ELECTRON MICROSCOPY AND X-RAY DIFFRACTION CHARACTERIZATION OF FeAl -BN NANOCOMPOSITES PRODUCED BY MECHANICAL ALLOYING.

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ABSTRACT
Structural characterization of Fe, Al + BN powders mechanically milled from Fe, Al and BN powders as raw materials was performed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The analyses indicated the production of particles measuring approximately 20 nm. After long milling times a well-dispersed nanostructure was obtained. The high resolution TEM (HRTEM) analysis indicated that some intermetallic particles are coated BN particles similar to a core-shell structure.

Key words: Fe-Al intermetallic/BN, Nanocomposites, Mechanical milling, XRD, HRTEM.

CARACTERIZACIÓN POR MICROSCOPÍA ELECTRONICA Y DIFRACCIÓN DE RAYOS X DE NANOCOMPUESTOS FeAl-BN PRODUCIDOS POR ALEADO MECÁNICO

RESUMEN
Polvos de Fe, Al + BN preparados por aleado mecánico a partir de Fe, Al y BN, fueron caracterizados usando técnicas de difracción de rayos-X (DRX) y microscopia electrónica de trasmisión (MET). Los análisis mostraron un tamaño aproximado de 20 nm en las partículas obtenidas. Se observa una nanoestructura bien dispersa de ambos tipos de estructuras las cuales contribuyen establemente a la formación del nuevo material. Análisis realizados por MET indicaron la presencia de algunas partículas intermetálicas (FeAl) cubiertas por BN. Estas partículas presentan una estructura similar al núcleo-coraza.

Palabras clave: Intermetálico Fe-Al/BN, Nanocompuesto, Molienda mecánica, XRD, HRTEM.

INTRODUCTION

FeAl intermetallic alloy has been widely studied because of its excellent mechanical properties at high temperatures and the low cost of the starting material [1-4]. However, the poor ductility and low strength at different temperatures limit its applications as a structural material. The properties of this alloy have been improved by adding fine ceramic particles and reducing the crystal size to nanometric size ranges [5-6]. The mechanical alloying (MA) process is a technique that allows the production of homogeneous materials with nanometric size grains. Therefore, this technique has been used to investigate several intermetallic-ceramic nanocomposites [7-8]. It has been reported that BN displays a high plastic deformation as a consequence of formation of nanotubes [9], but until now there is no reported research on the mechanical milling of iron aluminide reinforced with boron nitride particles. We have observed that this material indeed displays good mechanical properties in the nanometric scale range, and in this document we present the microstructural characterization of Fe-Al intermetallic/BN ceramic nanocomposites mechanically milled from Fe, Al and BN powders as raw materials.

MATERIALS AND METHODS

FeAl intermetallic/BN ceramic nanocomposite was produced by mechanical milling starting from the Fe, Al and BN powders. Each component powders were previously mechanically milled in order to compare the individual components structures (FeAl and BN) before milling and the structure of the nanocomposite formed after milling. Thus, the raw powders of Fe and Al were milled for 12 h before the mechanical alloying. Similarly, boron nitride powders were milled for 32 h. The powder mixture of both components was milled for 12, 18, 25, 28 and 32 h in a high-energy ball mill SPEX 8000 using hardened-steel vials and balls, with the ball-to-powder weight ratio being 10: 1. Ethanol was used as processing-control agent to prevent welding. Fe and Al powders were mixed in quantities according to the intermetallic composition $Fe_{60}Al_{40}$ and the nominal nanocomposite composition was $(Fe_{60}Al_{40})_{0.90}(BN)_{0.10}$. Milled powders were analyzed by X-ray diffraction analysis in a Siemens D5000 equipment using monochromatic Cu kα radiation (λ=0.154 nm). The chemical analysis of the samples was performed with the x-ray energy dispersive spectroscopy (EDS) equipment NORAN-EDS attached to a scanning electron microscope (SEM) JEOL 6400. These samples were also observed under the transmission electron microscope (TEM) JEOL-FEG-2010-EX for high resolution TEM (HRTEM) observations. This microscope is equipped with a Schottky type field emission gun, an ultra-high resolution pole piece (Cs = 0.5 mm) operated at 200 kV. Some samples were also observed in the JEOL JSM transmission electron microscope. For the digital image processing, the Fast Fourier Transforms (FFT) analysis, and the statistical measurements, the Gatan Digital Micrograph (DM) software was used.

