

# Co-Pt-B Particles Prepared by Chemical Reduction

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**Abstract**—The magnetic and structural properties of ultrafine Co-Pt-B particles have been studied in samples near the equiatomic CoPt composition. The particles were prepared by the chemical reduction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{PtCl}_4$  with  $\text{NaBH}_4$ . The as-made powders had an fcc structure and they were magnetically soft. An fcc to fct phase transformation was observed after annealing at  $700^\circ\text{C}$  resulting in coercivities up to 17.8 kOe at room temperature. The variation of coercivity with particle morphology and structure has been investigated.

## I. INTRODUCTION

Among the various preparation methods for ultrafine magnetic particles, chemical reduction is widely used because it is simple and it usually leads to large amounts of powders[1]. Amorphous and crystalline particles with different particle size can be obtained by varying the concentration of the solutions and/or the preparation procedure[2].

Co-Pt alloys at or near the equiatomic range are well known as permanent magnet materials. Early studies on bulk Co-Pt alloys have shown that a phase transformation from the original disordered face centered cubic (fcc) phase to an ordered face centered tetragonal (fct) phase results in coercivities up to 5 kOe which have been attributed to the high anisotropy of the tetragonal phase ( $K \approx 2-4 \times 10^7 \text{ erg/cm}^3$ ) [3,4]. Lately Co-Pt thin films have been extensively studied because of their potential applications in high-density magneto-optical recording media[5].

In this paper, we have prepared ultrafine Co-Pt-B particles by chemical reduction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{PtCl}_4$  with  $\text{NaBH}_4$ , and we have studied their magnetic and structural properties.

## II. EXPERIMENTAL METHODS

Fine Co-Pt-B particles were produced by a two step procedure. First, a  $\text{NaBH}_4$  aqueous solution (with a molarity in the range of 0.006–0.06 M) was rapidly added to a mixed solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{PtCl}_4$  (with a molarity in the range of 0.002–0.02 M). The reactions were carried out in air. The black precipitates were rinsed with distilled water and subsequently in acetone. The powders were dried at

room temperature in a flow of Ar gas. Different Co/Pt ratios were obtained by varying the  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{PtCl}_4$  ratio in the solutions. The powders were then sealed in a quartz tube under vacuum ( $10^{-5}$  Torr) for further heat treatment.

An x-ray diffractometer(XRD) was used to determine the phases present in the particles. A Jeol-100CX transmission electron microscope(TEM) equipped with an EDXA detector was used to determine the particle size and the Co/Pt ratio. The chemical composition of the particles was determined by ICP spectroscopy. A SQUID magnetometer and a VSM magnetometer with a maximum applied field of 55 kOe were used in the temperature range 10-1000 K for the magnetic measurements.

## III. RESULTS and DISCUSSION

Chemical composition studies showed that the particles had a Co/Pt atomic ratio between 0.5 and 2.5 with a boron content in the range of 9–15 at%. X-ray diffraction patterns showed that all the as-made particles had a fcc structure (Fig.1). The powders were magnetically soft with a low coercivity  $H_c \approx 130 \text{ Oe}$  at room temperature. After annealing the powders at  $600^\circ\text{C}$  for 1 hour, the crystal structure of the particles with Co/Pt $\approx$ 0.5–1 was found to transform from disordered fcc to an ordered fct phase. X-ray diffraction patterns showed clearly the superlattice reflections of fct (002), (202). The percentage of fct phase in the samples was found to depend on the annealing temperature. X-ray diffraction patterns showed weak and broad peaks present in samples annealed for short time and lower temperature. The sharper peaks were present in samples annealed at higher temperatures and longer aging times. This indicates that the particle size is increased and a completed fcc-fct phase transformation has occurred. The crystal lattice parameters of the sample  $\text{Co}_{43}\text{Pt}_{43}\text{B}_{14}$  were found to be  $a=3.806 \text{ \AA}$ ,  $c=3.699 \text{ \AA}$  with  $c/a=0.972$  (AuCu type indexing). A trace of  $\text{Co}_2\text{B}$  and  $\text{CoPt}_3$  phases were also present in samples with Co-Pt off the equiatomic range (Fig.1). The particle size and morphology of as-made and annealed samples is consistent with the XRD data(Fig.2). In as-made samples the particle size is around 80  $\text{\AA}$  and the particles agglomerate together to form chain/dendrites with the dendrite frame diameter 200–250  $\text{\AA}$ . Spherical particles with an average size about 220  $\text{\AA}$  were present in the sample annealed at  $700^\circ\text{C}$  for 3

