Amorphous Transition Metal-Boron Ultrafine Particles Prepared by Chemical Methods

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Ultrafine amorphous transition metal-boron (TM-B, TM = Co, Ni, Fe) powders have been prepared, under identical experimental conditions, by chemical reduction of Co^{2+}, Ni^{2+}, and Fe^{2+} ions with potassium borohydride in aqueous solution. The chemical compositions of the samples are close to $TM_{60}B_{40}$. The particles have a spheroidal shape with diameters ranging from 10 to 100 nm. X-ray diffraction and transmission electron microscopy investigations show that the Co-B and Ni-B samples are fully amorphous while in a few particles of the Fe-B sample the presence of α-iron microcrystallites are observed. Crystallization of the samples has been investigated by differential scanning calorimetry. Under anaerobic conditions the Co-B sample evolves toward t-Co_2B accompanied by a minor quantity of o-Co_3B; in the Ni-B and Fe-B samples, crystallization gives rise to a metallic component plus boride phases. A significant decrease of the boride phases and a corresponding increase of the metallic component are obtained in all samples when the thermal treatment is performed in the presence of traces of oxygen.

Introduction

Amorphous transition metal-boron (TM-B) alloys have been prepared as ribbons or films by melt spinning or by sputtering techniques.[1,2] Because of the increasing technological interest in these materials, new preparation methods have been developed and then improved or modified. Recent attention has focused on the preparation of amorphous alloy powders, which are preferable to ribbons and films for forming bulk amorphous samples.[3]

It has been known for a while that chemical reduction of metal ions by alkaline borohydrides leads to the precipitation of fine metallic powders,[4] some of which have recently been shown to be amorphous.[5] This discovery has renewed interest in this method of preparation, and several papers have recently appeared: the influence of BH_4/TM ion ratio, pH, temperature, mixing of reagents, washing, and drying procedures on the powders stoichiometries, morphology and structure have been investigated.[6-16]

We have reported the preparation of TM-B-O alloys (TM = Fe, Co, Ni) by chemical reduction of TM^{2+} ions with KBH_4 in aqueous solution.[17] The oxygen content, mainly due to the presence of borates, was in the range 6-12 wt%. Samples rigorously prepared in identical experimental conditions were amorphous when the TM was cobalt or nickel but mainly crystalline when the TM was iron.

We report herewith the results of further investigations on the preparation of Co-B, Ni-B, and Fe-B alloys and their morphological, structural and thermal characterizations.

Experimental Section

In a typical preparation procedure, 100 mL of aqueous 0.25 M $CoCl_2$, $NiCl_2$, or $FeSO_4$ was added dropwise (3-6 min) to 250 mL of aqueous 1 M KBH_4, which was in a large stoichiometric excess. The operation was carried out under an argon atmosphere in a three-neck round-bottom flask (1000 mL) equipped with a dropping funnel; borohydride solution was vigorously stirred while maintained approximately at 273 K with ice bath.

After the addition of the TM^{2+} solution was complete, the resulting fine black precipitate was filtered under argon in a Büchner funnel and washed first with distilled water and then with acetone in order to remove excess reagents. The washing procedure was carried out rapidly in order to shorten the contact time of the powders with water, which could lead to a reduction of boron content as a result of partial hydrolysis of the metal borides.[17,18]

Acetone-wet powders can be handled in air, while dry powders are highly pyrophoric. Stable powders are obtained by drying them at room temperature under a slow flow of argon containing