RESULTS AND DISCUSSION

Figures 1 shows two HREM images of the boron nitride powders milled for 32 and 28 h, respectively. The reduction of the hexagonal crystal size to the nanoscale range can be observed. Figure 1a shows a multilayer BN nanotube with a lattice distance of 0.34 nm. This distance corresponds to the (002) lattice plane of the hexagonal (hcp) crystalline structure of BN. Figure 1b shows a bending structure resembling the structural features of multilayer nanotubes. The structure tends to shrink, bending the layers toward the center of the particle. This type of structure is commonly observed in boron nitride nanostructures obtained after mechanical milling [9-10]. HREM images of the FeAl alloyed powders were also obtained. Previous studies have indicated that the intermetallic compound was formed after 6 or 7 h of mechanical alloying [11].

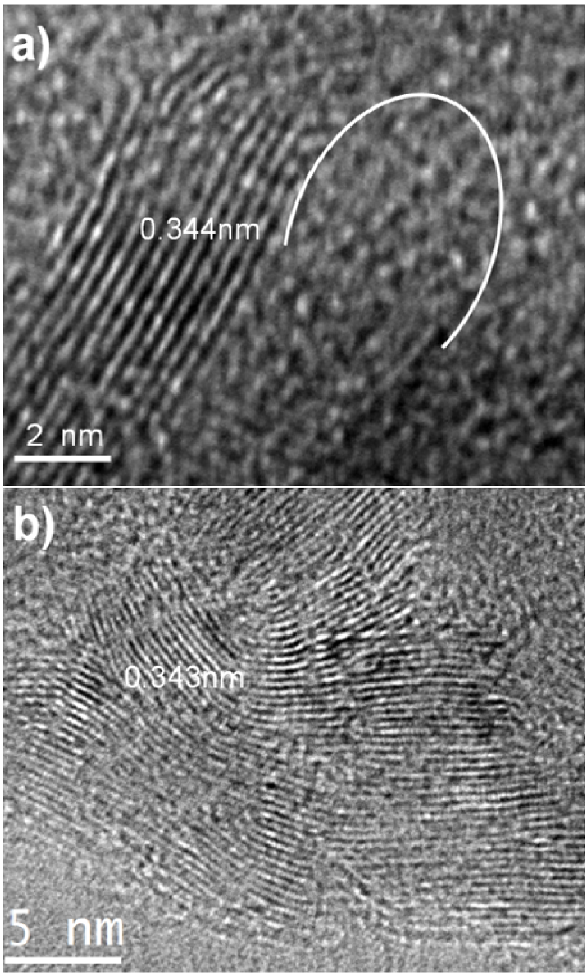

Fig. 1. HREM images of BN powders milled for 32 h (a) and 28 h (b). a) A multilayer BN nanotube with lattice distance of 0.34 nm for the (002) lattice plane of the hexagonal crystalline structure. b) A bending structure resembling the structural features of multilayer nanotubes.

Figure 2a shows a HREM image of the intermetallic compound milled for 12 h. Figure 2b shows the filtered image of the structure enhancing the structural characteristics. The interplanar spacing of 0.28 nm corresponds to that of the (110) planes of FeAl. Among the differences between the structure of the intermetallic and the one obtained in the boron nitride powders there is, for example, the straight rather than curved planes in the intermetallic structure. From the theoretical point of view, the mechanical behavior of boron nitride nanotubes should improve the poor ductility and low strength of the intermetallic alloy in the consolidation of the nanocomposite material. It is worth noting that 32 h of milling can be applied to achieve the BN particle dispersion in the FeAl intermetallic. Furthermore, after the 32 h milling the structural contribution of BN is better due to its structure with large planar defects.

