Magnetic properties of ultrafine Fe-Ni-B particles

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Ultrafine Fe-Ni-B particles were synthesized by reducing iron and nickel salts with $NaBH_4$ in aqueous solutions. The particles had diameters in the range of 100–300 Å. X-ray diffraction patterns showed that particles with boron concentration 18 at. % or more were amorphous; otherwise they were crystalline. It was also found that the amorphous particles contain less than 50 at. % of Fe. The coercivity of Fe-B particles was increased by an addition of a small amount of Ni to the system. The room-temperature coercivity and saturation magnetization for particles of composition $Fe_{63}Ni_{24}B_{13}$ and of diameter 100 Å were 1275 Oe and 70 emu/g, respectively.

INTRODUCTION

In recent years great interest has been associated with ultrafine magnetic particles. This follows from the fact that the magnetic properties of ultrafine particles could be different from the bulk. Magnetically, bulk $Fe_{80}B_{20}$ alloys are very soft (coercivity less than 5 Oe),[1] but in the fine particle form they are at least two orders of magnitude harder.[2] For Fe-Ni-B ribbon the maximum reported coercivity (H_c) was 50 Oe.[3] The saturation magnetization (M_s) gradually decreased from 160 to 58 emu/g when 60% of Fe in $Fe_{80-x}Ni_xB_{20}$ ribbon was replaced by Ni.[4] In this work we present results for fine particles of Fe-Ni-B prepared by a chemical method. Although it was not possible to maintain a constant B concentration in the fine particles, we wanted to study the trend of H_c and M_s when Ni was added to Fe-B particles.

EXPERIMENT

Ultrafine Fe-Ni-B particles were made by using a "Y" junction through which aqueous solutions of $FeCl_3$ and $NiCl_2$ were mixed with a $NaBH_4$ solution. The solution molarity of $NaBH_4$ was kept constant at $0.2M$ and the molarity for the mixture of $FeCl_3$ and $NiCl_2$ together was kept constant at $0.08M$. These molarities pertain to the total solution after mixing. Detailed procedure for the sample preparation technique can be found elsewhere.[2]

A SQUID magnetometer was used to measure the magnetic properties. Particle diameters were determined by the Brunauer–Emmett–Teller (BET) nitrogen adsorption method. To calculate the diameters, it was assumed that the particles were monodispersed and of spherical shape. X-ray diffraction patterns were used to determine the phases present and chemical analysis for the compositional properties of the particles.

RESULTS AND DISCUSSION

Figure 1 shows the composition of the particles as a function of different molarity of the Ni salt solution, $M(Ni)$. These compositions have been normalized to a total of 100%. The unknown fraction varied between 20% and 40%

and was most likely oxygen. Since the total molarity of Fe plus Ni was kept at $0.08M$, the Fe molarity was $0.08 - M(Ni)$. Figure 1 shows that as $M(Ni)$ increased the B concentration in the particles also increased along with the Ni concentration.

Figure 2 shows the particle diameter as a function of $M(Ni)$. For concentrations up to $0.05M$, the particle diameter remained constant at about 110 Å. For higher $M(Ni)$, the particle diameter increased to about 300 Å at about $0.07M(Ni)$. Further increase of $M(Ni)$ did not change the particle diameter. This change of particle diameter can be explained by the reaction rate of Fe and Ni cations. Higher reaction rates yield smaller particles. This occurs because at higher reaction rate more nuclei are formed and fewer metal atoms are available to make the particles grow.[5] In the experiment it was found that the molar ratio of Fe/Ni solutions was always less than the atomic ratio of Fe/Ni in the particles. This suggests that the Fe reduces faster than Ni, as could be corroborated by visual observation of the color change. Thus, the reaction rate was slower with larger $M(Ni)$ and hence the particles were bigger. This finding is opposite that of Kim and Brock.[5]

