Available online at www.sciencedirect.com

Journal of Solid State Chemistry 177 (2004) 382–388

JOURNAL OF SOLID STATE CHEMISTRY

http://elsevier.com/locate/jssc

Preparation of Fe/B powders by mechanical alloying

J. Abenojar,[*] F. Velasco, J.M. Mota, and M.A. Martínez

Departamento de Ciencia de Materiales e Ingeniería Metalúrgica, Universidad Carlos III de Madrid, Av Universidad 30. E-28911 Leganés, Spain

Received 18 October 2002; received in revised form 24 January 2003; accepted 24 January 2003

Abstract

Steels with a high boron content are valuable as a neutron shield in waste containers and as control absorbers in nuclear reactors. The purpose of this study was to obtain by mechanical alloying an iron powder with 50% boron (by weight) and then powder-metallurgy materials. The elementary powders were mixed in a high-energy mill for 36 h in an inert atmosphere. Samples were withdrawn at intervals, and the powder was characterized by differential thermal analysis, X-ray diffraction and electron microscopy. The Fe/B powders withdrawn at different intervals of milling were diluted with further additions of iron up to a final content of 10% boron. The mixtures were uniaxially compacted at 500 MPa; their green density was verified, and they were sintered in argon at 1150°C. Their physical properties (density and dimensional change) and bending strength were evaluated and microstructural studies and fracture tests were performed.

Keywords: Mechanical alloying; Powder metallurgy; Boron steel

1. Introduction

Boron, with an effective cross-section of 755 barns, is an ideal material for nuclear applications although its metallurgical properties have certain limitations. It is one of the few elements that does not emit γ-rays on being radiated [1]. The control absorbers in some reactors are made of steel with boron (a maximum of 4%) [2]. In other plants, a compound prepared by infiltration of B_4C preforms with molten aluminum is used [3]. A similar material, but with better properties, manufactured by powder metallurgy, is an alloy of Cu with 20% by weight of B_4C, encased in stainless steel [2].

Stainless steels have generally been used on account of their corrosion resistance [4,5]. Control bars were made of 304 stainless steel with 3% B by vacuum processing and rolling [6]. This provides a low-cost material, corrosion resistant and efficient as a neutron shield, but the boron content cannot exceed 3% as the material is extremely hard and brittle and cannot be rolled.

A number of reports describe the use of small amounts of boron in steels made by powder metallurgy. These works use a maximum of 0.8% by weight of boron which promotes the formation of the eutectic Fe–Fe_2B at 1175°C [7,8] and thus liquid-phase sintering that gives a density of up to 96–98% of the theoretical value [9]. Boron and carbon are used in steels as substitutes for copper to promote sintering; the mechanical properties and corrosion resistance are similar, and recycling is easier when these steels are used in the nuclear industry [10].

Mechanical alloying is now widely used to prepare amorphous materials or other non-equilibrium materials [11,12]. The Fe–B system lends itself to a detailed study of mechanical alloying. The alloys have been prepared by various techniques such as rapid solidification, sputtering, or vacuum evaporation [13,14] and their amorphization studied by the method of mechanical alloying. A number of reports have given the amount of boron required for the maximum degree of amorphization as percentages that range from 60% to 20%. Thermodynamic calculations estimate amorphization in the range 32–47% of boron [15–21]. The aim of our experimental work was to explore the possibility of using mechanical alloying coupled with powder technology, to manufacture steel with a high boron content useful in nuclear technology.

2. Experimental

As already stated, the materials were manufactured by powder metallurgy (P/M). The powders used were:

---

[*] Corresponding author. Fax: 34-91-624-9430.

E-mail address: abenojar@ing.uc3m.es (J. Abenojar).

0022-4596/$ - see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2003.01.001

iron ASC100.29, in the form of atomized powder of 99.9% purity, supplied by Höganäs (Sweden), particle size under 150 μm; amorphous boron, supplied by Strem Chemicals, 92–95% pure (a trace of magnesium), and natural graphite of particle size under 50 μm.