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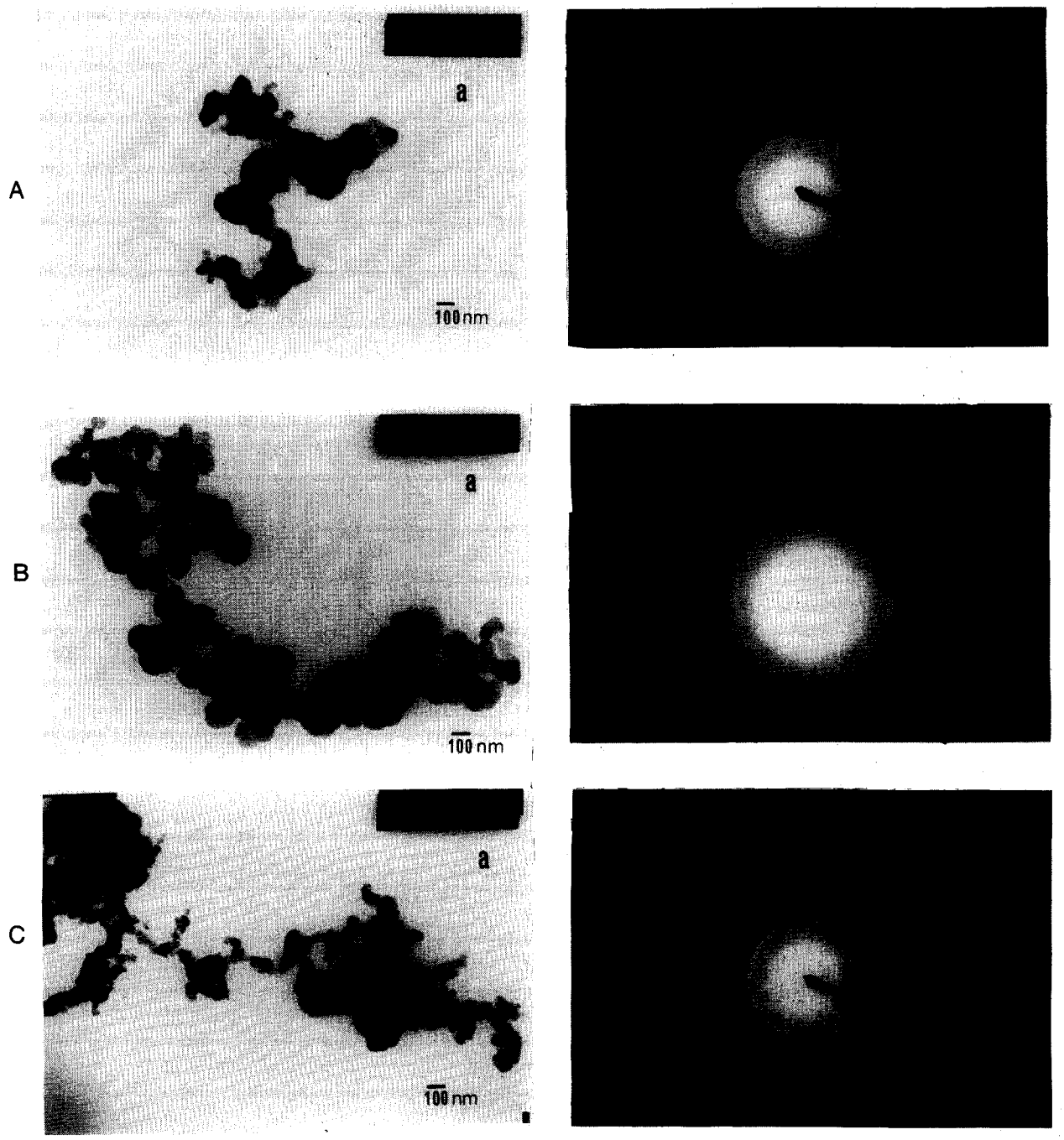

Figure 1. Bright-field image (a) and the corresponding SAD pattern (b) of the Co–B (A), NiB (B), and Fe–B (C) samples.

Table I. Composition of the Investigated Samples

	composition, wt %					
sample	Fe	Co	Ni	B	solvent	Δ
Fe–B	85(1)			12(1)	<1	2
Co–B		84(1)		11(1)	<1	4
Ni–B			85(1)	11(1)	<1	3

about 10 ppm of oxygen. Reaction, washing and drying procedures were kept rigorously constant in the preparation of all the samples.

Metal and boron content was determined by wet chemical analysis.[19] Traces of residual solvent were detected by thermogravimetry under a pure (99.9997%, N57) argon flux, using a Perkin-Elmer TGA7 instrument. Curie temperatures were measured according to the Faraday method.

Powders were investigated by transmission electron microscopy (TEM) using a JEOL 200CX microscope operating at 200 kV. Because of the small size of the individual particles, TEM observations were carried out directly on the as-prepared powders without any thinning procedure; powders were deposited on a carbon grid after being ultrasonically dispersed in octane.

X-ray diffraction (XRD) data were collected on a Siemens D500 powder diffractometer using Mo Kα radiation and a graphite monochromator on the diffracted beam. At least 50 000 counts at discrete scattering angles were collected on the as-prepared samples in order to obtain structure and radial distribution functions. Details on data collection and analysis have been described elsewhere.[20]

Thermal behavior and crystallization processes were examined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC7 apparatus with a heating rate of 10 K/min. Because of an enhanced tendency to oxidize during thermal treatment, the powders were sealed in aluminum pans under pure argon (N57).

