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Effects of boron addition on mechanical alloying and ordering behaviors of Fe–Al–(B) alloy powders

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Abstract

In this paper, mechanical alloying (MA) of Fe–50Al, Fe–49.5Al–1B, and Fe–47.5Al–5B (at.%) powders and their ordering behavior during annealing were investigated. The results showed that the alloying process was completed after 50h of milling and disordered Fe–Al–(B) solid solutions were developed. In addition, by increasing the boron content, more considerable crystallite refinement occurred in the course of MA. The ordering behavior of the powders milled for 80h was evaluated by annealing at various temperatures. The transformation of the disordered solid solutions to ordered Fe–Al–(B) intermetallics was a consequence of annealing. It was also found that the annealing temperature had no meaningful effect on the long-range order parameter. However, by increasing the boron content, the long-range order parameter decreased. It was also notable that the nanoscale structure of the powders was retained even after annealing, suggesting their thermal stability.

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Keywords: Nanostructured materials; Mechanical alloying; Transmission electron microscopy

1. Introduction

Fe–Al intermetallic compounds present attractive properties, such as high specific strength, excellent corrosion resistance, and good strength at intermediate temperatures [1–3]. Nevertheless, it has found that they possess relatively low strength at temperatures above 600◦C and low ductility at room temperature, limiting their applications [4,5]. The ductility of the Fe–Al polycrystals is affected by the nature of testing environment, strain rate, grain size, annealing temperature, cooling rate, and boron addition. It has been frequently reported that reducing the crystallite size to the nanometer range [6,7] and the addition of boron [8,9] improve the ductility considerably.

It is well established that MA is a capable method to produce nanostructures [10,11]. There are several reports in the literature on MA of Fe–Al [2,12,13]. MA produces disordered Fe–Al solid solution nanostructures which can be transformed to the ordered compounds by a suitable heat treatment. It has been reported that amorphous Fe–Al alloys (with 83% and 85% of Al) obtained by MA are crystallized to a mixture of $Al_{13}Fe_4$ intermetallic and Al during heating [14]. Furthermore, the microstructure and mechanical properties of mechanically alloyed Fe–Al alloys consolidated by spark plasma sintering [15,16] and vacuum hot pressing [17] have been investigated recently. Concerning the boron addition, Rico et al. [18] have reported the formation of a BCC solid solution and Fe_2B phase during MA of $Fe_{60}Al_{40-x}B_x$ alloys (x=2, 4, 6, 8, 10, 15, and 20) by X-ray diffraction and Mössbauer spectroscopy assessments. In this research, MA of Fe–Al with and without the boron addition was

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compared. Afterward, the ordering characteristics of the as-milled powders during annealing were evaluated.

2. Experimental procedures

Elemental high pure Fe, Al, and B powders (supplied by MERC) with nominal compositions of Fe–50Al, Fe–49.5Al–1B, and Fe–47.5Al–5B (at.%) were milled in a planetary ball mill under an argon atmosphere. A ball-to-powder mass ratio of 50:1 by seven hardened steel balls with a diameter of 20 mm was employed. Milling was conducted at a rotational speed of 300rpm for times of 20, 50, and 80 h. Phase changes in the powders were investigated by X-ray diffraction (XRD) (Philips Analytical PC-APD with a Cu K radiation (=0.1542 nm)) and transmission electron microscopy (TEM, JEOL-JEM 2010). The crystallite size was estimated by the Williamson–Hall method [19] and the long-range order parameter, S, was calculated from the XRD data by comparing the relative intensities of the superlattice (h + k + l odd) and fundamental (h + k + l even) peaks of the annealed powders with respect to the well-annealed reference material, according to:

$$S^2 = \frac{I_{S(dis)}/I_{F(dis)}}{I_{S(ord)}/I_{F(ord)}}$$

where $(I_S/I_F)_{dis}$ and $(I_S/I_F)_{ord}$ are the ratio of the intensities of the superlattice reflection to the fundamental line for the disordered (dis) and reference (ord) powders, respectively. For the determination of S, (200) and (100) reflections were chosen to minimize any texture effect [8].