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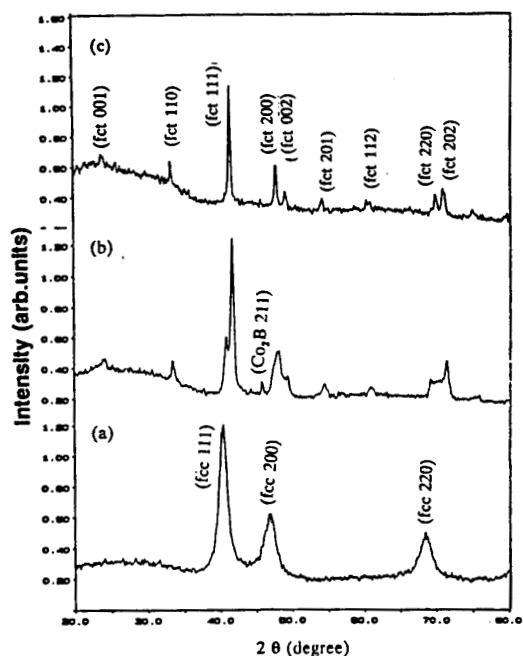


Fig.1 X-ray diffraction patterns of fine Co-Pt-B particles. (a) as-made (b) Co/Pt=0.54, annealed. (c) Co/Pt=1, annealed.

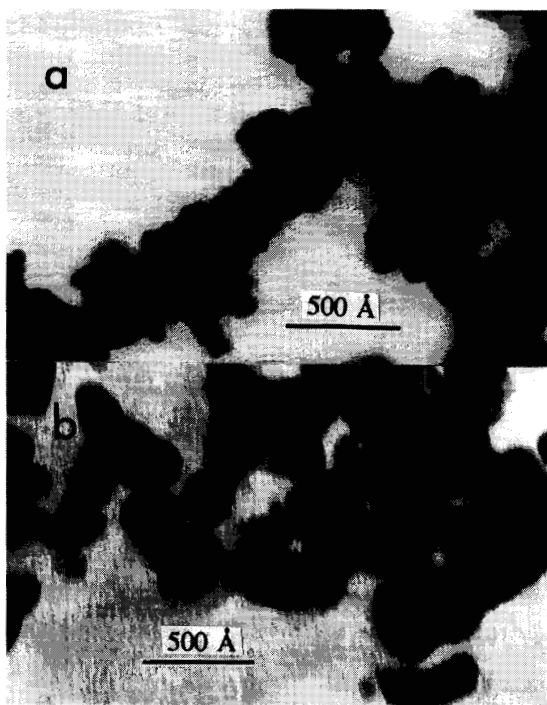


Fig.2 Morphology of Co-Pt-B particles (a) as-made (b) annealed.

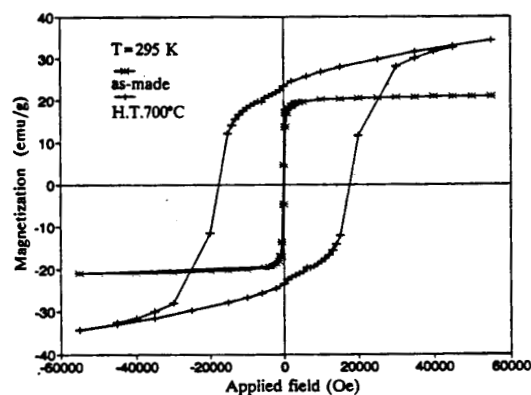


Fig.3 Hysteresis behavior of  $\text{Co}_{43}\text{Pt}_{43}\text{B}_{14}$  particles.

hours. The heat treatment led to the sintering of small particles and higher aging temperatures and aging times led to larger particles (size  $\sim 320$  Å).

Because permanent magnet properties are displayed in samples close to Co-Pt equiatomic range, the magnetic and structural properties were investigated on samples with Co/Pt=1. Typical hysteresis behavior of the fcc and fct  $\text{Co}_{43}\text{Pt}_{43}\text{B}_{14}$  particles is shown in Fig.3. The magnetization of the annealed particles was higher than that of as-made powders. The unsaturated magnetization curve (even at 55 kOe) indicates a high anisotropy in the particles. Fig.4 shows the magnetization and coercivity at 295 K of  $\text{Co}_{43}\text{Pt}_{43}\text{B}_{14}$  particles as a function of annealing temperature and time. The samples were annealed for 1 hour at different temperatures and at 700°C for different times to obtain the optimum annealing temperature and time. The magnetization

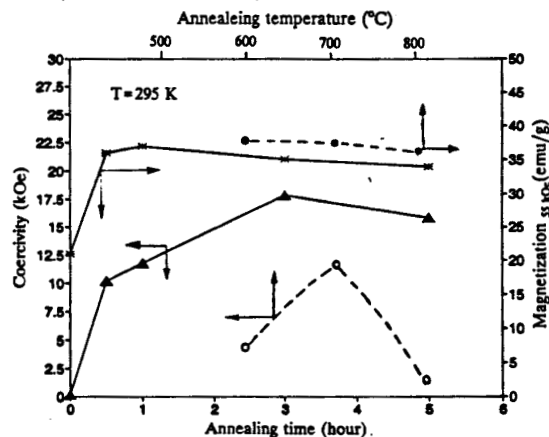


Fig.4 Magnetization at 55 kOe and coercivity of  $\text{Co}_{43}\text{Pt}_{43}\text{B}_{14}$  particles as a function of annealing temperature and time. (solid line for annealing time, dash line for annealing temperature, \* = magnetization, o = coercivity)

