

# Magnetic properties of fine Fe-Co-B particles prepared by chemical reduction

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The effect of chemical composition and particle size on the magnetic properties of Fe-Co-B fine particles has been studied. The powders were produced by chemical reduction of aqueous solutions of ferric chloride and cobalt chloride with sodium borohydride. The structure of the initially reduced powders varied from amorphous to crystalline bcc depending on the boron concentration. Chemical composition analysis showed a boron content in the range 5–30 at. %. The particle size was found to be 25 nm. The magnetization and coercivity of as-made powders were relatively low. After annealing, the maximum values of magnetization and coercivity obtained were about 160 emu/g and 1940 Oe, respectively. The temperature coefficient of coercivity varied from negative to positive with sample composition and packing fraction.

## I. INTRODUCTION

Dragieva *et al.*<sup>1</sup> reported in the past that amorphous transition-metal boron alloys can be produced by chemical reduction of aqueous solutions of transition-metal salts with  $\text{NaBH}_4$ . Since then, a number of studies have dealt with the magnetic and structural properties of Fe-B, Co-B, and Fe-Ni-B fine particles prepared by this technique.<sup>2–6</sup> These studies emphasized the structural properties, the composition, and in particular the B concentration and the change of magnetic properties caused by a crystallization heat treatment. The highest saturation magnetization obtained in Fe-B powders was 160 emu/g, but the maximum coercivity was only 1000 Oe. In Co-B powders, the maximum coercivity was 2000 Oe, but the saturation magnetization was lower than 100 emu/g.

In this paper, we have investigated the magnetic and structural properties of fine Fe-Co-B particles obtained by chemical reduction of  $\text{FeCl}_3$  and  $\text{CoCl}_2$  with  $\text{NaBH}_4$ . In particular the dependence of coercivity on temperature and packing fraction is discussed.

## II. EXPERIMENTAL METHOD

Fine Fe-Co-B particles were produced by a two step procedure. First, a 0.8-M  $\text{NaBH}_4$  aqueous solution was added dropwise to a 0.4-M mixed  $\text{FeCl}_3$  and  $\text{CoCl}_2$  aqueous solution while the pH value of the solution was kept at 8. The black precipitates were rinsed with distilled water and acetone, and dried in an Ar atmosphere chamber. The powders were then sealed in a quartz tube under vacuum for heat treatment. The crystallization temperature was determined by differential scanning calorimetry using a Perkin Elmer DSC7 thermal analysis system with a heating rate 10 °C/min. A SQUID magnetometer was used for magnetic measurements in the temperature range 10–300 K and in magnetic fields up to 50 KOe. The powders were mixed with wax for the magnetic measurements of isolated particles. For the packing fraction experiments, the powders were aligned and pressed, with the length of the spec-

imen made much larger than the thickness, to minimize shape effects. The crystal structure of the powders was examined by a Phillips APD 3520 X-ray diffractometer. A JEOL-100C transmission electron microscope (TEM) was used to study the particle morphology. The chemical composition was determined by plasma emission spectroscopy.

## III. RESULTS AND DISCUSSION

All the as-made powders were amorphous except those with boron content lower than 15 at. %. With varying Fe:Co ratio, the amount of boron was found to vary in the range 5–30 at. %. The dependence of Co and B content and particle size on the Fe:Co ratio is shown in Fig. 1. The saturation magnetization of as-made powders was relatively low, with a maximum value of about 90 emu/g. A coercivity of about 1100 Oe at 300 K was found in an as-made crystalline sample with boron content of about 10 at. %.

The crystallization behavior of the samples is shown in Fig. 2. An exothermic peak characteristic of crystallization is observed in all the samples with boron content greater than 10 at. %, indicating the amorphous structure of the samples. The onset crystallization temperature depends on the Fe:Co ratio, with the Co-rich samples having lower onset crystallization temperatures. A similar behavior has been also observed in amorphous  $R\text{-Fe}(\text{Co})$  samples.<sup>7</sup> Samples with boron content less than 15 at. % do not show any exothermic peaks indicating that they are already crystalline.