The powders milled for 80 h were used for ordering studies. The milled powders were encapsulated in sealed quartz tubes under an evacuated condition and then annealed at temperatures of 800, 900, 1000, and 1100◦C for 3 h. Heating was performed at a rate of 10

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◦C/min and then cooling was conducted in the same furnace to room temperature. The effect of the annealing temperature on the phase transformation, grain growth, and ordering was analyzed by the XRD method.

3. Results and discussion

Fig. 1 shows the XRD pattern of the Fe–50Al powders milled for 20, 50, and 80 h. The analysis of the results suggests that after 50h of milling, the alloying process is completed and disordered Fe–Al solid solutions are developed. The XRD analysis of the other powder samples depicted similar features. Because of the fact that during milling the powder particles are subjected to severe plastic deformation, the high density of defects and consequently the disordered solid solutions are generated.

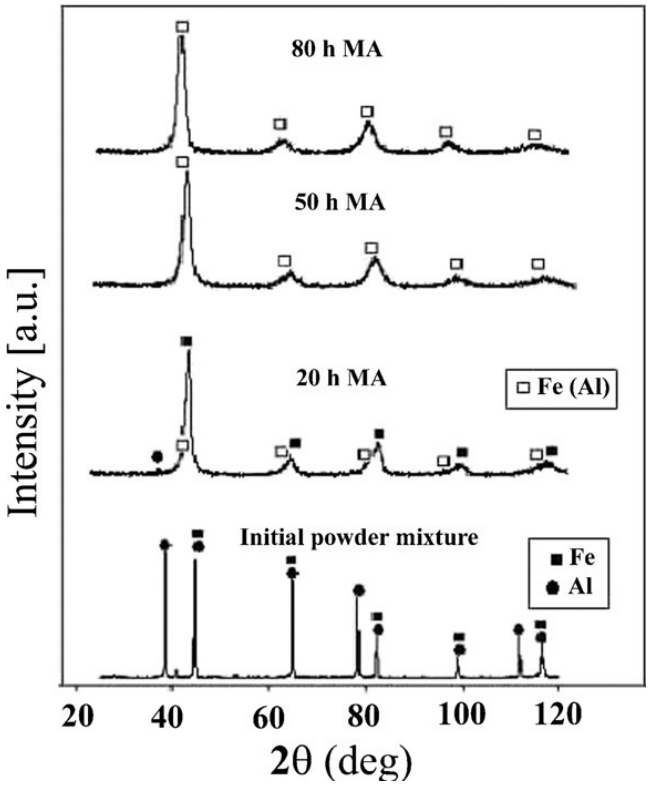

Fig. 1. XRD pattern of the Fe–50Al powders milled for 0, 20, 50, and 80 h.

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The crystallite size of the as-milled powders obtained from the XRD analyses is listed in Table 1, revealing crystallite sizes in the nanometric scale. During MA, the powder particles are subjected to severe plastic deformation and extreme cold working. The dislocation density increases to considerably high levels and shear bands containing a high dislocation density are formed. With continued milling, the lattice strain increases by increasing the dislocation density, leading to the formation of dislocation cells and subgrains separated by low-angle grain boundaries. After sufficient milling times, the transformation of the low-angle grain boundaries into those of the high-angle takes place by grain rotation, developing the nanostructures [11]. It is noticeable that by increasing the boron content, the grain refinement occurs more rapidly and more significantly. In the presence of B, a high percentage of B atoms infuses into the structure by diffusing down to dislocations and grain boundaries. The diffused B atoms are segregated into dislocations and grain boundaries. This phenomenon contributes to the fixing of dislocations and the stabilizing of grain boundaries. Afterward, the trickling down of running dislocations on the fixed dislocations leads to the nucleation of new boundaries. This results in a rapid grain refinement in the order of a few nanometers, by increasing the boron content. A severer grain refinement by interstitial nitrogen atoms has been recently reported during MA of Fe–Cr–Mn–N alloy powders [20]. Mohamed [21] has proposed that variations in some interatomic and structural properties, including hardness, self-diffusion activation energy, stacking fault energy, shear modulus, and milling temperature, are responsible for such differences in grain refinement kinetics during MA.

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Table 1. Crystallite size (nm) of the as-milled powders obtained from the XRD analyses.

