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Chemical synthesis and characterization of amorphous Fe-Ni-B magnetic nanoparticles

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We have synthesized Fe-Ni-B amorphous nanoparticles by chemical reduction of the transition metal solution. A compositional study shows that the nominal Ni/Fe ratio is preserved. The new preparation method used yields a much higher boron composition than the one obtained traditionally by rapid quenching and other chemical synthesis previously reported. For all compositions, the size of the particles is about 2.1 nm diameter with a narrow log-normal distribution. © *2001 Kluwer Academic Publishers*

1. Introduction

Materials composed by ultrafine particles have been studied extensively in the last years because of their novel properties and technological applications in catalysis, material processing and in optical, magnetic and electronic fields [1, 2]. Specifically, Fe-M-B (M = transition metal or rare earth) based nanoparticles give materials with a wide variety of magnetic behavior: hard magnetic materials (e.g., Nd-Fe-B used as permanent magnets [3]) as well as soft magnetic materials (e.g. FINEMET alloy [4]). Essential to the study of ultrafine particles is the production of samples with a narrow and reproducible size distribution. Fe-M-B amorphous alloys are usually synthesized by rapid quenching from the melt producing thin ribbons [5–7]. In Fe-B amorphous compounds case, the boron composition range is between 10 at.% to 30 at.% outside which various crystalline forms of Fe and Fe-B compounds may precipitate. On the other hand, the chemical route gives the possibility to obtain the alloys in the form of fine particles, more versatile for the technological applications and generally presents the advantage of leading to fine morphology, homogeneity, reproducibility in a wide range of compositions, and is a competitive process for potential applications. In particular, for preparing ternary transition-metal - boron amorphous alloys, the chemical reduction of aqueous solutions of metal salts by $NaBH_4$ has proved to be a successful method [8–16].

Particularly, Fe-Ni-B based amorphous alloys synthesized by rapid solidification exhibit soft ferromagnetic properties [6, 17]. The amorphous nanoparticles obtained by the chemical method will exhibit different morphology (i.e., size and shape) depending on its composition and synthesis conditions. Ideally, fine particles made by the chemical route can allow the study of its magnetic properties in a non-interacting range (i.e., dispersed particles) and strongly interacting regime (i.e., concentrated powder) which is partly our interest in the study of these materials [18, 19].

Within this context we report the preparation, their morphological and compositional characterization of a $(Fe_{1-x}Ni_x)_{100-y}B_y$ $(0 \leq x \leq 1)$ series of fine particles by a chemical reduction route.

2. Experimental procedure

Amorphous powders of Fe-Ni-B alloys were obtained by reduction of aqueous solutions of metallic salts of $FeSO_4$ and $NiCl_2$ with a $NaBH_4$ solution. The pH of the precursor solutions was accurately controlled. The reduction was carried out in an inert atmosphere (in order to prevent oxidation) by adding drop-by-drop 25 ml of the transition metal ion solution (pH = 6) to a one containing 25 ml of $NaBH_4$ (pH = 13). In order to obtain the total reduction of the transition metal ions, an excess of $NaBH_4$ with respect to the stochiometric reduction quantities was placed. The reaction temperature (273 K) and the dropping velocity were accurately controlled, fully performing the reaction in 30 min. During reaction the solution was vigorously stirred. A black powder was collected in a filter and washed with distilled water to remove residual ions, then it was rinsed with acetone to remove water and finally dried in vacuum. Because the particles are strongly pyrophoric a passivation with air was performed leaving the powder overnight under vacuum (∼100 mTorr) followed by controlled introduction of air.

The relative Fe/Ni composition was determined by energy disperse spectroscopy microanalysis (EDS) and the boron concentration, by atomic absorption analysis. The morphologic characteristics of the powder specimens were examined by transmission electron microscopy (TEM), X-ray diffraction (Cu Kα radiation) measurements and light scattering correlation.

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The TEM instrument was a Philips CM200 UT operated at 200 kV and the light scattering instrument is a commercial ZetaSizer 1000 working at 90 deg fixed angle.

