RAPID PUBLICATION

Structural Changes in Fe-B Powder Mixtures during Amorphization Process by Mechanical Alloying

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The main purpose of this work is to utilize EXAFS to observe the atomic-scale structural changes during the MA (mechanical alloying) process of two Fe-B powder mixtures: one is $\text{Fe}_{80}\text{B}_{20}$ (which is amorphized by RQ, but not by MA) and the second is $\text{Fe}_{50}\text{B}_{50}$ (which is amorphized by MA, but not by RQ). In the MA process of $\text{Fe}_{50}\text{B}_{50}$, the dissolution of B atoms into the α -Fe crystal was observed. Contrary to this, in the MA process of $\text{Fe}_{80}\text{B}_{20}$, the B atom dissolution into the α -Fe crystal was not observed.

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I. Introduction

Recently, it has been shown that the compositional ranges over which amorphous alloys can be formed vary with the preparation method used. For example, amorphous alloys of Fe-B can be prepared in the range 13–27 at%B by rapid quenching (RQ)⁽¹⁾, but not by the mechanical alloying (MA) of elemental powders. Conversely, alloys with 30–60 at%B can be formed by MA⁽²⁾⁽³⁾ but not by rapid quenching. The purpose of this work is to study the differences in the change of atomic arrangement of Fe-B alloys of different compositions during the MA process.

II. Experimental

Two alloy compositions were chosen for investigation: 20 at%B (which is impossible to prepare amorphously by MA) and 50 at%B (which can be prepared amorphously by MA). These two mixtures of pure Fe (99%, –200 mesh) and B (99%, <1 μm) powders were used as the starting materials in the MA process. The mixtures of Fe-B powder were milled in a SPEX vibratory mill (model 8000). Milling was performed with a hardened tool-steel vial and type 440 C martensitic stainless steel balls. The weight ratio of ball to powder was 30 to 1. The vial was sealed with a viton O-ring in an argon-filled glove box. Mechanically milled powders were characterized by X-ray diffraction measurements. A fine powder, screened to a particle size of less than 20 μm , was used for EXAFS

measurements. The powder was uniformly spread and sandwiched between adhesive tape. The transmission mode EXAFS spectra were measured at the Fe K edge (7.1112 keV) at room temperature on beam-line 23A2 at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, U.S.A., as a function of milling time. The stored electron-beam energy was 2.5 GeV. An Fe foil was used to calibrate the photon energy and the energy resolution ($\Delta E/E$) was 2×10^{-4} for the EXAFS. A double-crystal monochromator with Si(220) crystal was used to define the photon energy. Both incident and transmitted X-ray intensities were measured simultaneously in different ionization chambers, 17 cm long for the incident, and 31 cm long for the transmitted, both filled with pure nitrogen gas. The changes in the radial distribution function (RDF) around the Fe atom were derived by the Fourier transform of the EXAFS function, $k^3\chi(k)$, as a function of milling time.

III. Results and Discussion

The X-ray diffraction patterns of Fe-B mixed powders during MA are presented in Figs. 1(A) and (B). The intensity of the Fe(110) and (200) peaks decreased and both peaks also broadened with milling time. No peak from a B crystal was observed, because the B in the starting material is originally in the amorphous state. In the case of $\text{Fe}_{50}\text{B}_{50}$, the Fe(200) peak disappeared after 5h of milling. But in the case of $\text{Fe}_{80}\text{B}_{20}$, the Fe(200) peak retained a very low intensity to the end of the MA process. These X-ray patterns were compared with those of an amor-

Fig. 1 (A) X-ray diffraction patterns of the $\text{Fe}_{80}\text{B}_{20}$ alloy produced by mechanical alloying as a function of milling time. (B) X-ray diffraction patterns of the $\text{Fe}_{50}\text{B}_{50}$ alloy produced by mechanical alloying as a function of milling time.

phous $\text{Fe}_{80}\text{B}_{20}$ prepared by RQ⁽⁴⁾. The peak width of the Fe(110) peak of $\text{Fe}_{50}\text{B}_{50}$ is larger than that of $\text{Fe}_{80}\text{B}_{20}$ at 5h of milling, and is almost the same as the value of the amorphous $\text{Fe}_{80}\text{B}_{20}$ prepared by RQ. This indicates that the amorphization reaction occurred in the mixture of $\text{Fe}_{50}\text{B}_{50}$ after only 5h of milling.

In the case of $\text{Fe}_{80}\text{B}_{20}$, the intensity of $k^3\chi(k)$, the background-subtracted Fe K-edge EXAFS spectra, decreased gradually with MA time. In contrast, in the case of $\text{Fe}_{50}\text{B}_{50}$, the intensity of $k^3\chi(k)$ decreased drastically after 5h of MA time, and the phase of the spectra changed significantly at the same time. This suggests that a drastic change in the structure of $\text{Fe}_{50}\text{B}_{50}$ occurred after 5h of MA. Figures 2(A) and (B) show the radial distribution functions (RDF) around an iron atom provided by the Fourier transform of the EXAFS spectra, $k^3\chi(k)$, ($3.5 \sim 14.8 \times 10^{10} \text{ m}^{-1}$) as a function of milling time. The arrows indicate the first, second, third and fourth nearest neighbors around an iron atom in the crystalline phase. The intensity of the peaks in the RDF around an iron atom decreased gradually with MA time in the case of $\text{Fe}_{80}\text{B}_{20}$, but the b.c.c. structure of α -iron remained to the end of the MA process in this composition. However, in the case of $\text{Fe}_{50}\text{B}_{50}$, a small peak, shown by an arrow, appeared on the shorter-distance side of the main peak (Fe-Fe atomic pair) after 5h from the commencement of milling, as shown in Fig. 2(B). This indicates the dissolution