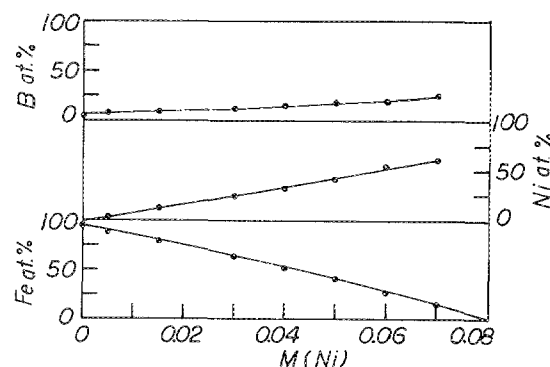Figure 3 shows the x-ray diffraction patterns for different $M(Ni)$. It shows that the particles became amorphous

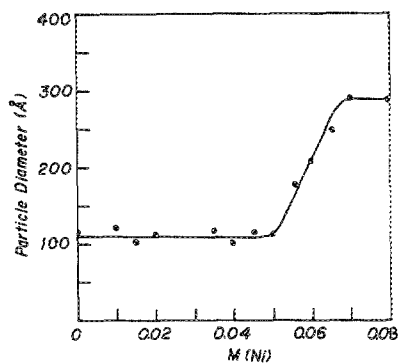FIG. 1. Normalized composition of the particles as a function of different molarity of the Ni salt solution, $M(Ni)$.

FIG. 2. Particle diameter as a function of $M(Ni)$.

FIG. 4. Coercivity and saturation magnetization as a function of different $M(Ni)$.

for $0.055M(Ni)$ or greater. This concentration was also where the particle diameter started increasing. Also it can be noticed, (Fig. 1) that in this region the B concentration was more than 20 at. %, which is known to give an amorphous structure.[6] For lower $M(Ni)$, the particles were crystalline and showed a bcc α-Fe structure. No sharp oxide peaks were observed which suggest that the oxides present in the particles were in the amorphous state.

Figure 4 shows the H_c and M_s as a function of $M(Ni)$. The maximum H_c and M_s were 1550 Oe and 110 emu/g at 10 K, respectively. For pure Fe-B the H_c and M_s were 1050 Oe and 125 emu/g, respectively. Thus, by adding Ni to the system, the H_c increased and reached a maximum. After the maximum, the decreasing rate of H_c was sharper for the
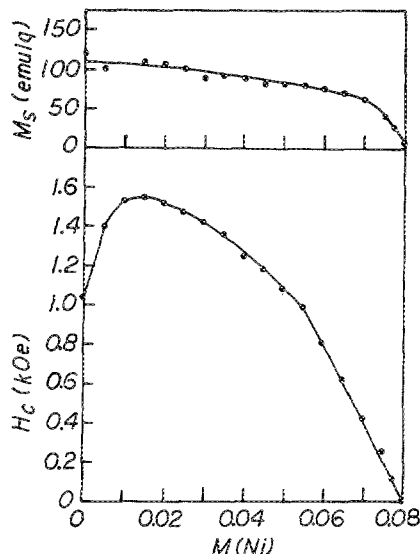
range of 0.055–0.08 $M(Ni)$ compared to the range of 0.02–$0.055M(Ni)$. The particle diameter remained more or less constant for the range of 0–$0.05M(Ni)$. We calculated the anisotropy energy using the law of approach to saturation. At low $M(Ni)$, the anisotropy energy increased with increasing $M(Ni)$, and then started to decrease at about $0.05M(Ni)$. This increase of anisotropy energy is perhaps responsible for the increase of H_c in the range of 0–$0.015M(Ni)$. The change of composition of the particles for
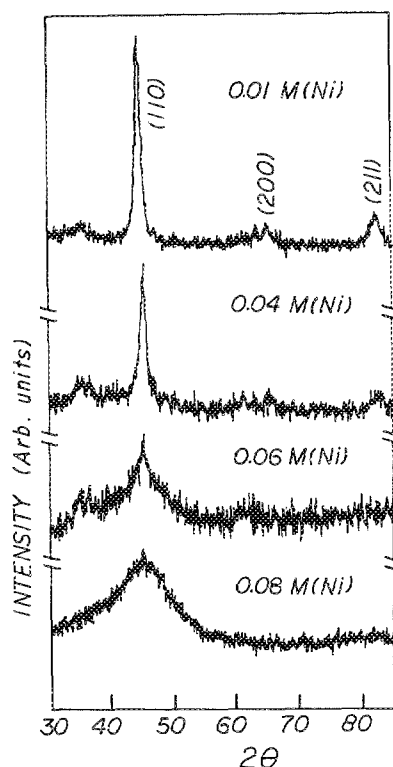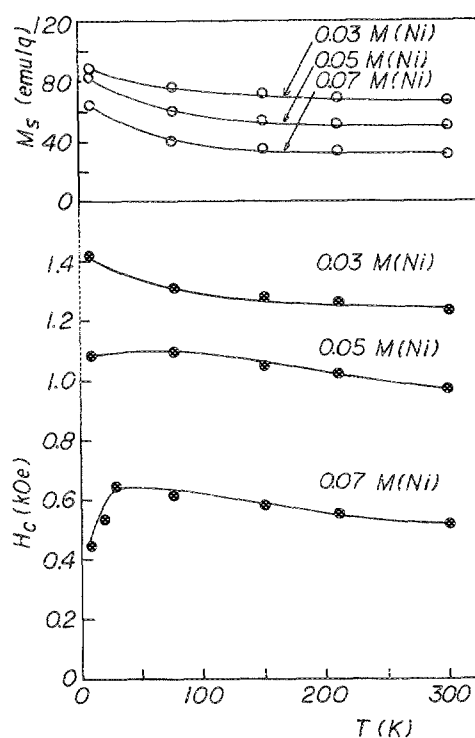