Milling time (h)	Fe–50Al	Fe–49.5Al–1B	Fe–47.5Al–5B
20	19	16	15
50	23	15	13
80	15	10	7

The TEM micrograph and corresponding selected area diffraction (SAD) pattern of the samples milled for 80h are shown in Fig. 2. In contrast to the other samples, the TEM picture of the powder containing 5% B suggests the formation of an amorphous phase. There is a competition between the formation of an amorphous phase and the precipitation of crystallites. Apparently, when that Gibbs free energy of the amorphous phase is lower than that of the crystallites, solid-state amorphization takes place during MA. The amorphization reaction can be explained by high energies given to the powders during milling. Th severe plastic deformation and extreme structural refinement, which have occurred during milling, increase the density of defects and the constraint of the neighboring crystallites [20], thereby decreasing the stability of the crystalline structure and promoting amorphization. Nonetheless, the B-free sample does not show detectable amorphization, reflecting that the contribution of boron to amorphization is significant. As mentioned above, boron intensifies the structural refinement, aiding amorphization, on the one hand. Moreover, boron in the Fe–Al–B alloy system increases the atomic size mismatch and negative heat of mixing among the constituent elements, encouraging amorphization significantly. It would be worth mentioning that the same effect has been reported for nitrogen in the Fe–Cr–Mn–N alloy system [20].

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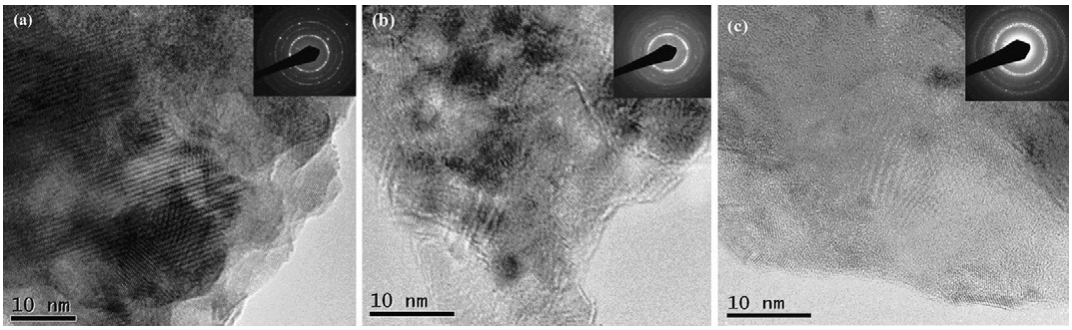

Fig. 2. TEM micrograph and corresponding SAD patterns of the as-milled samples. (a) The B-free powder; (b) the powder containing 1% B; (c) the powder containing 5% B.

For confidence in homogenous alloying, the powders milled for 80 h were used for the ordering evaluations. Fig. 3 demonstrates the XRD trace of the 80 h Fe–47.5Al–5B as-milled powder and the related samples annealed for 3h at 800, 900, 1000, and 1100 ◦C. This implies that the disordered solid solutions are transformed

to ordered intermetallics with a B2 structure, due to the recovery of defects by an increase in the atomic diffusivity during annealing. Table 2 tabulates the crystallite size of the intermetallics after annealing. It can be seen that the crystallites have remained in the nanometric scale and the samples containing the higher B concentration have smaller crystallites. Since the solubility of B is limited in the crystalline structure, B atoms tend to segregate toward grain boundaries to decrease strain energy. The accumulation of considerable B contents at grain boundaries retards grain growth. In addition, it is expected that very fine boride precipitations have been dispersed in the structure (especially in the Fe–47.5Al–5B samples), suppressing fast grain growth via decreasing grain boundary mobility. Nonetheless, since the content of these probable precipitations is very low (if they exist), they were not detected by the applied characterization method.

