXPERIMENTAL

The Sm_2Fe_{17}-based alloys were prepared by induction-melting of the constituent elements and subsequent heat-treatment at temperatures of between 1000 and 1200 °C. For the study of the "Sm_2Fe_{17} + H_2 and/or N_2" solid-gas reactions, a constant volume reactor (Isochoro-Thermal Analyzer[7-14] (ITA)) was used which is similar to the thermopiezic analyzer (TPA) used by other researchers (see ref. [1]). Phase analysis was performed by X-ray (CuK_α) powder diffraction (XRD). Hysteresis loops were obtained with a Vibrating Sample Magnetometer (VSM) in fields up to 15 kOe. The final pulverization of the powders was done by hand in air or by ball milling under liquid medium.

3. RESULTS AND DISCUSSION

The process for the production of magnetically anisotropic $Sm_2Fe_{17}N_3$-based powders involves three major steps:

1) The preparation of sub-single grain powders from bulk Sm_2Fe_{17}-based alloys.
2) Saturation of the Sm_2Fe_{17}-based powders with nitrogen producing $Sm_2Fe_{17}N_3$-based powders.
3) Reduction of the size of the $Sm_2Fe_{17}N_3$-based powders to below 5 μm for development of the hard magnetic properties.

3.1. Sub-single grain powders-IHAD process

Sm_2Fe_{17}-based sub-single grain powders can be prepared by ball milling or other higher energy milling processes. Such milling methods can produce particles with high defect densities especially on their surface. Such defects may increase the mobility of the Fe and Sm atoms facilitating the formation of stable α-Fe and SmN during the nitrogenation process. Also, any milling process can introduce a considerable amount of contamination such as oxygen, hydrogen, carbon etc. The amounted defects and contamination have a negative effect on the final magnetic properties as well as on the long-term stability of the magnet-products. Therefore, Sm_2Fe_{17}-based sub-single grain particles should be produced in a way that the defect density and contamination are kept to a minimum. Such a process will be described below and is based on the following observations made during the study of the reactions between the Sm_2Fe_{17} [10] and $SmFe_3$ [9] phases with hydrogen:

1) In the case of Sm_2Fe_{17}-hydride, a reversible Interstitial Hydrogen Absorption and Desorption (IHAD) occurs in the temperature range of 25 and 500 °C. The corresponding volume expansion between Sm_2Fe_{17} and the fully developed hydride ($Sm_2Fe_{17}H_5$) is 3.4 %.

2) In the case of $SmFe_3$-hydride, a reversible IHAD occurs between 25 and 400 °C. The corresponding volume expansion between $SmFe_3$ and the fully developed hydride ($SmFe_3H_4$) is as large as 19 %.

Temperature cycling (between 25 and 500 °C, termed herein as cycled IHAD) of the Sm_2Fe_{17} bulk alloy under hydrogen atmosphere causes its repeated expansion and contraction which results in the formation of cracks (Fig. 1a) mainly along the grain boundaries (intergranularly) and within the grains (transgranularly) up to a certain extent. Under these conditions the bulk alloy retains its integrity (it does not decrepitate) but becomes extremely friable. If a Sm_2Fe_{17} bulk alloy containing very little $SmFe_3$ phase is used instead (Fig. 1b), decrepitation occurs very violently and powders are produced. The huge expansion of the $SmFe_3$ phase introduces stresses within the sample which are relieved by rapture and formation of powders. For alloys containing the $SmFe_3$ phase, the temperature cycling is performed at the maximum temperature of 400 °C in order to avoid decomposition of this phase into α-Fe and Sm-hydride. At the end of the cycled IHAD, hydrogen is desorbed by heating the interstitial hydrides under vacuum at about 150-250 °C.

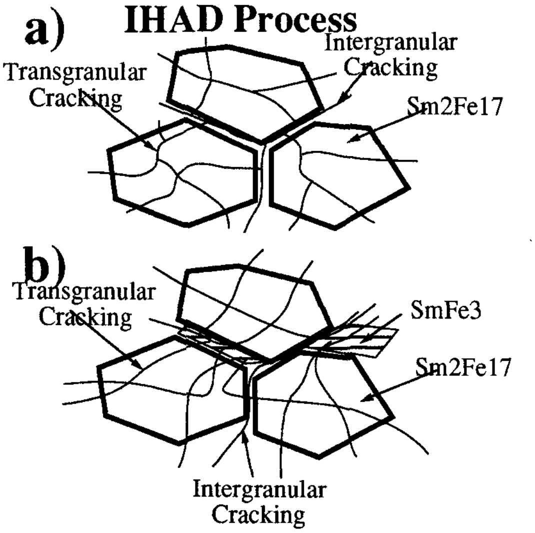

Figure 1. Intergranular and transgranular cracking during the Interstitial Hydrogen Absorption (IHAD) process: a) Sm_2Fe_{17}, b) Sm_2Fe_{17}+$SmFe_3$.