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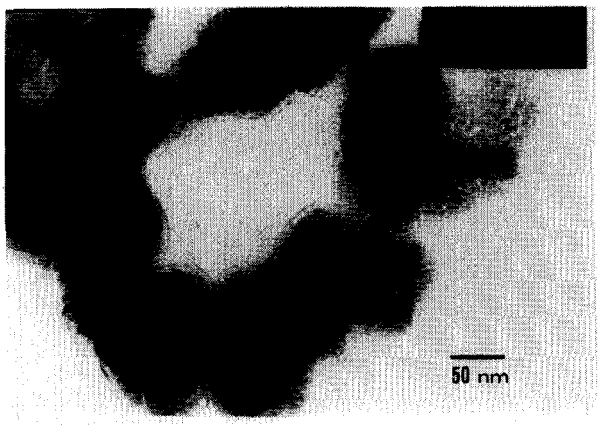

Figure 2. Bright-field image of the Co–B sample.

Table II. Curie (T_c) and Crystallization (T_x) Temperature by TGA Data

sample	T_c (K)	T_x (K)
Fe–B	735	745
Co–B	513	735

Results and Discussion

The chemical compositions of the three samples are very close. According to the results reported in Table I, the stoichiometries of the as-prepared powders are roughly $TM_{60}B_{40}$ with an uncertainty of about 2 at. %. TM+B sum is ~95–97 wt % with the difference to 100% due to residual solvent (below 1 wt % in all samples) and to oxygen. The drop in oxygen content with respect to the previously reported samples[16] (from 12 to 4 wt %), comes from different operational conditions such as concentration of reagents, KBH_4/TM^{2+} molar ratio, order of reagent mixing, and washing and drying procedures (which were improved in the light of recent developments in the knowledge of this complex redox reaction[6–17]).

The bright-field electron micrographs and pertinent selected area diffraction (SAD) patterns are shown in Figure 1. The particles have a spheroidal shape and diameters ranging from 10 to 100 nm with narrow particle size distribution centered around 30 nm (half-width around 15 nm). The Co–B and Fe–B particles appear connected to each other in chainlike form and those of Ni–B are in a more globular form. This behavior could originate from the difference in magnetic properties since the Co–B and Fe–B samples are ferromagnetic at room temperature (see Curie temperatures in Table II), while Ni–B is paramagnetic. The SAD patterns show that the Co–B and Ni–B samples are completely amorphous. In a few scattered particles of Fe–B sample the presence of α-Fe microcrystallites is confirmed by the presence of rings in the diffraction pattern.

The porosity in all samples was imaged by the TEM technique of defocus contrast.[21] Particles in all samples appear to be porous as shown in Figure 2 for the Co–B sample. A coating around each particle, due to superficial borates or boron oxides, is also evident in all Co–B, Ni–B, Fe–B samples.

The XRD spectra of the as-prepared samples are shown in Figure 3. The first halo in the Fe–B sample is slightly sharper as a consequence of the presence of a small fraction of crystalline material. The crystalline component gives

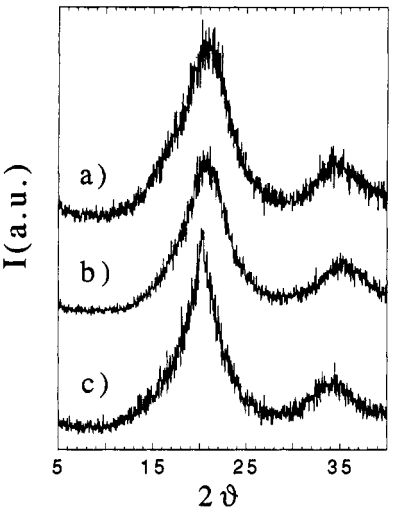

Figure 3. XRD spectra of the Co–B (a), Ni–B (b), and Fe–B (c) samples.

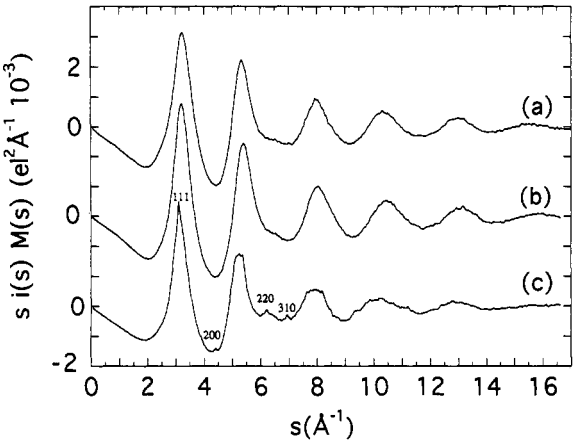

Figure 4. Structure functions $si(s)$ of the Co–B (a), Ni–B (b), and Fe–B (c) samples.