The base powders, iron and boron (50% by weight, from now on, Fe/B) were mixed in an attritor at 700 rpm, in argon atmosphere, with a charge/ball ratio of 15:1 and with the addition of 1.5% of the lubricant. The mechanical mixing was done in two stages: the first for the study of the Fe/B system before the amorphization of the iron, and the second at the amorphous stage and the formation of intermetallic compounds.

During the first stage that lasted for 12 h milling, samples were withdrawn at 2 h intervals for their characterization by X-ray diffraction and scanning electron microscopy (SEM).

After each 2 h of mixing, the powders were diluted with Fe until the boron content was 10% by weight. Then 0.3% of carbon was added, and samples were compacted at 500 MPa and the green density (density of as-compacted materials) [22] was measured. They were then sintered for 30 min at 1150°C in argon atmosphere. This temperature was chosen from previous work [23], as DTA of these materials give no special information (sintering takes place in solid state). The sintered samples were then submitted to measurements of the physical and mechanical properties—sintering density, dimensional change and bending strength—and finally their microstructure and fracture characteristics were determined. All these values were compared with those of the materials obtained by simple mixture of powders of the same composition (indicated as '0 h' in the figures of the results).

This first stage was followed by a second longer milling, replacing the ASC100.29 powder by ASC300 which is much finer, and adding 1% carbon. The milling was continued until the iron reached the amorphous state. Samples of the powder were withdrawn at intervals of 6 h for characterization by X-ray diffraction and SEM.

The powder submitted to mechanical alloying for 36 h, which by that time was amorphous, was also diluted with iron to reach a composition of 10% boron by weight, and then compacted and sintered in the same conditions as before. In all cases, results are the average of at least four samples tested.

3. Results and discussion

3.1. Fe/B powder milled for up to 12 h

As described in the experimental section, the first stage consisted in the mechanical mixing of Fe with 50% boron by weight for 12 h, with withdrawal of samples every 2 h. Fig. 1 shows micrographs of the powder at different stages of milling. Figs. 1a and b (2 and 4 h milling) show the typical deformation of the iron particles with the milling, while the boron particles remain separate and form agglomerates. There is no close mixing of the elements, and as always occurs in mechanical alloying when one of the constituents is ductile (Fe in this case), this constituent is deformed in the first stages. Starting from 6 h (Fig. 1c), the particles of iron and boron begin to merge, and those of iron undergo no further deformation as the boron surrounds their surface. From 8 h of milling until 12 h (Figs. 1d–f), the roughly equiaxial particles of iron are enveloped in boron, with a morphology characteristic of the last stages of mechanical alloying. The unusual feature is that the boron particles are not trapped within those of iron, as occurs in most processes of alloying of hard particles with fragile ones, but envelop the iron particles, and prevent their bonding. The particle size diminishes notably with the milling time.

X-ray diffraction (Fig. 2) of the powders at the different intervals of milling shows no significant change in the iron peaks, although the intensity of the second peak (200) decreased and it was a little wider. Hardly any amorphous state is observed. Since amorphous boron was used, it was impossible to study boron peaks, and, as observed by SEM, no borides were formed.

3.2. Fe/B powder milled for 36 h

Milling was continued, with withdrawal of powder samples at 6 h intervals, until the iron was amorphous. The state of the powder after 36 h milling (Fig. 3), may be compared with the more or less crystalline state in Fig. 1. This is also shown by X-ray diffraction (Fig. 4). From 12 h milling, the peaks of Fe had begun to weaken, and at 36 h they were further diminished as is shown in the non-normalized diffractograms (Fig. 4, above). Peaks of borides appear after 30 h milling: see the normalized diffractograms in the lower part of Fig. 4. This was generalized at 36 h which was taken to be the optimum time of mechanical alloying.

