Characterization of mechanical nanocrystallization process of amorphous Fe–Mo–Si–B alloy by transmission Mössbauer spectroscopy

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The nanocrystallization process of the amorphous Fe–Mo–Si–B alloy under ball milling is characterized by means of transmission Mössbauer emission spectroscopy (TMES) in the present paper. It was found that a single α–Fe phase with the bcc structure is formed under ball-milling the amorphous Fe–Mo–Si–B alloy. A significant increase in the relative area of the subspectra of 8Fenn and 7Fenn and a remarkable decrease in isomer shift and half linewidth of the subspectra of various Fe configurations, especially in the case of 6Fenn, were observed during the ball-milling process. The diffusion of metalloid atoms from the bcc α–Fe phase to the remaining amorphous phase and α–Fe/α–Fe grain boundaries is suggested to occur during the mechanical crystallization of the current amorphous alloy based on the above TMES investigations.

I. INTRODUCTION

Two technical routes are now available for crystallizing the amorphous metallic alloys to produce extremely fine nanocrystals, namely thermal crystallization1–3 and mechanical crystallization.4,5 Up to now, the thermal crystallization process of amorphous materials has been well characterized by various techniques. Micromechanisms for it have been studied intensively.2,6 However, it seems little is known about the nanocrystallization process of the amorphous materials induced by the mechanical deformation. Transmission Mössbauer emission spectroscopy (TMES) has been proved to be a powerful tool in the study of hyperfine structures in solids. It has been successfully applied to investigate the microstructures of nanocrystalline materials.7,8 In order to understand the mechanisms responsible for the structural change occurring during ball milling, we investigate the mechanical crystallization process of the amorphous Fe–Mo–Si–B alloy, of which the thermal crystallization process is known,9 by means of transmission Mössbauer spectroscopy.

II. EXPERIMENTAL PROCEDURES

The amorphous Fe77.2Mo0.8Si9B13 (at. %) alloy ribbons (25 μm thick and 8 mm wide) were prepared by means of the melt-spinning technique on a single copper roller. The amorphous nature of the as-quenched ribbons was confirmed by x-ray diffraction and transmission electron microscope. The ribbons were cut into small pieces (5 × 5 mm2) and sealed in the milling vial under an argon atmosphere. The ball-milling experiment was performed in a WL-1 planetary ball mill. A stainless steel vial and hardened steel balls were used in the present work with a ball-to-sample mass ratio of 40:1. The milling process was interrupted at various time intervals in order to remove some powders for analysis and characterization.

 Structural characterization of the milled powder samples was carried out on an Elscint-Promeda-II computerized Mössbauer spectrometer with a 1.5 × 108 Bq 57Co radiation source. The Mössbauer spectra for the amorphous and the milled samples were recorded at room temperature. The spectrum for the amorphous was fitted by the modified Hess program, and the spectra for the powder samples were fitted by using the Gauss–Newton program.

III. RESULTS AND DISCUSSION

A. Crystallization of the amorphous Fe–Mo–Si–B alloy under ball milling

The Mössbauer spectrum and the fitted result of the as-quenched amorphous Fe–Mo–Si–B alloy was given in Fig. 1. It is seen that the spectrum is composed of six well-defined but broadened lines, which is typical of the
Fe-based amorphous alloy. The hyperfine magnetic fields exhibit a wide distribution as shown in the inset in Fig. 1 with an average value of 23.0 T. This is compatible with our previous report.9

Figure 2 illustrates the Mössbauer spectra of the Fe–Mo–Si–B samples after milling for 65 h (a), 102 h (b), and 262 h (c), respectively. Compared with Fig. 1, one can see that when the amorphous sample is subjected to ball milling, crystallites precipitate within the amorphous matrix, reflected by the appearance of complicated peaks in the recorded spectra [Figs. 2(a)–2(c)].

The spectrum of the sample milled for 65 h [Fig. 2(a)] is well fitted by using four sets of subspectra as in Fig. 3, corresponding to different Fe configurations or iron-containing phases. The fitted hyperfine parameters are presented in Table I. In Table I, $H_{hf}$ represents the hyperfine magnetic field, IS and $SQ$ are isomer shift (which is relative to the center of $\alpha$–Fe) and quadrupole splitting, respectively, and AREA is the relative area of the subspectrum which corresponds to the fraction of iron atoms in an iron configuration relative to all iron atoms. In order to analyze the nature of these subspectra, some other experiments10 were performed on the milled sample by using x-ray diffraction, a transmission electron microscope, and a differential scanning calorimeter. These investigations revealed that the as-milled sample is partially crystallized. The crystalline phase is $\alpha$–Fe with an average grain size of 4 nm. No other crystalline phases can be detected. Based on the above result and the information from the literature,11 one can see that the first three subspectra in Table I correspond to 8Fenn, 7Fenn, and 6Fenn of the $\alpha$–Fe phase, respectively. Here, 8Fenn, 7Fenn, and 6Fenn refer, respectively, to the Fe configurations with eight, seven, and six nearest iron neighbors. The splitting of the subspectrum of $\alpha$–Fe is due to the solubility of Si and/or Mo atoms in the $\alpha$–Fe phase. Another evidence for the solubility of Si and/or Mo atoms in the $\alpha$–Fe phase is its decreased lattice constant (which is 0.28655 nm) relative to that of pure $\alpha$–Fe (which is 0.28664 nm). The fourth subspectrum in Table I can be considered to be the contribution of the remaining amorphous phase in the sample because the hyperfine magnetic field of which (23.1 T) is almost the same as that of the amorphous before milling (which is 23.0 T). In the present sample, the fraction of iron