Alloys containing $SmFe_3$ decrepitate even at room-temperature (Fig. 2) with the $SmFe_3$ forming $SmFe_3H_4$ and a portion (Fig. 2b-c) of the Sm_2Fe_{17} forming $Sm_2Fe_{17}H_x$ ($0<x\leq5$). In alloys containing excessive amount of $SmFe_3$, the Sm_2Fe_{17} phase becomes fully hydrogenated (Fig. 2d). Although the Sm_2Fe_{17} phase does not absorb hydrogen at room-temperature (Fig. 2a), the presence of the $SmFe_3$ phase causes hydrogen to penetrate from the $SmFe_3$ grains inside the Sm_2Fe_{17} grains. That is due to the coherent interfaces between the $SmFe_3$ and Sm_2Fe_{17} grains. The penetration of hydrogen into the Sm_2Fe_{17} grains terminates at the point where the building strain energy (due to the $Sm_2Fe_{17}H_x$) causes loss of coherency in the $Sm_2Fe_{17}H_x$-Sm_2Fe_{17} interfaces. By employing cycled IHAD, sub-single grain (5-200 μm) powders can be produced which are almost free of defects and contamination.

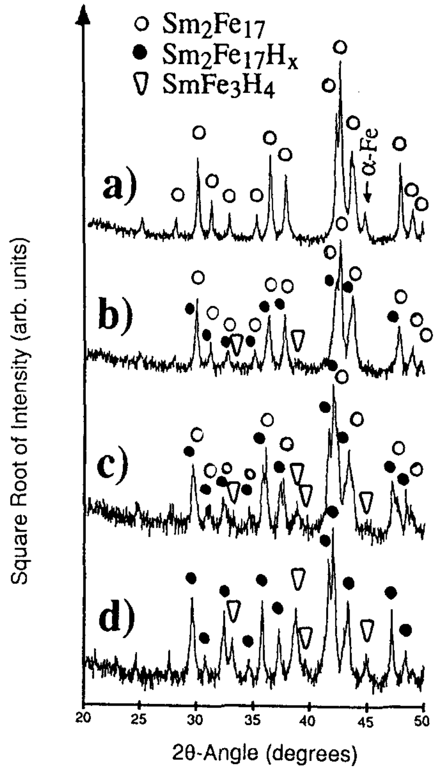

Figure 2. XRD patterns of alloys hydrogenated at 25 °C: a) Sm_2Fe_{17}, b) $Sm_{2.04}Fe_{17}$, c) $Sm_{2.22}Fe_{17}$ and d) Sm_3Fe_{17}.

3.2 The Nitrogenation and nitro-hydrogenation process

Nitrogenation of the Sm_2Fe_{17} phase produces nitrides but nitro-hydrogenation produces nitro-hydrides [5, 11-13]. The use of hydrogen together with nitrogen was employed based on the idea that, initially a Sm_2Fe_{17}-hydride will be formed facilitating nitrogen atoms to interstitially enter the structure. Furthermore, if one employs cycled nitro-hydrogenation it is possible to constantly create new surfaces which can be saturated easily by nitrogen.

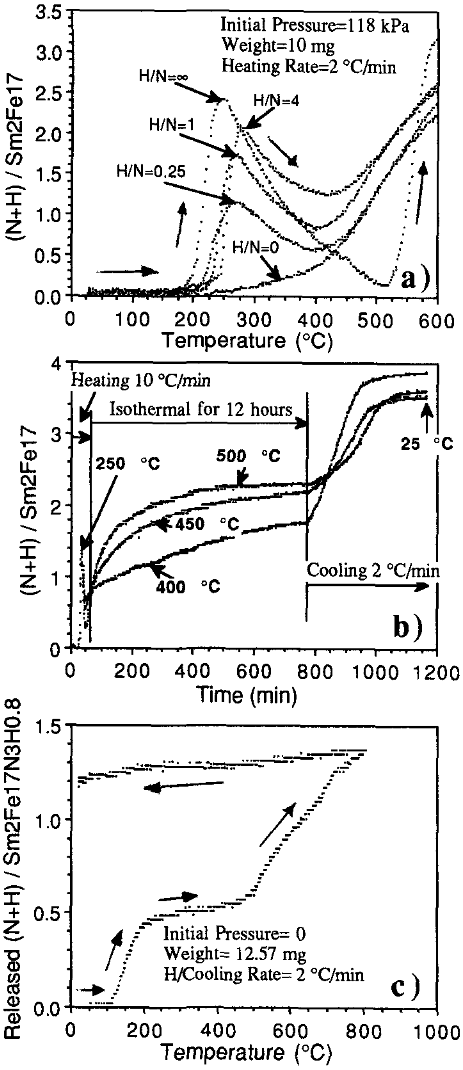

Figure 3. ITA traces: a) "Sm_2Fe_{17} + N_2+ H_2" with H/N= 0, 0.25, 1, 4 and ∞, d) "Sm_2Fe_{17} + N_2+ H_2" with H/N=1 at 400, 450, and 500 °C, c) $Sm_2Fe_{17}N_3H_{0.8}$ under initial vacuum conditions.