3.3. Processing of the materials. Properties obtained

As described in the experimental section, the powders withdrawn at 2 h intervals of milling (up to 12 h) were diluted with Fe until a 10% concentration by weight was reached. An addition of 0.3% carbon was made. This operation was repeated with the powders after 36 h milling. Fig. 5a shows the green density of the samples compacted at 500 MPa.This varied very little between the samples, and in all of them the relative density was above 65%. This is a notable improvement over the density of the elemental mix of powders of the same composition, without mechanical alloying (0 h in the

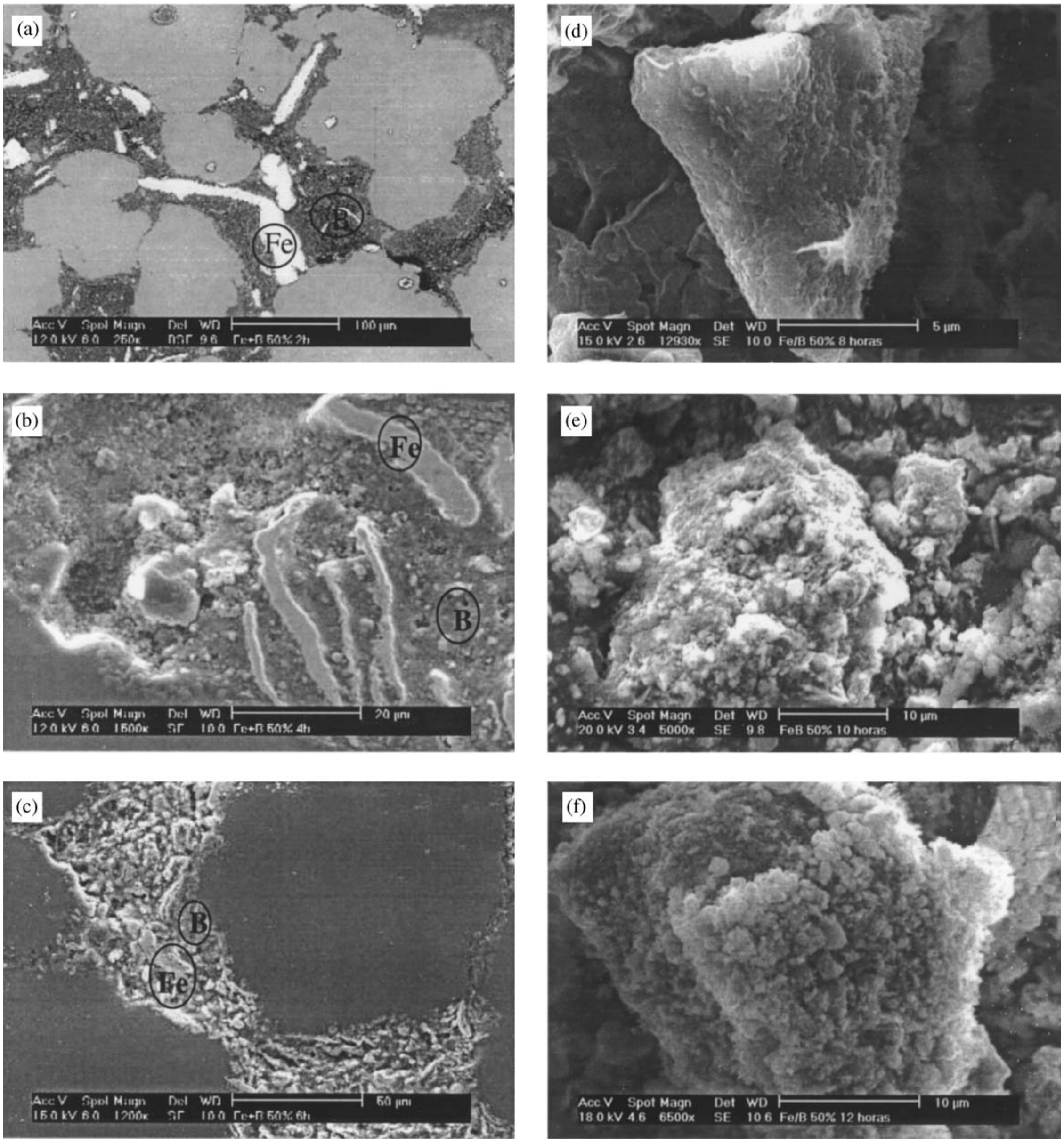

Fig. 1. Microstructural analysis of Fe/B powder, after (a) 2 h; (b) 4 h; (c) 6 h; (d) 8 h; (e) 10 h; and (f) 12 h of milling.

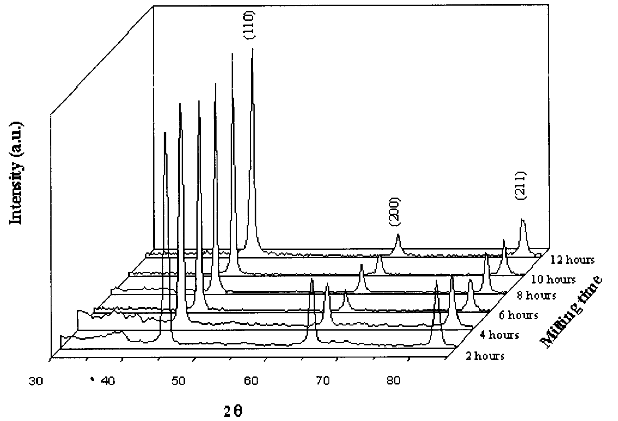

Fig. 2. Diffractogram of Fe/B powders at milling times of up to 12 h.

