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Magnetic properties of rare-earth transition-metal borides

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Magnetic properties of rare-earth transition-metal borides

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The magnetic and structural properties of quaternary $RCo_{4-x}Fe_xB$ alloys with R = Nd, Sm, Er have been examined with magnetometry and x-ray diffraction. The $CeCo_4B$-type phase is found for all x in Er, for $x \leqslant 3$ in Sm, and for $x = 0$, 1, and 2 in Nd. Maximum coercivities have been obtained in a crystallized $SmFe_2Co_2B$ sample with $H_c > 17$ kOe at room temperature.

INTRODUCTION

The magnetic and structural properties of as-cast[1-3] and melt-spun[4] RT_4B alloys, where B and T denote rare-earth and transition-metal, respectively, have been recently studied. It was found that for Co-containing alloys the hexagonal $CeCo_4B$-type phase is formed with all R except Eu and Yb. For the Fe alloys the phase is formed only in Er-Fe-B.

In the present study we investigate the magnetic properties of quaternary $RCo_{4-x}Fe_xB$ alloys in the as-cast and melt-spun state. The idea was to partially substitute Co with Fe in an attempt to stabilize the 1:4:1 phase in the Fe-containing alloys and study its magnetic properties.

EXPERIMENT

Alloys with composition $RCo_{4-x}Fe_xB$ where R = Nd, Sm, Er were prepared by arc-melting the pure constituents under argon atmosphere. Ribbon samples were made by melt-spinning small pieces from the as-cast alloy. For the Nd-Fe-B system, splat-cooled samples were also made using the piston and anvil technique. The ribbons and splat-cooled samples were heat-treated at a temperature of about 600 °C for optimum magnetic hardening.

The crystal structure of the alloys was determined by x-ray diffraction using Co$K\alpha$ radiation. The magnetic properties were measured with a vibrating-sample magnetometer in magnetic fields up to 80 kOe and in the temperature range of 4.2–700 K. Thermomagnetic data (M_H vs T) were obtained by measuring the magnetization in a small constant field H as a function of temperature.

RESULTS AND DISCUSSION

$NdCo_{4-x}Fe_xB$

The x-ray diffraction patterns showed that the samples generally have a two-phase structure with the $CeCo_4B$ structure as the majority phase in the $x = 0,1,2$ alloys. The Curie temperature of the phase increased from 200 °C in $NdCo_4B$ to 380 °C in $NdCo_2Fe_2B$. Diffraction lines not fitting the $CeCo_4B$-type phase could be indexed with an $(Fe,Co)_2B$ phase. This is also consistent with M-vs-T data which showed a Curie temperature of about 740 °C for this phase. There is no diffraction evidence for a 2:14:1 phase.

The two-phase microstructure of the samples resulted in constricted hysteresis loops. Figure 1 shows the hysteresis loops of a splat-cooled and subsequently heat-treated $NdFe_2Co_2B$ sample parallel and perpendicular to the plane of the foil. The sample is strongly anisotropic with an easy axis along the plane of the foil. The coercivity of the sample after crystallization is much larger than 8 kOe. Low-temperature hysteresis loop measurements (Fig. 2) showed an H_c value of 16 kOe at 200 K, which is decreased upon cooling to 4.2 K. The anomalous structure of the hysteresis loop could be attributed to the presence of the $(Fe,Co)_2B$ phase

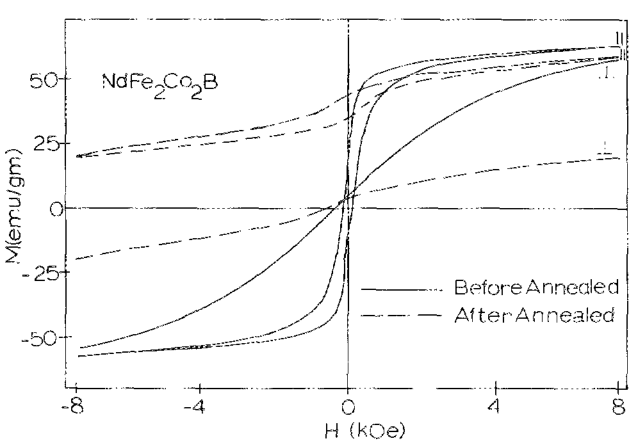

FIG. 1. Hysteresis loops of a splat-cooled and heat-treated Nd-Fe-Co-B sample along and perpendicular to the sample plane.