The DSC data were found to agree with x-ray and electron diffraction measurements that showed broad peaks in all the as-made amorphous samples (Fig. 3), and sharp peaks in the as-made crystalline samples. According to the DSC results, the samples with a different Fe:Co ratio were annealed at temperatures in the range 450–530 °C. After the heat treatment, the bcc Fe diffraction peaks of the crystalline samples became sharper and their intensity increased. The amorphous powders were crystallized into a

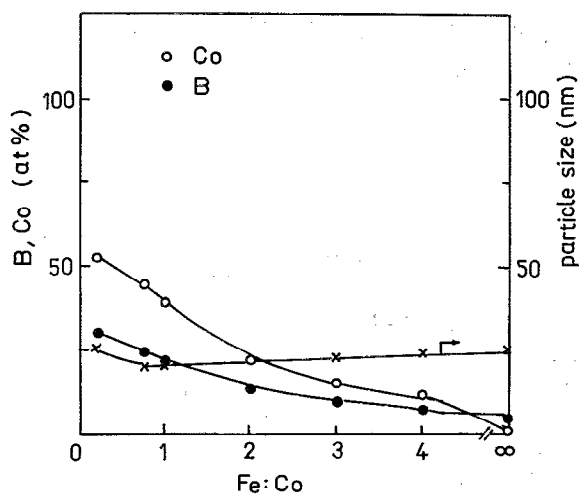


FIG. 1. Dependence of composition and particle size on Fe:Co ratio.

bcc Fe-Co phase, too.

The magnetic properties of amorphous and crystallized isolated particles as a function of Fe:Co ratio are shown in Fig. 4. The maximum saturation magnetization obtained is 160 emu/g for a sample made with Fe:Co = 4 which corresponds to 10 at. % B. This is much different from bulk Fe-Co alloys where the maximum is obtained at 30 at. % Co,<sup>8</sup> but similar to the Nd-Fe(Co)-B alloys where the maximum is at about 12 at. % Co.<sup>9</sup> The saturation magnetization of any composition corresponds to 75%–80% of that of bulk iron-cobalt alloys. The other 20% is probably an oxide, but none of the oxide peaks were detected by

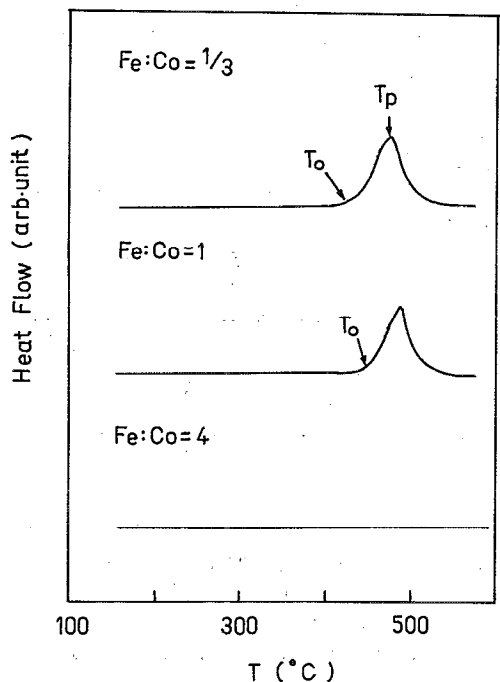


FIG. 2. Crystallization behavior of Fe-Co-B powders ( $T_0$  = onset crystallization temperature,  $T_p$  = peak crystallization temperature).

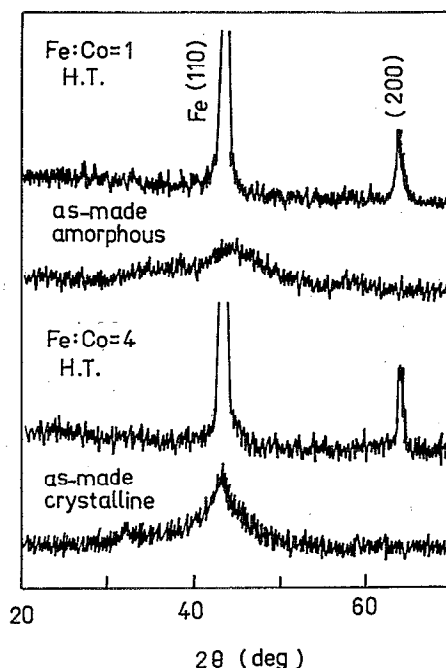


FIG. 3. X-ray-diffraction patterns of different composition powders.

x-ray diffraction possibly because they are too broad and diffused. The maximum coercivities obtained for the isolated particles were 1655 Oe at 10 K in a 25-at. % Co powder, and 1940 Oe at 300 K in a 35-at. % Co sample.