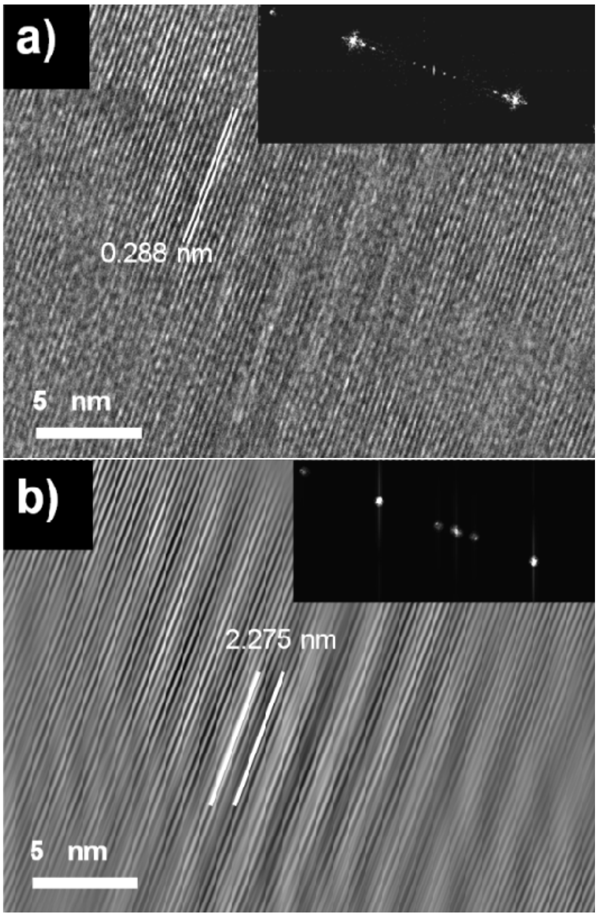

Fig. 2. a) HREM image of the intermetallic compound milled during 12 h. b) Filtered processed image from (a) to enhance the structural characteristics. The interplanar spacing of 0.28 nm corresponding to that of the (110) planes of FeAl is observed.

Figure 3a shows a series of X-ray diffraction patterns of FeAl + BN specimens for 12, 18, 25, 28, and 32 h of ball-milling time respectively. Note that after 12 h of milling, the XRD pattern shows few peaks. A shift of the diffraction peaks to higher angles and the presence of the (110), (200) and (211) diffracted peaks of the FeAl intermetallic structure indicate the BCC structure formation. No evidence of BN structure and/or the formation of other phases were observed. This is probably due to atomic number differences between the FeAl and BN phases. As the milling time increases, the intensities of the diffraction peaks decrease and become very broad, suggesting the crystal size decrease and the introduction of a large number of crystalline defects into the structure. Figure 3b shows the dependence of the crystal size on the milling-time obtained by the Scherrer equation, which does not take into account the microstrain contribution. After 12 h of mechanical alloying, the average crystal size was 77 nm, dropping to less than 58 nm after 32 h.

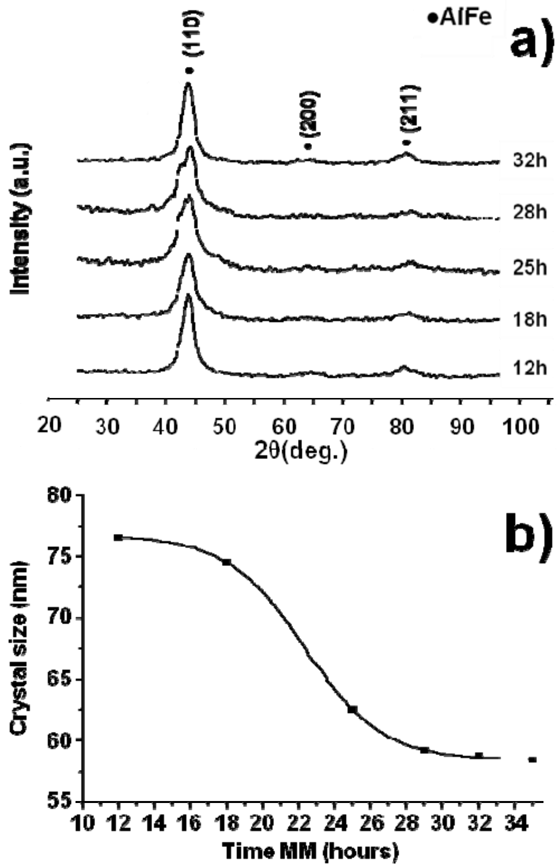

Fig. 3. a) X-ray diffraction patterns of FeAl + BN specimens for 12, 18, 25, 28, and 32 h of ball-milling time respectively, b) Graph of the milling-time dependence on the crystal size obtained by the Scherrer equation.

Transmission electron microscopy has also been used for the structural characterization of the nanocomposite milled powders. Figure 4 shows the bright and dark field images and the electron diffraction pattern of the FeAl+BN nanocomposite powder milled for 32 h. The dark field image shows the presence of less-than-50 nm crystalline particles. The indexation of the polycrystalline diffraction pattern suggests a B2-type cubic structure. The measured crystal size was smaller than the values obtained from X-ray measurements. Few bright spots (indicated by arrows) are emerging from the material matrix. This suggests a large disorientation of the material grains, indicating an incoherent matrix between intermetallic and ceramic grains, maybe due to the incorporation of ceramic particles into the rigid structure of the intermetallic compound.