3. Results and discussion

The X-ray powder diffraction patterns were obtained, for all samples, at room temperature. Only some broad peaks are observed showing a similar pattern for all the samples (Fig. 1). The positions and widths of those peaks suggest the presence of nickel-boron, iron and nickel borates and nickel oxide (which can be expected in the particle surface due to the passivation process) all of which show a short crystalline order $D < 3$ nm. In Fig. 1 we present, as example, the diffraction patterns for $x = 0.75$, $x = 0.5$ and $x = 0.25$ compositions which exhibit essentially the same pattern. We conclude that no long-range crystalline order is observed, as expected for amorphous compounds.

In order to clarify the morphology of the Fe-Ni-B powders, TEM observations were carried out on the samples with different iron-nickel composition. Powder electron diffraction presents a broad and diffuse pattern confirming the amorphous nature of the nanoparticles. Bright-field micrograph shows, for all compositions, nearly spherical shape nanoparticles. Their mean diameter was in the range of 1.2–1.7 nm. In Fig. 2 we show the TEM results for $x = 0.75$ and $x = 0.5$. The TEM observations give us a picture of the size and shape of the nanoparticles. Because of the small size of nanoparticles and their amorphous nature, the resolution of the size distribution is very poor to determine a histogram of size population. For this reason we also performed light scattering measurements in an aqueous suspension of particles, which yield the size distribution of our samples. In Fig. 3 the results obtained on an aqueous suspension of the $(Fe_{0.25}Ni_{0.75})_{100-y}B_y$ sample. This method yields a narrow size distribution centered at 2.5 nm and comprised within the 2–4.5 nm range. One of the most common distribution used to describe the size distribution of fine-particle systems is the log-normal distribution:

$$f(\phi) = \frac{\exp\left[-\frac{\sigma^2}{2}\right]}{\sqrt{2\pi}\sigma\phi_0} \exp\left[-\frac{\ln^2\left(\frac{\phi}{\phi_0}\right)}{2\sigma^2}\right] \qquad (1)$$

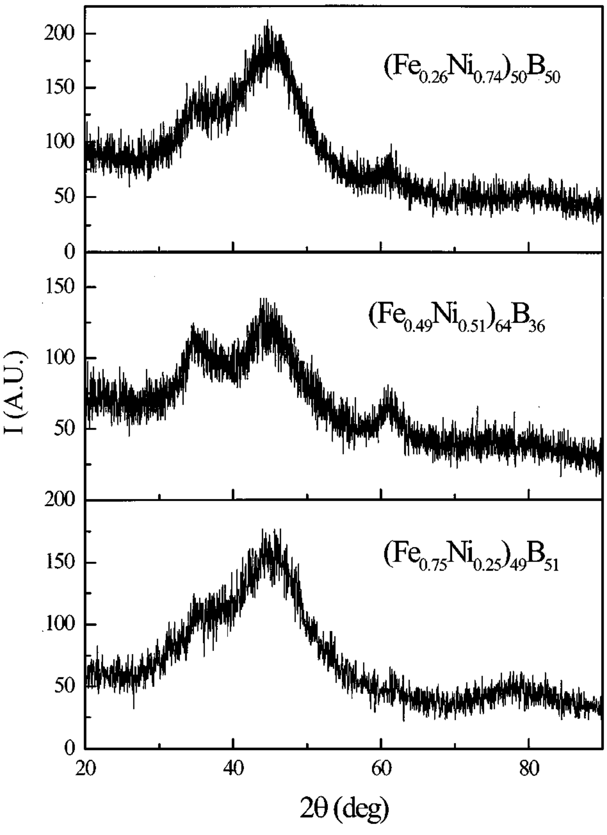

Figure 1 X-ray powder diffraction pattern (Cu K-α radiation) of the $(Fe_{1-x}Ni_x)_{100-y}B_y$ samples for $x = 0.75$, $x = 0.625$ and $x = 0.5$.