figure), probably due to the small size of the added particles of Fe. The figures are the normal ones in green P/M materials. The property is not modified by the longer milling time, probably because the particle size hardly changes between 10 and 36 h milling.

After sintering, the density (Fig. 5a) was similar to that of the green material, and remained low at around 70–75%. There was even a slight loss in materials milled for up to 6 h. The density rose, however at 0, 8, 10 and 12 h and again at 36 h. This is in agreement with the study of dimensional change (Fig. 5b) which indicated a strong swelling of the materials milled between 2 and 6 h and a shrinkage between 8 and 12 h, which was coincident with the morphological study. While the particles of Fe are deformed and those of boron poorly

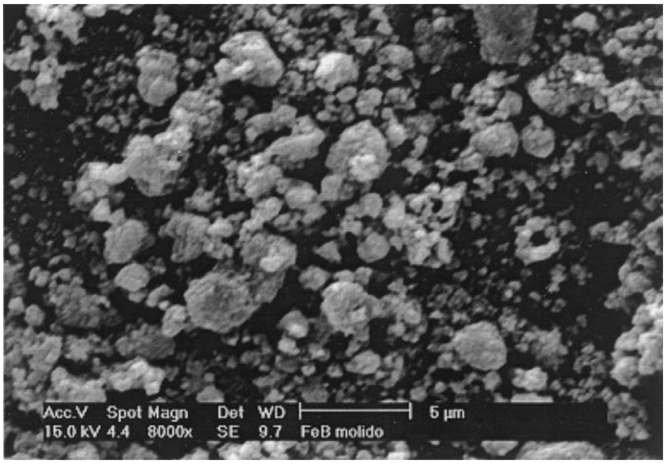

Fig. 3. Microstructure of Fe/B powder milled for 36 h.