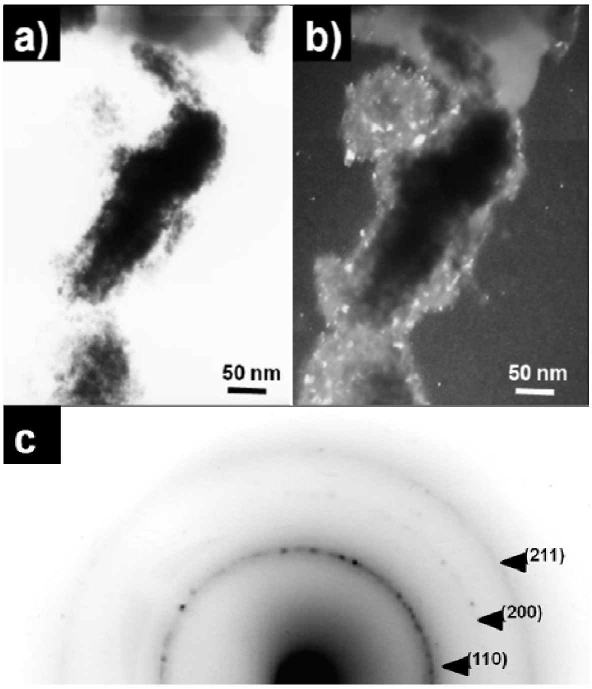

Fig. 4. Bright (a) and dark (b) field images, (c) the corresponding electron diffraction pattern of the FeAl+BN nanocomposite powder milled for 32 h. Note the presence of less-than-50 nm crystalline particles in the dark field image. The indexation of the polycrystalline diffraction pattern suggests a B2-type cubic structure.

Figure 5 shows two bright-field TEM images of both the BN and FeAl + BN samples after 32 h of milling. As it is observed in this figure, the BN particles have a greater agglomeration than the particles in the nanocomposite. This may be a result of the curvature of the particles shown in Figure 1a, where the particles are intertwined and bend to have higher attraction energy between them. In the case of nanocomposite particles in a rigid matrix, they behave in such a way that agglomerates are not formed.