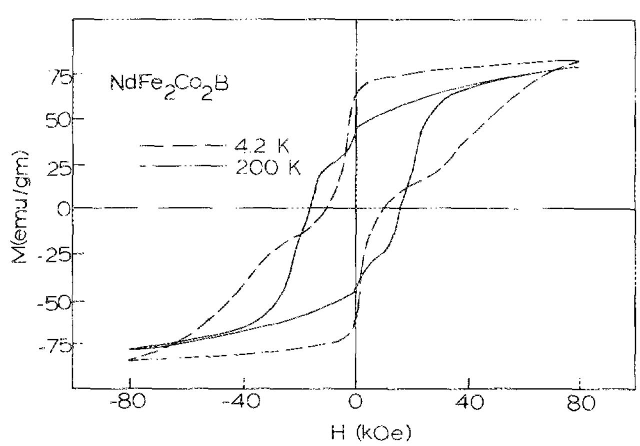

FIG. 2. Temperature dependence of hysteresis in $NdFe_2Co_2B$.

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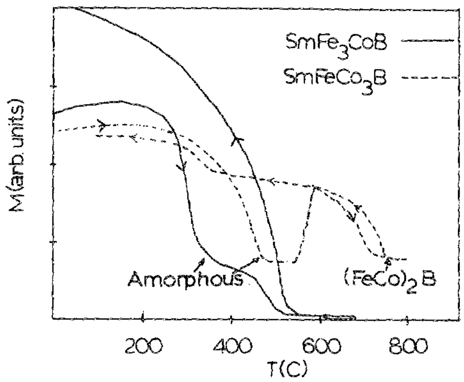

FIG. 3. Thermomagnetic data in $SmFeCo_3B$ and $SmFe_3CoB$ melt-spun samples.

or to a spin reorientation of the 1:4:1 phase. The coercivity of a fine $NdCo_2Fe_2B$ powder was also measured and a value of 2 kOe was found. Magnetization curves obtained parallel and perpendicular to the alignment direction showed an anisotropy field of about 80 kOe. The coercivity of crystallized $NdCo_4B$ ribbons was below 1 kOe. This result was unexpected since the coercivity of crystallized ribbons of anisotropic rare-earth alloys is much higher.[5] It could be that the crystallization temperature of these alloys is higher than 600 °C and therefore a heat treatment at higher temperatures is required to fully crystallize the sample.

$SmCo_{4-x}Fe_xB$

For this system the 1:4:1 phase is found to form over a wider range of compositions, up to $x = 3$ (Fig. 3). The Curie temperature of the Fe-substituted alloys is also found to increase with Fe content (Fig. 4). This is in contrast to the 2:14:1 compounds where T_c decreases with Fe content.[6] The Fe_2B-type phase was strongly present in the $x = 1$ alloy after crystallization (Fig. 3).

Figure 5 shows the magnetic properties of as-cast samples. Maximum coercivity was obtained in the $x = 0$ sample.

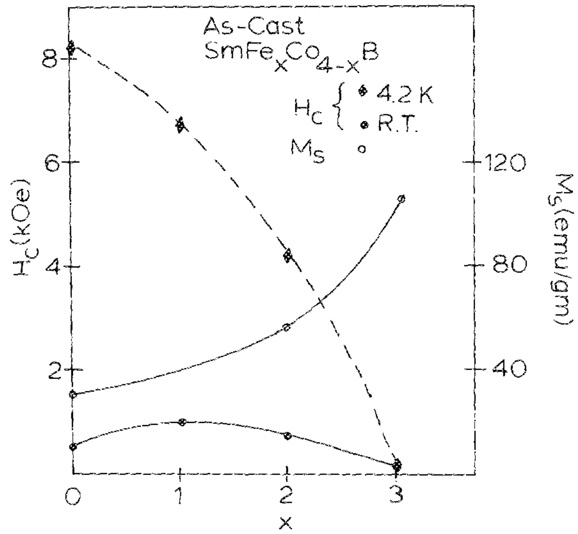

FIG. 5. Coercivity and saturation magnetization in $SmFe_xCo_{4-x}B$ alloys.