Figure 3a shows the ITA traces for the "Sm_2Fe_{17} + H_2 + N_2" system, with the atom ratio of H/N= 0, 0.25, 1, 4, and ∞. The effect of the nitro-hydrogenation temperature is shown in the ITA traces (Fig. 3b) for the "Sm_2Fe_{17} + H_2 + N_2" with H/N= 1, obtained at the temperatures of 400, 450 and 500 °C. In the lower temperature range, for example at 400 °C, a mixture of a nitro-hydride and a hydride is produced. The hydrides are formed during cooling from the reaction between the $Sm_2Fe_{17}N_x$ and H_2. When the nitro-hydride ($Sm_2Fe_{17}N_3H_{0.8}$) is subjected to heating under initial vacuum conditions (Fig. 3c), interstitial hydrogen desorption begins at about 110 °C. At higher temperatures and apart from hydrogen, nitrogen is also released [11] due to the decomposition of the nitride itself into SmN+Fe+N_2. By heating the $Sm_2Fe_{17}N_3H_{0.8}$ in the temperature range of 110 and 220 °C under continuous vacuum conditions, it is possible to preferentially remove the H atoms and form a pure $Sm_2Fe_{17}N_3$.

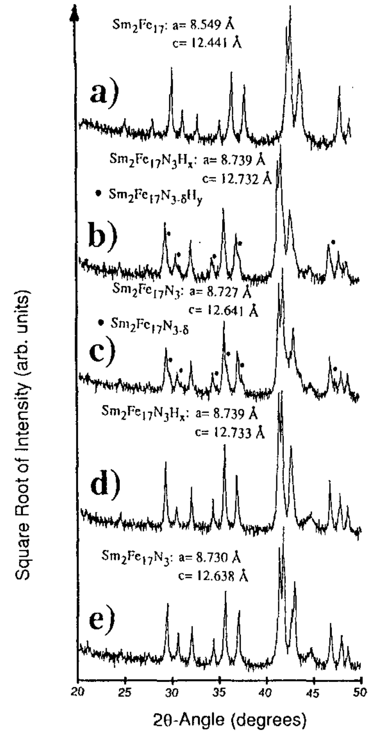

Figure 4. XRD patterns: Starting alloy (a), nitro-hydrides prepared at 450 °C (b) and 475 °C (d) under H/N=1, and corresponding nitrides (c and e).

Nitro-hydrogenation (at 450 and 475 °C) and subsequent dehydrogenation (at 200 °C in vacuum) of the IHAD-produced powders (<45 µm) showed (Figs. 4 and 5) that the M_{15} for the nitro-hydrides is slightly larger than that of the nitrides, but the ${}_iH_c$ is lower. The Sm_2Fe_{17}-nitro-hydride is expanded in the c-axis. The "a" lattice parameter remains essentially the same. This is because hydrogen enters the vacant 18g sites of the structure causing an expansion in the c-direction. Hydrogen can also enter the 9e sites, but they are already populated by the nitrogen atoms [13] which hold on to them by strong bonding with the Sm atoms. A typical hysteresis loop with ${}_iH_c$ of 8.4 kOe and $(BH)_{max}$ of 36 MGOe (assuming full density) is shown in Fig. 6. Powders prepared by employing cycled nitro-hydrogenation and final ball milling showed similar energy products but greater ${}_iH_c$ (>11 kOe). These powders are essentially anisotropic and very suitable for the preparation of anisotropic bonded magnets.

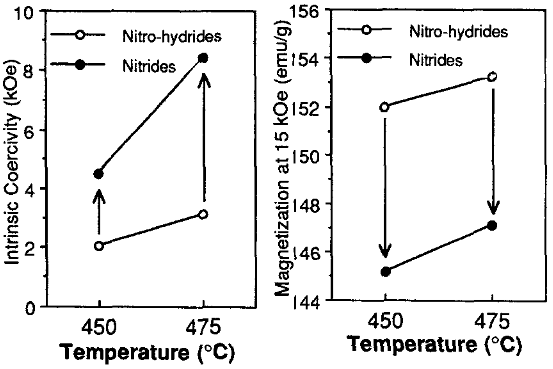

Figure 5. ${}_iH_c$ and M_{15} of nitro-hydrides and corresponding nitrides.

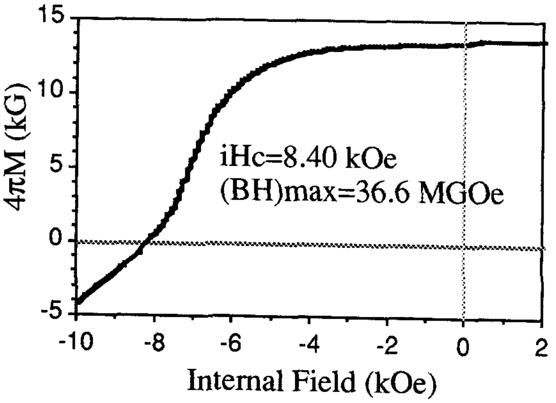

Figure 6. Hysteresis loop of anisotropic $Sm_2Fe_{17}N_3$ powder.

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