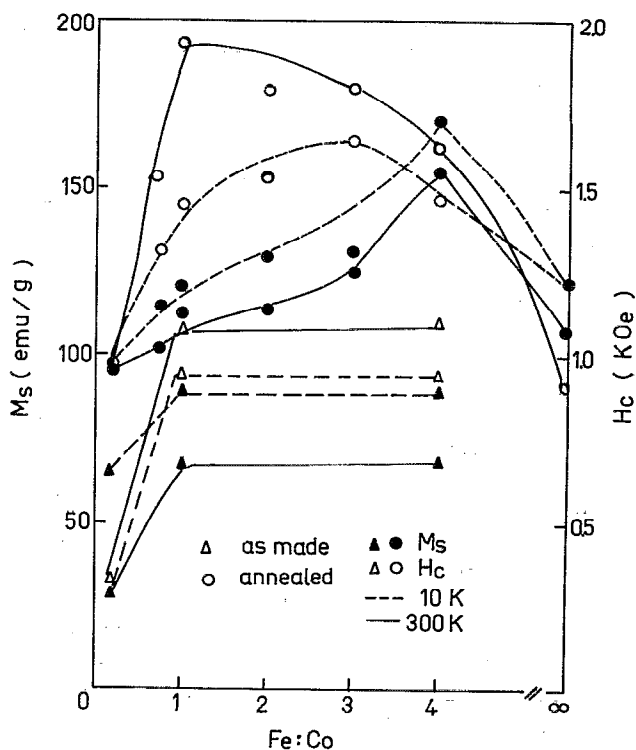


FIG. 4. Saturation magnetization and coercivity as a function of Fe:Co ratio.

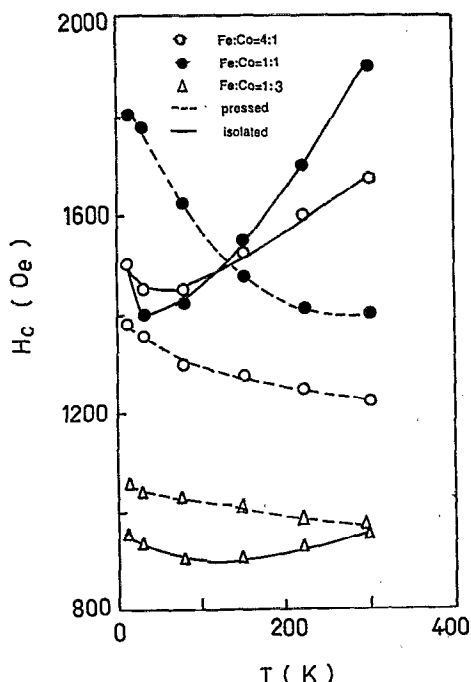


FIG. 5. Coercivity of isolated and packed particles as a function of temperature.

The maximum coercivity is shifted to Co-rich powders when the temperature is increased from 10 to 300 K.

The coercivity as a function of temperature for both annealed isolated and pressed particles is shown in Fig. 5. An anomalous behavior is observed with the temperature coefficient of coercivity depending on the Fe:Co ratio. When the powders contain only one transition metal, such as Fe-B or Co-B,<sup>3,4</sup> the temperature coefficient of coercivity is negative, with the coercivity at low temperatures being greater than that at high temperatures. However, when the powders contain binary transition metals (Fe,Co), regardless of composition, the coefficient gradually changes to positive. The temperature coefficient of coercivity in pressed powders is always found to be negative with different ratio of Fe:Co. This behavior is similar to that for most bulk magnets.<sup>8</sup>

The magnetic hardness of fine particles is probably due to both shape and crystal anisotropy. The law of approach to saturation was used to estimate the anisotropy constant  $K$  of the particles by plotting  $M$  vs  $H^{-2}$ .<sup>10</sup> The crystal anisotropy  $K$  was found to change slightly with the Fe:Co ratio, and has a negative temperature coefficient. The particle morphology studies obtained with TEM showed the formation of chains consisting of 10–40 particles, with a

diameter of 20–30 nm. Fe-rich powders form longer chains. According to the theoretical model, the expression for the coercive field for single-domain particles is given by

$$H_c = 2K/M_s - NM_s \quad (1)$$

where  $K$  is the anisotropy constant and  $N$  is the demagnetization factor.<sup>11</sup> Using the values of  $M_s$  and  $K$  found in the Fe-Co-B particles, one can show that both terms in Eq. (1) are equally important in determining  $H_c$ . In fact, the anisotropy contribution is larger at low temperatures but it decreases at high temperatures and becomes lower than the demagnetization contribution, which is almost constant in the temperature range studied (Fig. 5). This behavior cannot explain the positive temperature coefficient of  $H_c$  using the formula of Eq. (1). It is possible that this behavior is due to the surface anisotropy of small particles which is expected to be quite large. This behavior is observed in Fe-Co-B alloys and not in Fe-B and Co-B because of their higher magnetization. Further studies are needed to clarify this issue.

#### IV. SUMMARY

Both amorphous and crystallized Fe-Co-B fine particles can be produced by reducing  $\text{FeCl}_3$  and  $\text{CoCl}_2$  mixed solutions with  $\text{NaBH}_4$ . The particle size is about 20–30 nm. The maximum coercivity of annealed 35-at. % Co powders is 1940 Oe at 300 K. The temperature coefficient of coercivity behaves anomalously changing from negative to positive with packing fraction.

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