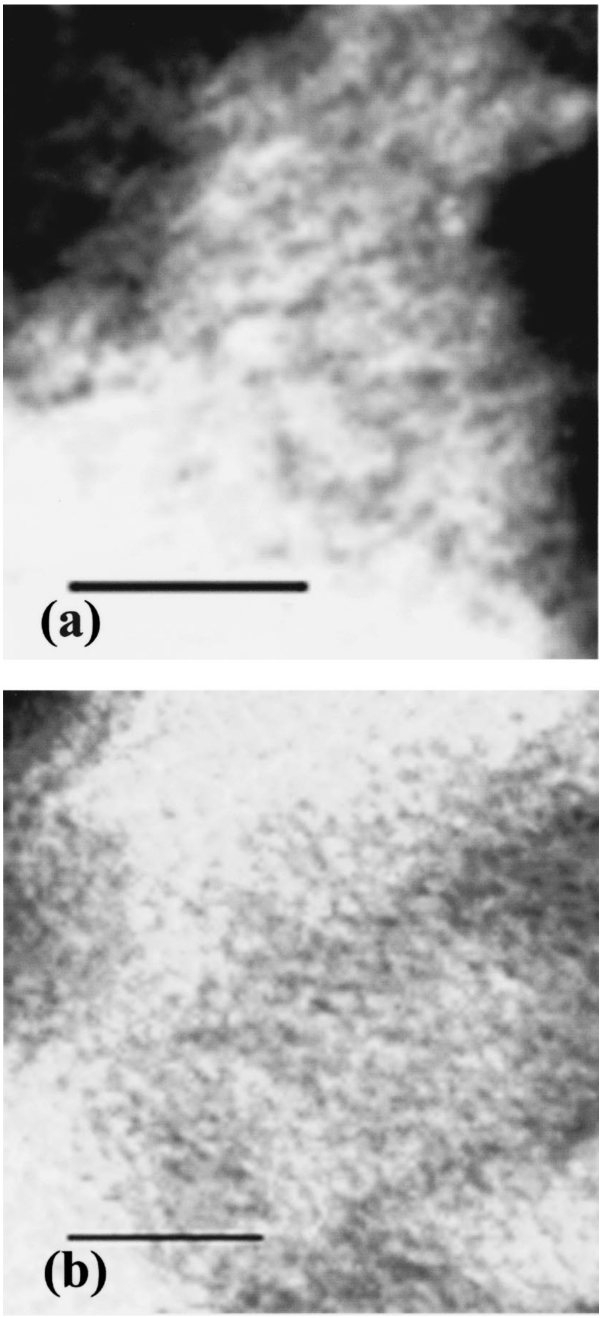

Figure 2 Bright-field micrograph showing nearly spherical particles of $(Fe_{1-x}Ni_x)_{100-y}B_y$ samples with mean diameter of 1.5 nm for (a) $x = 0.75$ and (b) $x = 0.5$ samples. The black segment represents a length of 10 nm.

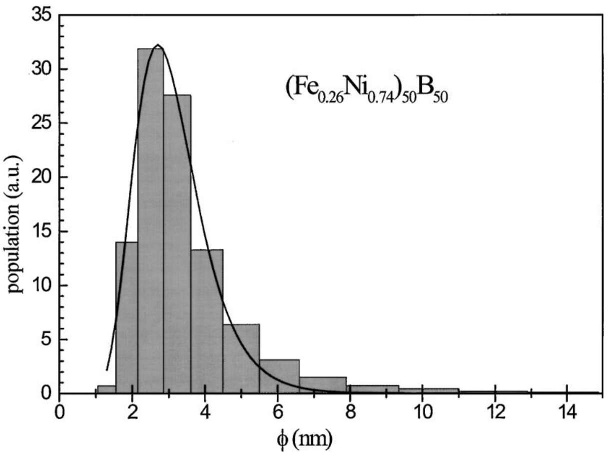

Figure 3 Size distribution of the $(Fe_{0.25}Ni_{0.75})_{100-y}B_y$ nanoparticles measured by light scattering method (open circles). The solid lines correspond to the least-square fitting of the data with a log-normal distribution (Equation 1).