As the Fe content is increased, the magnetization increases but the coercivity is reduced, as expected. However, in crystallized ribbons the maximum coercivity was obtained for the $x = 2$ alloy (Fig. 6). The room-temperature coercivity was much higher than 17 kOe, but it dropped to below 10 kOe at 4.2 K. At 4.2 K a magnetic field of 80 kOe was not sufficient to saturate the sample. This is because the true H_c is much higher at cryogenic temperatures and therefore much higher fields are needed to saturate the magnetic moments; this behavior results in an "apparent" smaller H_c. The anisotropy field for these alloys was estimated[3] to be around 400 kOe. High coercivities were also obtained in fine powders (Fig. 7). The size corresponding to the highest H_c was found to be in the range 1.5–4.5 μm.

$ErCo_{4-x}Fe_xB$

The 1:4:1 phase was found in all alloys studied. The Curie temperature of the Co-containing alloys (Fig. 4) is

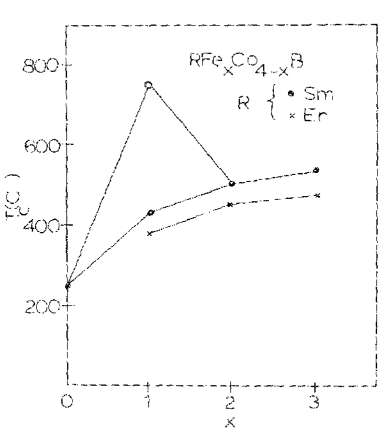

FIG. 4. Curie temperatures in $RFeCo_{4-x}B$ alloys. The O point is believed to be the Curie temperature of the Fe_2B-type phase.

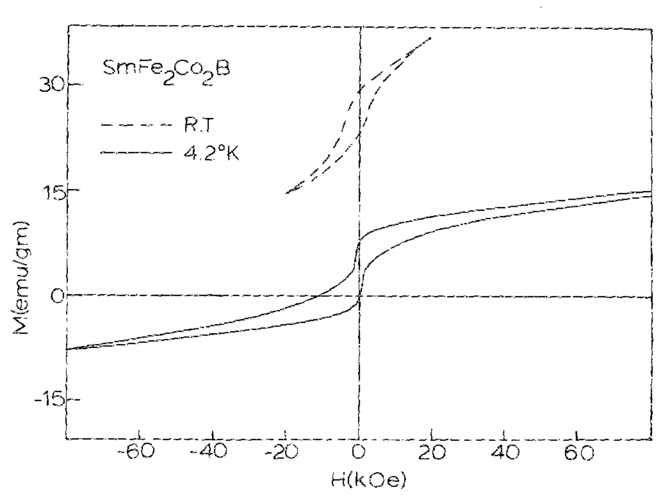

FIG. 6. Hysteresis loops in a crystallized $SmFe_2Co_2B$ sample.

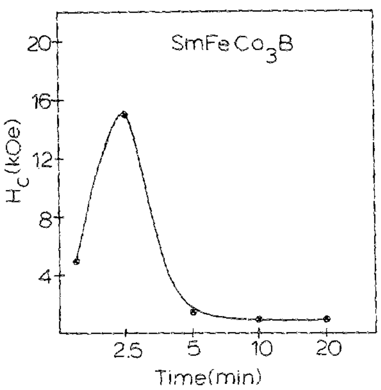

FIG. 7. Coercivity as a function of milling time in $SmFe_2Co_2B$.

higher than the Curie temperature reported[7] for $ErFe_4B$. However, H_c of the former samples is much lower. A coercivity of 6 kOe has been reported[4] for $ErFe_4B$. Relatively high coercivities (2–5 kOe) were also obtained in fine powders. The anisotropy fields found from magnetization measurements on aligned powders are shown in Table I.

The magnetic phase diagram of all alloys studied is presently being examined with ac susceptibility. These data together with microstructure studies are required to understand the results of coercivity in these systems.

TABLE I. Anisotropy fields of $ErCo_{4-x}Fe_xB$ alloys.

x	M_s (emu/g)	H_a (kOe)
0	30	47
2	30	40
3	38	38

ACKNOWLEDGMENTS

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