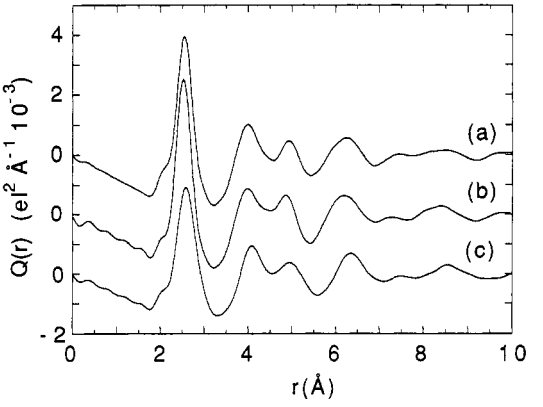

Figure 5. $Q(r)$'s of the Co–B (a), Ni–B (b), and Fe–B (c) samples.

rise to the few faint, defined peaks in the structure function $si(s)$ of Fe–B sample,[22] which is shown in Figure 4 together with those of Co–B and Ni–B samples. The general pattern of these functions, as well as that of the pertinent radial functions, $Q(r)$ (Figure 5), is typical of amorphous substances. The $Q(r)$'s of the Ni–B and Co–B samples are almost identical to those of the two samples which were prepared under a slightly different procedure and were characterized by a lower boron and a higher oxygen content.[17]

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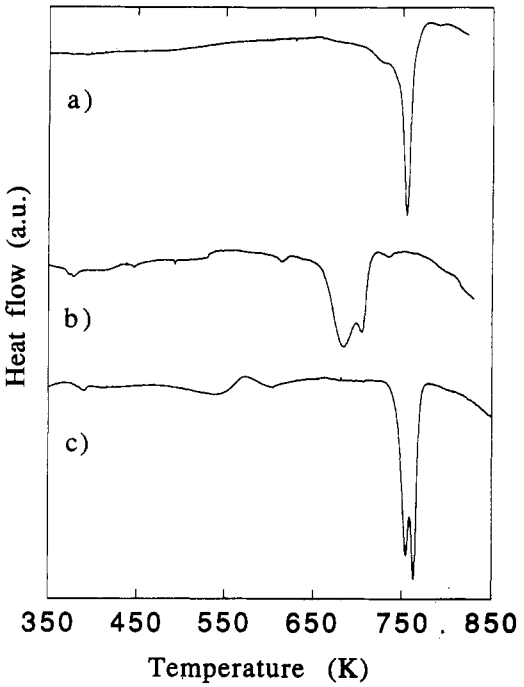

Figure 6. DSC traces of the Co–B (a), Ni–B (b), and Fe–B (c) samples.

Table III. Temperature of Crystallization T_x(onset) and Associate Enthalpy ΔH_x by DSC Data

sample	T_x (K)	ΔH_x (J/g)
Fe–B	743	176
Co–B	745	134
Ni–B	666	124

The $Q(r)$'s of all samples are very close to those of metal–boron alloys obtained by rapid quenching.[23] In particular the $Q(r)$ of Ni–B sample is very similar even in the minor details to that of a quenched sample of close composition.[24] The similarity of $Q(r)$'s in amorphous TM–B samples obtained either by chemical reduction or by rapid quenching suggests that metal–metal structuring, the dominant contribution to these curves, is similar in all samples.

All DSC traces given in Figure 6 show an exothermic signal due to sample crystallization. The onset crystallization temperature and crystallization enthalpy values, calculated from the peak areas, are given in Table III. The presence of two overlapping peaks in the Ni–B and Fe–B samples reveals a crystallization behavior which is more complex than in Co–B, which shows a sharp single peak.

XRD spectra of the powders which were treated in the DSC up to 853 K and then rapidly cooled to room temperature are shown in Figure 7. The most significant diffraction peaks in the Co–B spectrum are due to t-Co_2B,[25] and they are accompanied by faint peaks of o-Co_3B.[26] No peaks due to metallic cobalt can be identified. On the contrary, face-centered cubic (fcc) nickel[27] and α-iron peaks are present in the diffraction spectra of the Ni–B and Fe–B powders respectively. In the Ni–B sample both metal and a significant quantity of o-Ni_3B[28] are present. In the