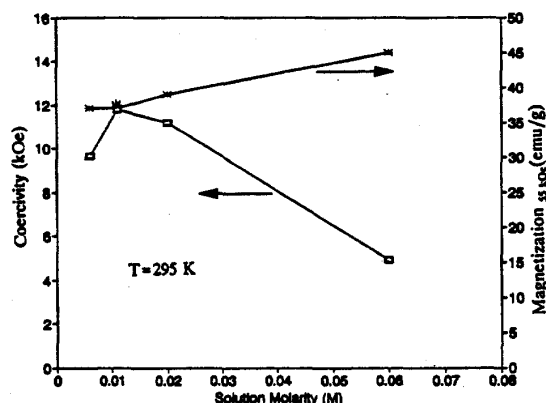


Fig. 5 Magnetization and coercivity as a function of initial solution molarity.

of the particles was found to be insensitive to annealing temperature. However, the coercivity increases from about 4 kOe after annealing for 1 hour at 600°C to a maximum value of 17.8 kOe (295 K) annealing at 700°C for 3 hours and then decreases at higher temperatures. The saturation magnetization was found using the law of approach to saturation by plotting  $M$  as a function of  $1/H^2$  and extrapolating to infinite fields;  $M_s = 40.2$  emu/g and  $K = 2.11 \times 10^7$  erg/cm<sup>3</sup>.

In the borohydride reduction of metallic cations, a higher concentration solution normally produces smaller particles [6], because at higher concentrations the reduction rate is higher and more nuclei are formed and fewer metal atoms are available to make the particles grow. In this system a series of samples were made to study their magnetic and structural properties as a function of the concentrations of the initial cation solutions while the initial ratios of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{PtCl}_4/\text{NaBH}_4$  were kept constant. The composition of the as-made powders was found to vary slightly with  $\text{Co}/\text{Pt} \approx 1.02$ –1.05, boron in the range of 9–15 at% with the lower boron content corresponding to higher molarity concentrations, the boron content of the different samples A–E are: A=9 at%B, C=13 at%B, D=14 at%B and E=15 at%B. The average particle size of the as-made powders was around 70–100 Å. After annealing at 700 °C for 1 hour, the particle size of sample A increased to around 170 Å and that of samples C, D, E to around 200 Å. X-ray diffraction patterns showed the presence of fct phase in all the samples. The magnetic properties especially the coercivity varied with the solution molarity, as shown in Fig. 5. Higher reduction rates lead to a higher magnetization and lower coercivity. The thermomagnetic data of a sample are shown in Fig. 6. The initial increase of magnetization with temperature is due to Hopkinson effect. The Curie temperature of the annealed particles (fct structure) was found to change slightly in the

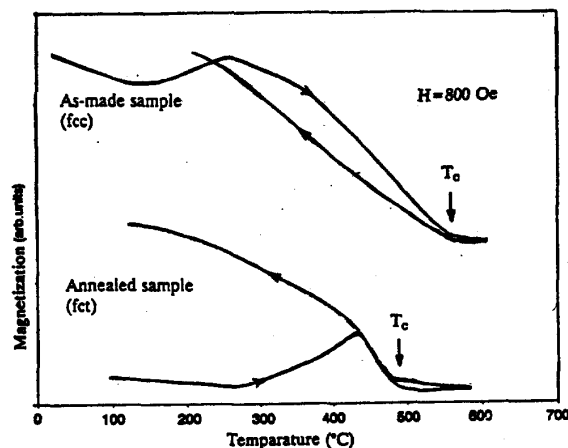


Fig. 6 Thermomagnetic behavior of Co-Pt-B particles.

different samples having the following values: for sample (A)  $T_c \approx 510^\circ\text{C}$ , (C)  $T_c \approx 500^\circ\text{C}$ , (D, E)  $T_c \approx 480^\circ\text{C}$ . These temperatures are slightly lower than those of as-made powders (530–560°C). This behavior is similar to that of bulk alloys reported by F. Bolzoni et al [4]. These variations are probably due to the different chemical composition and particle morphology of the powders.

#### IV. SUMMARY

Fine Co-Pt-B particles near the equiatomic CoPt composition can be produced by the chemical reduction technique. A disordered fcc to an ordered fct phase transformation results in high coercivities with an optimum  $H_c$  of 17.8 kOe at room temperature and 23.7 kOe at 10 K. The dependence of magnetic properties on the solution molarity is due to the change of both the composition and morphology of the particles with concentration.

#### V. ACKNOWLEDGMENTS

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