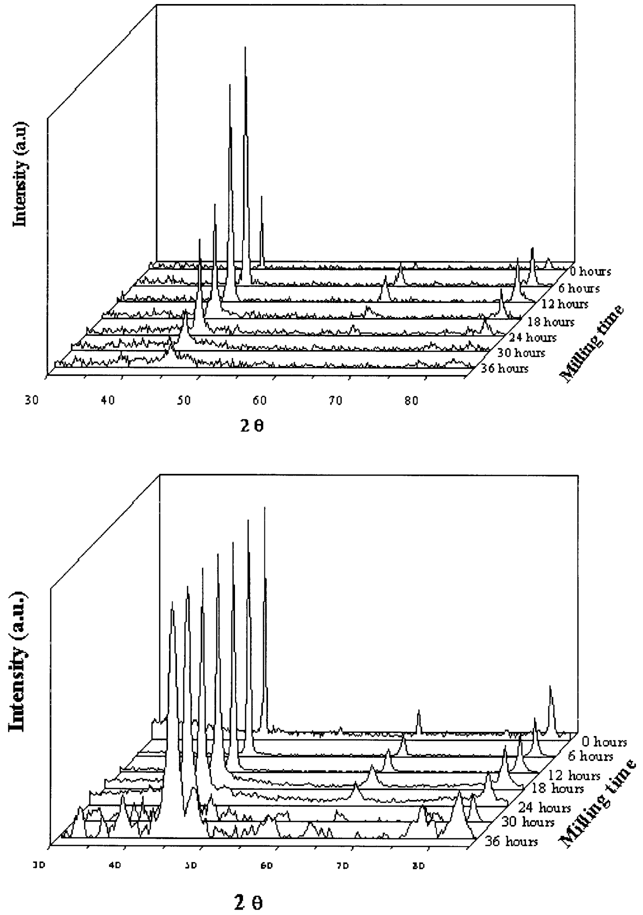

Fig. 4. Diffractograms of Fe/B powders, at milling times of up to 36 h. Above, non-normalized diffractograms; below, normalized diffractograms.

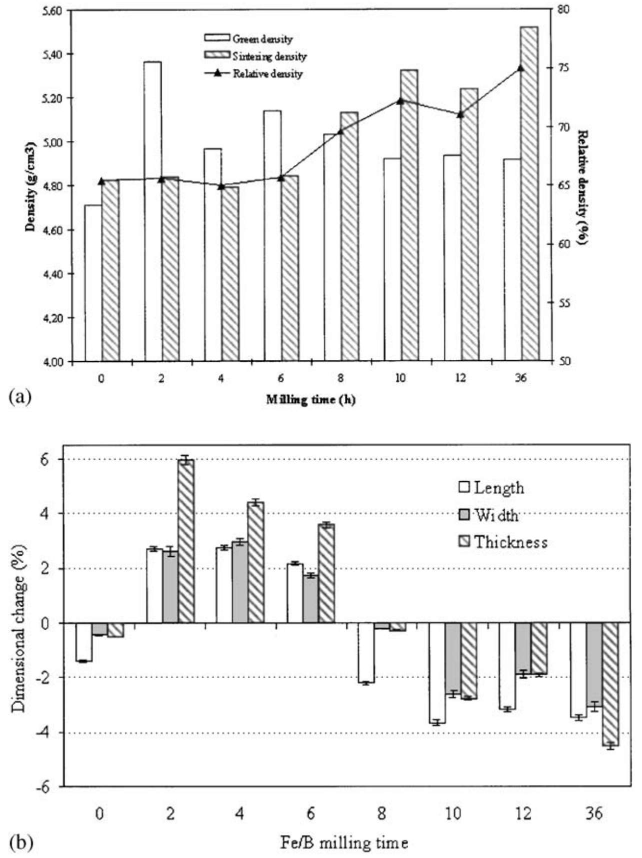

Fig. 5. (a) Green density, sintering density and relative sintering density of Fe + 20% Fe/B material, at different Fe/B milling times, after sintering in argon at 1150°C. (b) Dimensional change of Fe + 20% Fe/B material, at different Fe/B milling times, after sintering in argon at 1150°C.

distributed (up to 6 h milling), sintering does not affect the density. Once the Fe particles are coated with boron, the homogeneity and easy diffusion of the B allow the densification, and this is slightly greater at 36 h.