TABLE I Mixing composition of transition metal ions in aqueous solution and the analyzed composition of the chemically synthesized powders

TM ions mixing composition	TM resulting composition	Boron composition	Alloy composition
Fe_0Ni_1	Fe_0Ni_1	46 at.%	$Ni_{54}B_{46}$
$Fe_{0.25}Ni_{0.75}$	$Fe_{0.26}Ni_{0.74}$	50 at.%	$(Fe_{0.26}Ni_{0.74})_{50}B_{50}$
$Fe_{0.375}Ni_{0.625}$	$Fe_{0.35}Ni_{0.65}$	48 at.%	$(Fe_{0.35}Ni_{0.65})_{52}B_{48}$
$Fe_{0.5}Ni_{0.5}$	$Fe_{0.49}Ni_{0.51}$	36 at.%	$(Fe_{0.49}Ni_{0.51})_{64}B_{36}$
$Fe_{0.625}Ni_{0.375}$	$Fe_{0.63}Ni_{0.37}$	60 at.%	$Fe_{0.63}Ni_{0.37})_{40}B_{60}$
$Fe_{0.75}Ni_{0.25}$	$Fe_{0.75}Ni_{0.25}$	51 at.%	$(Fe_{0.75}Ni_{0.25})_{49}B_{51}$
Fe_1Ni_0	Fe_1Ni_0	54 at.%	$Fe_{46}B_{54}$

where ϕ_0 is the most probable diameter of the particles and σ is the logarithmic standard deviation. We perform a least-square fit of these data with this distribution function with good agreement (Fig. 3, solid line) obtaining values of $\phi_0 = 2.7$ nm and $\sigma = 0.31$.

All these measurements indicate that the product of the synthesis consists in nanoparticles of approximately 2-3 nm. With all techniques we obtain the same nanoparticle size magnitude but, due to the characteristics of each method, we obtain different sizes for each one. In the TEM measurements, the contrast is produced by the variation of the densities, as the particles are amorphous. Also the samples are placed on a C-coated FormVar foil which contribute to the amorphous background. Then, considering the low resolution to observe the surface layer of the particles, the size measurement may result lower than the real value. The X-ray powder diffraction technique sees the more crystalline part of the sample corresponding to the oxides and borates at the surface of the particles or, probably, also to fully oxidized particles. In this case, this method is more sensitive to the larger particles and therefore the measurement tends to raise the calculated particle size. An average of the two more relevant experiments (TEM and light scattering) gives an average particle size of 2.1 nm, which we assume as the mean nanoparticle size. We emphasize that this result agrees with independent magnetic granulometry measurements [18, 19].

The transition-metal compositional analysis was perform by energy dispersion spectroscopy (EDS) resulting an iron-nickel composition close to the nominal one (Table I). The analyzed compositions of the transition metal elements agree with the mixed composition indicating that it is relatively easy to control the iron/nickel ratio. The atomic absorption analysis reveals that the boron concentrations are as high as 36 at.% to 60 at.% (Table I). The boron composition in our samples is notoriously higher than the values found in literature produced by reduction of transition metal salts in aqueous solution using KBH_4 or $NaBH_4$ [8, 14–17]. In references [14–17] the samples were prepared adding a KBH_4 (or $NaBH_4$) aqueous solution to the metallic salt solutions. In these cases, the boron composition goes from 18 at.% to 32 at.% depending on the preparation conditions. Instead, samples synthesized by adding the iron salt solution to the borohydride solution yields a boron content of about 34–38 at.% (references [16] and [8] respectively). Particularly, Wells *et al.* [16] discuss the fact that when an iron salt solution is added to the borohydride solution the boron concentration results greater than the inverse case and the resultant composition is irrespective of the borohydride concentration. Our samples were synthesized dropping the metallic salt solution in the $NaBH_4$ but our results show that the boron concentration is still greater. Conversely to what is cited in literature, we have used an excess of the reducting media when the reaction takes effect in order to secure that the samples do not oxidates. This excess of $NaBH_4$, combined with the preparation method, may cause the large boron concentration detected in our samples.

4. Conclusion

We have synthesized $(Fe_{1-x}Ni_x)_{100-y}B_y$ $(0 \leq x \leq 1)$ amorphous nanoparticles by chemical reduction method. The size of the particles is, for all compositions, ~2.1 nm diameter with a narrow log-normal distribution ($\sigma = 0.31$). The chemical reduction route shows that the transition metals are homogeneously distributed and their proportion is preserved. Notoriously, the boron composition observed is much higher than the one obtained by other comparable chemical reduction of transition-metal salts in aqueous solution of borohydride synthesis reports.

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