FIG. 3. X-ray diffraction patterns for different $M(Ni)$.

FIG. 5. Temperature dependence of coercivity and saturation magnetization for samples with different $M(Ni)$.

different $M(\text{Ni})$ may also contribute to the coercive field. For the range $0.055-0.08M(\text{Ni})$, the drop of H_c was sharper, perhaps due to the added effect of increased particle diameter. Magnetization data show a monotonic decrease in M_s from 120 to 60 emu/g for the range of $0-0.07M(\text{Ni})$. After this, M_s decreased rapidly from 60 emu/g to almost 0 for the range of $0.07-0.08M(\text{Ni})$.

Figure 5 shows the temperature dependence of H_c and M_s for samples with different $M(\text{Ni})$. Change of M_s with temperature for samples with high $M(\text{Ni})$ was more rapid (52%) than those with lower $M(\text{Ni})$ (30%). It also can be noticed that most of the change occured in the temperature range of 10–77 K. Coercivity data show that there was a trend for H_c (10 K) to be smaller at lower temperatures than that at higher temperatures as $M(\text{Ni})$ increase. We are investigating this effect with Mössbauer measurements at low temperature to check whether this effect was due to the ordering of a magnetically soft phase at low temperature which lowered the coercivity or a true particle size effect.

In summary, the H_c of Fe-B particles can be increased by adding Ni to the system. The coercive field obtained in fine Fe-Ni-B particles were larger than reported for metallic glasses (50 Oe) having similar composition. A high coercivity of about 1275 Oe and a saturation magnetization of about 70 emu/g were obtained for particles of composition $Fe_{63}Ni_{24}B_{13}$ and of diameter 100 Å.

[1] F. E. Luborsky, J. J. Becker, J. L. Walter, and D. L. Martin, IEEE Trans. Magn. MAG-16, 521 (1980).
[2] S. Nafis, G. C. Hadjipanayis, C. M. Sorensen, and K. J. Klabunde, IEEE Trans. Magn. 25, 3641 (1989).
[3] F. E. Luborsky, H. H. Liebermann, and J. L. Walter, Organ. Comm. Central Res. Inst. Phys. 1, 203 (1980).
[4] R. C. O'Handley, R. Hasegawa, R. Ray, and C. P. Chou, Appl. Phys. Lett. 29, 330 (1976).
[5] S. G. Kim and J. R. Brock, J. Colloid Interface Sci. 116, 431 (1987).
[6] C. D. Graham and T. Egami, Ann. Rev. Mater. Sci. 8, 423 (1987).

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