This is explained by the microstructural study (Fig. 6). After a short time of milling, the materials have a large number of pores (Figs. 6b–d) caused by the iron borides during the diffusion of the boron, which leave voids in

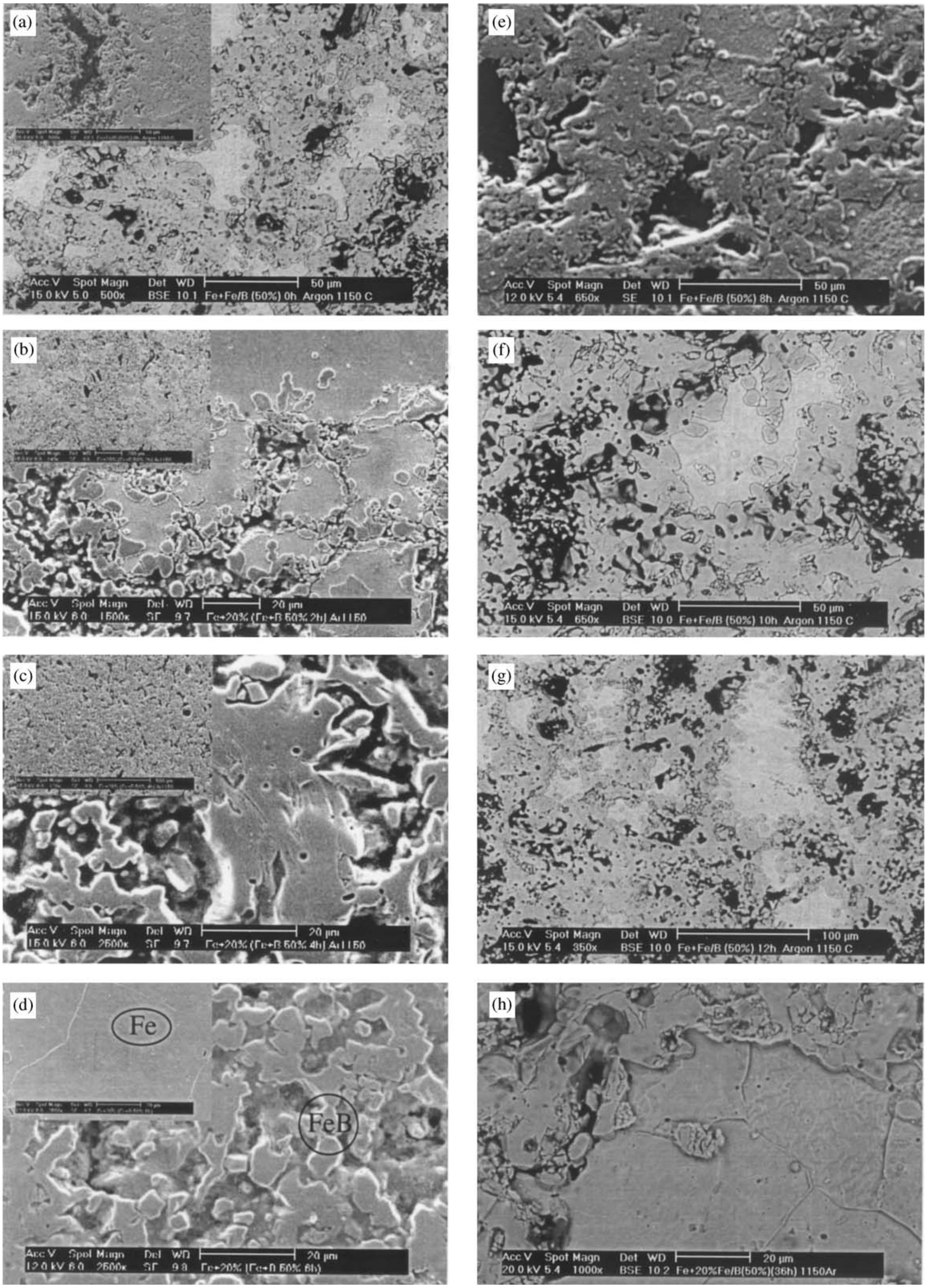

Fig. 6. Microstructural analysis of Fe + 20% Fe/B material after sintering in argon at 1150°C, at different Fe/B milling times: (a) 0 h; (b) 2 h; (c) 4 h; (d) 6 h; (e) 8 h; (f) 10 h; (g) 12 h; (h) 36 h.

the original particles. With longer milling, the Fe/B becomes more homogeneous, and on sintering the number of pores decreases (Figs. 6e–g). The material formed from the elemental powder mix (0 h, Fig. 6a) is free of the clusters of boron produced by the short milling, so they sinter better and acquire higher density.

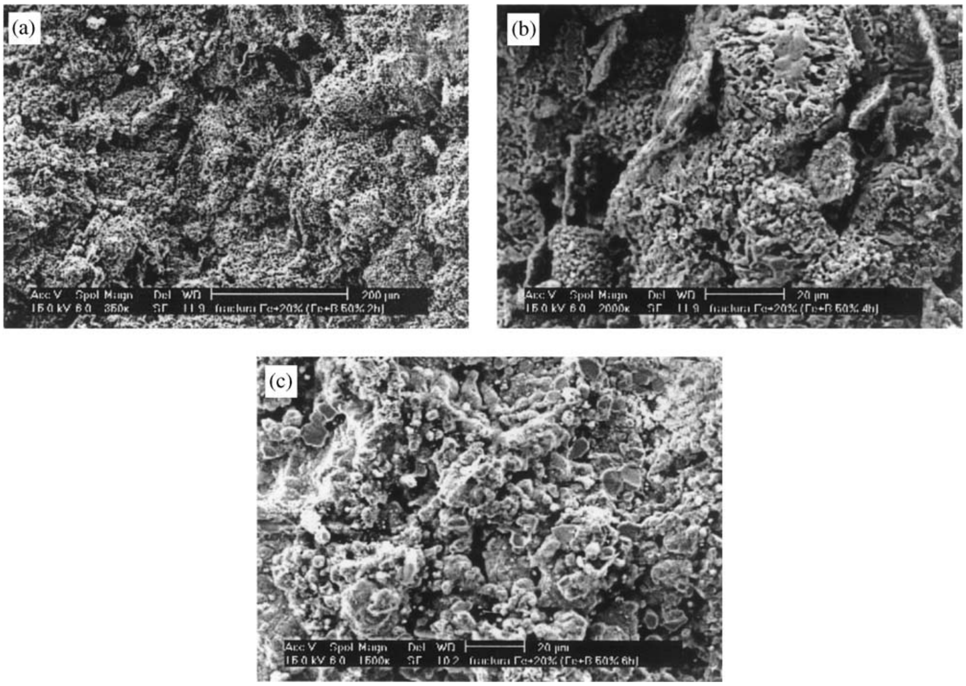

Fig. 7. Fracture analysis of Fe + 20% Fe/B material, at different Fe/B milling times after sintering in argon 1150°C. (a) 2 h; (b) 4 h; (c) 6 h of milling.

The study of the microstructure shows particles of ferrite and of borides in all the materials, the ferrite coated with the intermetallic compounds.

Hardness cannot be measured in these materials as the brittle samples break on being placed in the hardness-meter; measurement was possible only in the Fe + 10%B, 36 h, where it was found to be 63 HRA. The bending strength is controlled by the presence of brittle borides. The porous structures formed in short milling times were more brittle, but this improved between 6 and 10 h, and reached a maximum at 36 h. The materials with Fe/B milled for 2 – 4 h appear poorly sintered as is shown by their fracture (Figs. 7a and b) by particle decohesion due to porosity. The higher density reached with longer milling time improves the strength of the materials although brittle fracture predominates as the borides cause intergranular fracture (Fig. 7c).