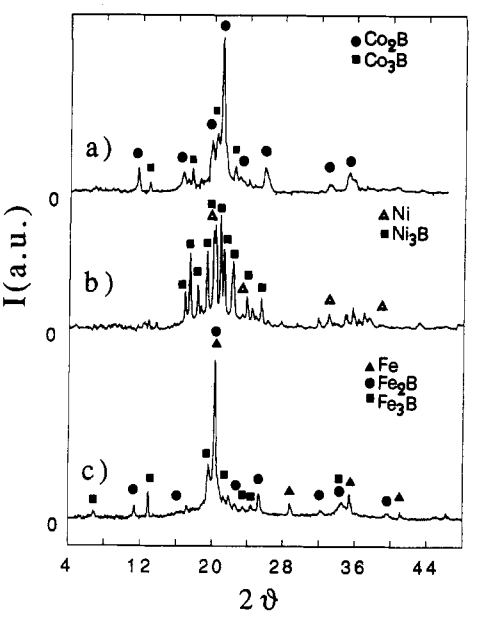

Figure 7. XRD spectra of the Co–B (a), Ni–B (b), and Fe–B (c) thermally treated samples.

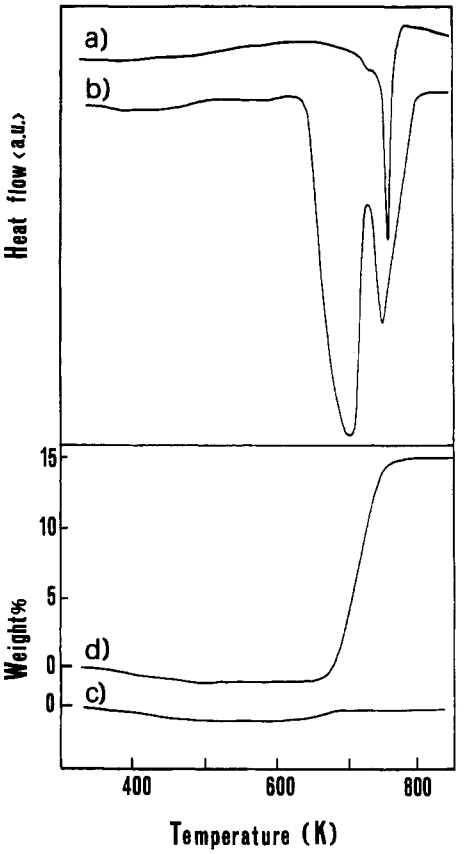

Figure 8. DSC (a, b) and TG (c, d) curves of the Co–B sample. Curves a and c refers to anaerobic condition.

Fe–B sample the dominant α-iron peaks are accompanied by those of t-Fe_2B[29] and by faint peaks arising from metastable Fe_3B.[30] These findings agree with those reported for Ni–B and Fe–B samples prepared by a similar procedure.[31,12]

To check the powders' stability at high temperatures in the presence of traces of oxygen, two different portions of

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each sample were examined by DSC and TGA under a flow of argon containing about 10 ppm of oxygen (the same gas used for drying and passivating the powders). The DSC and TGA thermograms of the Co–B sample are reported in Figure 8. The maximum of the large exothermic DSC peak falls at the same temperature (708 K) at the inflection point in the TGA, where a weight increase of about 15% occurs. The Ni–B and Fe–B samples show a similar behavior under the same experimental conditions. Neither the DSC peak nor the TGA inflection were observed in the analogous experiments carried out under a pure (N57) argon atmosphere. The powders which result from the two experiments have a completely different appearance: those thermally treated under pure argon maintain the characteristics of the as-prepared samples, i.e., very fine, metallic-black powders, while those treated in the presence of oxygen become granular, grey, and opaque. A comparison of the XRD spectra of the two Co–B samples which underwent different thermal treatments show that the oxidized powder has a much larger fraction of fcc metallic cobalt than t-Co_2B. This is the only component present in the nonoxidized sample. In the case of the Ni–B and Fe–B samples, oxidation leads to a significant decrease of the boride phases and a corresponding increase in the metallic component. These results suggest that the TM_2B are converted to metallic particles and boron oxide through the following reaction:[7]

$$4TM_2B + 3O_2 \rightarrow 8TM + 2B_2O_3$$

As revealed by XRD, the products of all samples which form upon anaerobic crystallization have a boron content less than $TM_{60}B_{40}$. This could originate from the segregation of elemental boron which, because of its small scattering power, is not detectable by XRD. Boron could also partially form a solid solution with metals.[32] Analysis of the diffraction peak positions of both fcc nickel and α-iron shows no variations of their cell parameters.[33] This would apparently exclude the second hypothesis and suggests that excess boron segregates in an elemental form.

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