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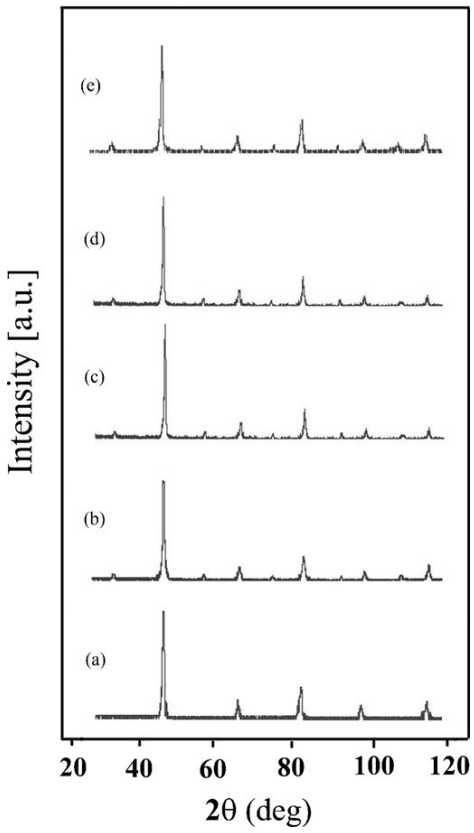

Fig. 3. XRD trace of the Fe–47.5Al–5B as-milled powder (a) and the related samples annealed at 800 (b), 900 (c), 1000 (d), and 1100 ◦C (e) for 3 h.

Fig. 4 presents the TEM image of the 5% B-containing sample annealed at 1100◦C. It can be seen that an amount of the amorphous phase has been retained in grain boundaries. This suggests the considerable stability of the amorphous phase, which can affect the observed grain growth kinetics and accordingly properties.

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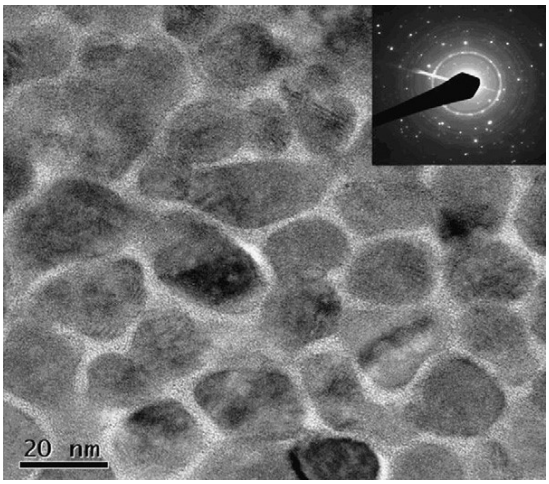

Fig. 4. TEM image of the 5% B-containing sample annealed at 1100 ◦C.

The long-range order parameter of the annealed samples is listed in Table 3, obtained from the XRD analyses. The annealing temperature has no meaningful effect on the long-range order parameter for each alloy. The same ordering parameter is owing to the equilibrium cooling from the annealing temperatures. This allows defects, particularly vacancies, in all the samples to reach equilibrium contents. That is, the equilibrium cooling causes a same configuration of vacancies for each alloy. It would be worth mentioning that Fe–Al contains a unique thermal vacancy concentration compared to all iron aluminides [22]. This is due to a low enthalpy of vacancy formation which decreases by Al content ($H_f \approx 34$ kJ/mol for Fe–50 at.% Al) [23]. On the other hand, it can be seen that by increasing the boron concentration, the long-range order parameter decreases. Boron atoms occupy interstitial sites of the lattice, increasing the packing of the lattice. This leads to a decrease in the atomic diffusivity that is required for ordering. Therefore, by increasing the boron content the ordering parameter decreases due to the suppressing of diffusion. This is in good agreement with the work reported by Anna et al. [24].

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4. Conclusions

The outcome of this study can be summarized as following:

1. MA of elemental Fe–50Al, Fe–49.5Al–1B, and Fe–47.5Al–5B(at.%) powder mixtures was completed after 50h of milling, developing the disordered nanostructures.

2. The addition of boron led to more crystallite refinement during MA.

3. In the sample containing 5% B, partial amorphization was detected after MA.

4. The transformation of the disordered solid solution to the ordered Fe–Al–(B) intermetallics was found after annealing.

5. The amorphous phase in the sample containing 5% B showed a considerable stability.

6. The annealing temperature had no considerable effect on the long-range order parameter, due to slow cooling to room temperature.

7. By increasing the boron content, the long-range order parameter decreased, due to a decrease in atomic diffusivity.

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