4. Conclusions

The preparation of sintered components from mechanically alloyed Fe/B powders with optimal properties requires 36 h of high-energy milling. The materials obtained by this procedure are particularly brittle.

Iron powder reaches the amorphous state and forms the intermetallic compound with 36 h of milling.

The properties attained with the addition of mechanically alloyed material to an iron matrix are better than those attained with the direct addition of boron in the same proportion.

References

[1] H.C. Cowen, Nucl. Eng. 1 (1959) 11–17.
[2] M. López, F. Pascual, Materiales Nucleares, Junta de Energía Nuclear, Madrid, 1971.
[3] S. Glasstone, Ingenieria de Reactores Nucleares, Reverté, Madrid, 1990.
[4] L.B. Prus, E.S. Byron, J.F. Thompson, Nucl. Sci. Eng. 4 (1958) 415–428.
[5] D.N. Dunning, W.K. Anderson, P.R. Mertens, Nucl. Sci. Eng. 4 (1958) 402–414.
[6] N. Balai, Nucl. Sci. Eng. 1 (1958) 429–438.
[7] D.S. Madan, R.M. German, W.B. James, Prog. Powder Metall. 42 (1986) 267–283.
[8] D.S. Madan, R.M. German, Adv. Powder Metall. 1 (1989) 147–161.
[9] M. Selecká, H. Danninger, R. Bures, L. Parilák, Proceedings of Powder Metallurgy World Congress, EPMA, Shrewsbury, 1998, p. 638.
[10] H. Kuroki, H.Y. Suzuki, K. Shinozaki, Proceedings of Powder Metallurgy World Congress, EPMA, Shrewsbury, 1998, p. 293.
[11] A.W. Weeber, H. Bakker, Physica B 153 (1988) 93–135.
[12] E. Hellstern, H.J. Fecht, Z. Fu, W.L. Johnson, J. Appl. Phys. 65 (1989) 305–310.
[13] T. Kemeny, I. Vineze, B. Fogarassy, S. Arajs, Phys. Rev. B 20 (1979) 476–478.
[14] C.S. Fetzer, L. Granasy, T. Kemeny, E. Kotai, M. Tegze, I. Vineze, W. Hoving, F. van der Woude, Phys. Rev. B 42 (1990) 548–554.

[15] M.T. Clavaguera-Mora, M.D. Baro, S. Surinach, N. Clavaguera, Colloque Phys. 4 (1990) 49–54.

[16] J. Jing, A. Calkn, S.J. Campbell, J. Phys.: Condens. Matter 38 (1991) 7413–7420.

[17] H. Okumura, K.N. Ishihara, P.H. Shingu, H.S. Park, S. Nasu, J. Mater. Sci. 27 (1992) 153–160.

[18] T. Nasu, M. Sakurai, K. Suzuki, C.C. Koch, A.M. Edwards, D.E. Sayers, Mater. Trans. 36 (1995) 1088–1090.

[19] J. Balogh, T. Kemeny, I. Vineze, L. Bujdoso, L. Toth, G. Vineze, J. Appl. Phys. 77 (1995) 4997–5003.

[20] P. Ruuskanene, O. Heczko, J. Non-Cryst. Solids 224 (1998) 36–42.

[21] R. Gupta, A. Gupta, Mater. Sci. Eng. A 304–306 (2001) 442–445.

[22] R.M. German, Powder Metallurgy of Iron and Steel, Wiley, New York, 1998.

[23] J. Abenojar, F. Velasco, M.A. Martínez, in: J.M. Torralba (Ed.), New Developments on Powder Technology, 2001, p. 1313.