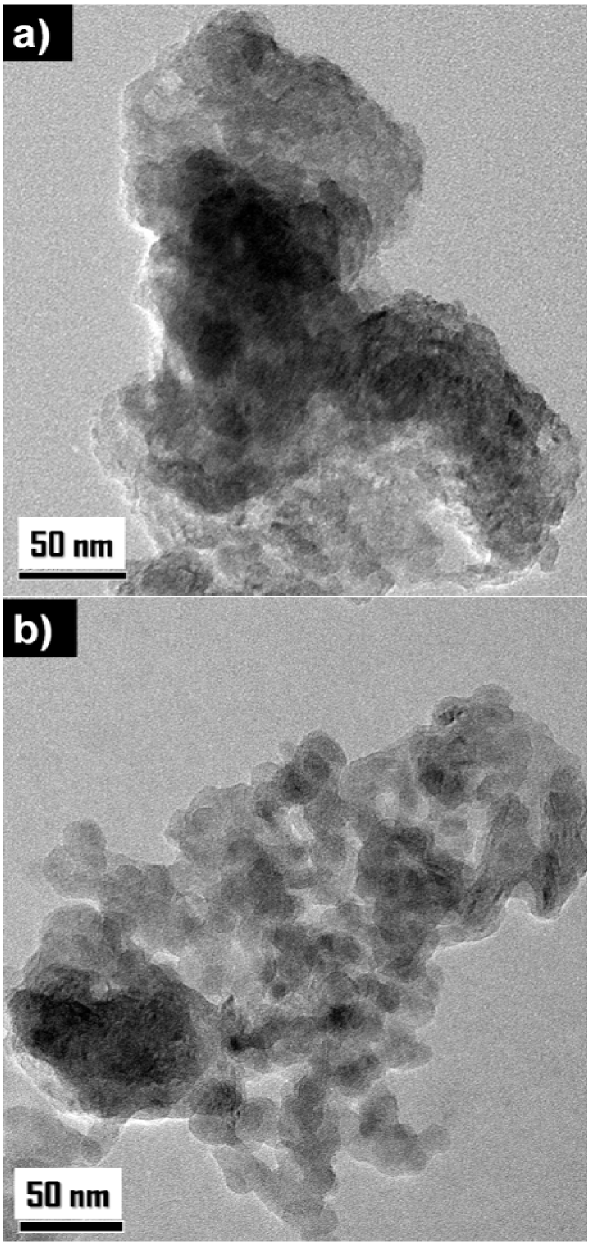

Fig. 5. Bright-field TEM images of the BN (A) and FeAl + BN (B) samples after 32 h of milling. Note that the BN particles have a greater agglomeration than the particles in the nanocomposite.

Figures 6a and b show two HRTEM images of the FeAl + BN sample. The structural features of the intermetallic and ceramic structures are clearly observed. The periodic distances measured were about 0.206 nm and 0.34 nm, which are associated with the (110) interplanar distance of the intermetallic phase and with the (002) interplanar distance of the BN phase, respectively. After milling, both materials retained their nanostructural features: the intermetallic structure appears with its straight planes, while the ceramic material does with their bent planes.

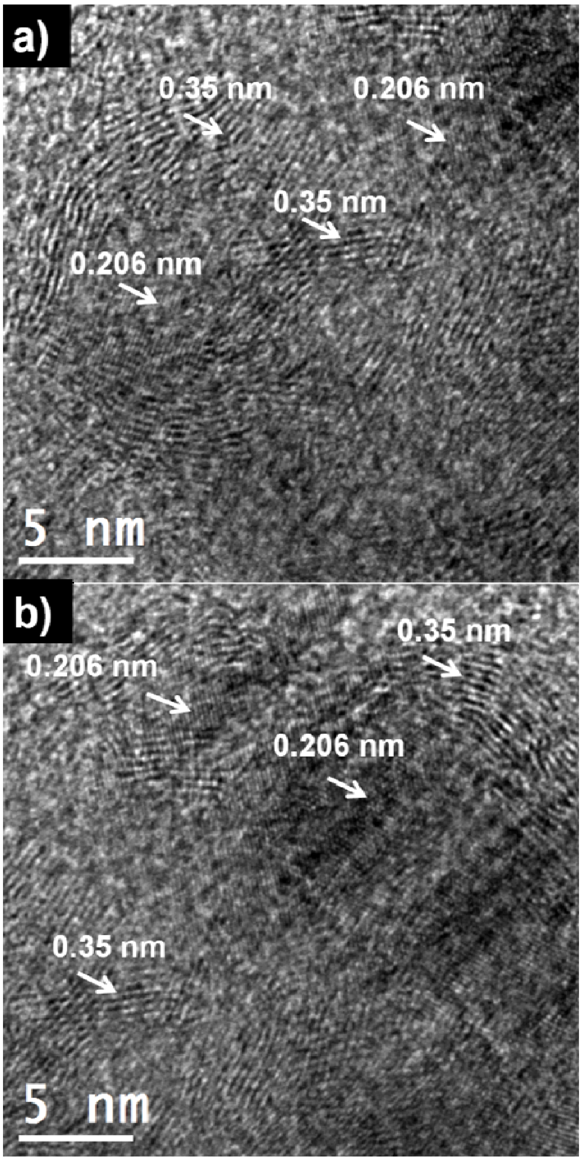

Fig. 6. a) HRTEM image of the FeAl + BN sample. The distances of 0.206 nm and 0.34 nm are associated with the (110) interplanar distance of the intermetallic phase and with the (002) interplanar distance of the BN phase, respectively, b) HRTEM image from another region of specimen.

All these results confirm the presence of both structures in the conformation of the nanocomposite material. During the HREM analysis this new structure was commonly found randomly distributed. However, some particles have a structure similar to core-shelter type (see figure 6a). As can be seen from the results presented here, the presence of the BN structure leads to a decrease in the FeAl crystal size. The incoherence of the lattice planes was also evident.

CONCLUSIONS

The TEM and XRD characterization of the FeAl intermetallic/BN ceramic produced by mechanical milling from Fe, Al and BN powders, indicated the production of nanocomposite particles (FeAl + BN). After long milling times and from the contribution of both structures (FeAl and BN), a well-dispersed nanostructure was obtained. This result can improve the FeAl mechanical properties after the nanocomposite consolidation.

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