Fig. 2 (A) Fourier transform of $k^3\chi(k)$ of the $\text{Fe}_{80}\text{B}_{20}$ alloy produced by mechanical alloying as a function of milling time. (B) Fourier transform of $k^3\chi(k)$ of the $\text{Fe}_{50}\text{B}_{50}$ alloy produced by mechanical alloying as a function of milling time.

of B atoms which are forced into the α -Fe crystal by MA. Simultaneously, the second, third and fourth nearest neighbour peaks in the α -Fe crystal structure decreased and disappeared suddenly. Only the main peak and the small peak, corresponding to the short range order around the Fe atom, remained at the end of the MA process. This indicates that the B atoms diffuse into the α -Fe crystal by MA, and then the medium- and long-range order of the α -Fe crystal disintegrate, changing into an amorphous structure.

The phase-diagram of the Fe-B system shows that the $\text{Fe}_{50}\text{B}_{50}$ composition correspond to the compound $\text{FeB}^{(5)}$. The free energy of formation for FeB is $-38 \text{ kJ/mol}^{(2)}$. Contrary to this, the $\text{Fe}_{80}\text{B}_{20}$ composition does not correspond to any compound. These facts are correlated with the ability of these compositions to be mixed at the atomic level. Eventually, the mixing of Fe and B at the atomic level in $\text{Fe}_{50}\text{B}_{50}$ lowers the free energy of the system, so that the mixing at the atomic level occurs very smoothly in this case. The strain energy in the α -Fe crystal is increased by the dissolution of the B atoms which is brought about by MA. The amorphization reaction then occurs due to this increase in strain energy. Contrary to this, in the case of $\text{Fe}_{80}\text{B}_{20}$, the composition does not correspond to any compound, so the decrease in free energy of the system by mixing at the atomic level is relatively small compared with the case of $\text{Fe}_{50}\text{B}_{50}$. No changes that would suggest the B dissolution into the α -Fe crystal were observed in the RDF obtained from the EXAFS measurement. The peaks corresponding to the medium- and long-range order of the α -Fe crystal in the RDF remained to the end of the MA process. In the MA process of $\text{Fe}_{80}\text{B}_{20}$, the B atom does not diffuse into the α -Fe crystal. These results suggest that the B atoms are condensed at the grain boundary of the α -Fe crystal in the MA process of $\text{Fe}_{80}\text{B}_{20}$. Consequently, the strain energy stored in the α -Fe crystal is not large enough to cause the amorphization reaction to occur.

Egami and Waseda suggested that there are two conditions for amorphization of the alloy by RQ, one is the atomic size ratio of constitutional atoms, and the second is the shift from eutectic composition in the phase diagram⁽⁶⁾. In the case of $\text{Fe}_{80}\text{B}_{20}$, the composition is very close to the eutectic composition (17 at%B) in the phase diagram of this system, the atomic size ratio $R_{\text{B}}/R_{\text{Fe}}$ is 0.77. These values satisfy the conditions for amorphization of the alloy by RQ and subsequently the $\text{Fe}_{80}\text{B}_{20}$ alloy amorphized by RQ. However, mixing at the atomic level does not occur in the solid state reaction caused by MA, and the powder mixture is not amorphized as mentioned above. In the case of $\text{Fe}_{50}\text{B}_{50}$, the composition is far away from the eutectic composition in the phase dia-

gram. Consequently, amorphization does not occur in this composition by RQ. However, mixing at the atomic level occurs very smoothly by MA, and the mixture amorphized by the accumulation of strain energy due to the B dissolution into the α -Fe crystal.

IV. Conclusion

The atomic structural changes in two Fe-B powders mixtures ($\text{Fe}_{80}\text{B}_{20}$, which is amorphized by RQ, but not by MA, and $\text{Fe}_{50}\text{B}_{50}$, which is amorphized by MA, but not by RQ) were observed by EXAFS during the MA process. In the MA process of $\text{Fe}_{50}\text{B}_{50}$, a peak which indicates the dissolution of B atoms into the α -Fe crystal appeared clearly in the RDF. Subsequently strain energy accumulated in the α -Fe crystal, the intensity of the peaks corresponding to medium- and long-range order of α -Fe crystal decreased, and the structure changed into the amorphous phase. Contrary to this, in the MA process of $\text{Fe}_{80}\text{B}_{20}$, the B atom dissolution into the α -Fe crystal was not observed in the RDF and the amorphization reaction did not occur.

These results suggest that the amorphization reaction by MA depends on the possibility of atomic mixing and the free energy for mixing of the constituent elements.

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