<table>
<thead>
<tr>
<th>Number</th>
<th>Subspectrum</th>
<th>$H_{hf}$, T</th>
<th>IS, mm/s</th>
<th>$SQ$, mm/s</th>
<th>AREA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8Fenn</td>
<td>33.4</td>
<td>0.01</td>
<td>−0.01</td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>7Fenn</td>
<td>30.7</td>
<td>0.05</td>
<td>−0.01</td>
<td>15.8</td>
</tr>
<tr>
<td>3</td>
<td>6Fenn</td>
<td>27.4</td>
<td>0.11</td>
<td>−0.05</td>
<td>17.7</td>
</tr>
<tr>
<td>4</td>
<td>res. am.</td>
<td>23.1</td>
<td>0.09</td>
<td>0.01</td>
<td>59.0</td>
</tr>
</tbody>
</table>

FIG. 1. Mössbauer spectrum and the fitted result of the as-quenched amorphous Fe–Mo–Si–B alloy. The inset shows the distribution of hyperfine magnetic fields. (---) Experimental, and (—) fitted.

FIG. 2. Mössbauer spectra of the Fe–Mo–Si–B samples after milling for 65 h (a), 102 h (b), and 262 h (c).

FIG. 3. The fitted Mössbauer spectrum of Fig. 2(a).
As the milling proceeds, the peaks due to the further crystallization of the remaining amorphous phase become sharper and sharper as in Figs. 2(b) and 2(c). The fitted spectrum of Fig. 2(b) is illustrated in Fig. 4. The fitted parameters are presented in Table II. It is clear from Table II that the fraction of the iron atoms in the remaining amorphous phase in this case is decreased to 36.3%.

The fitted spectrum of Fig. 2(c) is presented in Fig. 5. The fitted parameters are listed in Table III. In this case, the amorphous phase cannot be detected in the sample; i.e., the amorphous is completely transformed into a single bcc $\alpha$–Fe nanophase. Table IV summarizes the percentage of Fe atoms in different Fe-containing phases for the as-quenched amorphous and the milled samples. Clearly, the fraction of iron atoms in the remaining amorphous phase decreases remarkably with the prolonged milling. We can qualitatively regard the percentage of iron atoms in the amorphous phase as the volume fraction of the amorphous phase remaining in the milled samples. The crystallized fraction can be plotted against the milling time as in Fig. 6. Here, the solid circles are from DSC measurements, and the open circles are from the present TMES measurements. Interestingly, the crystallized fraction of the amorphous Fe–Mo–Si–B alloy increases linearly with milling time. Our present TMES results agree with the previous DSC data.

The crystallization behavior of the amorphous alloys has been successfully described in terms of kinetic theories. Nucleation and nuclei growth are responsible for the crystallization process upon heating in all systems. The transformation from a crystalline phase to an amorphous or a nanocrystalline phase induced by ball milling has been well investigated. Several mechanisms, such as the production of a large number of structural defects and the presence of a high “local effective temperature” at the collision site, have been proposed to explain the amorphous reaction which takes place during the high-energy mechanical alloying of some pure elemental powders or intermetallic compounds. It has been accepted that the stored energy due to the heavy deformation and the enhanced interface areas increase the free energy of the system. Trudeau et al. introduced for the first time the mechanical milling to crystallize amorphous Fe–(Ni, Co)–Si–B metallic alloys to produce nanocrystals. Nanocrystallization of the bcc Fe phase and the subsequent formation of Fe$_2$B or Fe$_3$B phase was observed. Grigoriev and Jachimowicz studied the mechanical nanocrystallization process of the amorphous Fe$_{78}$Si$_9$B$_{13}$ alloy by means of the pair function method. Only two crystalline phases, $\alpha$–Fe and Fe$_3$B, were observed in their work.
Table IV. Percentage of Fe atoms in the Fe-containing phases for the as-quenched amorphous and milled samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>AM, %</th>
<th>α–Fe, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-quenched am.</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>65 h milled</td>
<td>59.0</td>
<td>41.0</td>
</tr>
<tr>
<td>102 h milled</td>
<td>36.3</td>
<td>63.7</td>
</tr>
<tr>
<td>262 h milled</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

Up to now some attempts have been tried to explain the mechanisms dominating the mechanical crystallization process of the amorphous alloy. By incorporating some crystalline elements (Co and Ni) to the Fe–Si–B amorphous alloy, Trudeau et al. investigated the compositional dependence of the mechanical crystallization process of the Fe–Si–B glass. They found that the mechanical crystallization kinetics was accelerated by the addition of Co and impeded by Ni. Grigoriew and Jachimowicz reported two stages responsible for the mechanical crystallization of the amorphous Fe–Si–B alloy: the first stage is the creation of defects in the amorphous phase, and the second is the bulk nucleation in the amorphous matrix. Huang et al. also suggested that two stages, namely bending-induced bands in the early stage and wear-like mechanism for further crystallization, occur in the mechanical crystallization of the amorphous Fe78Si9B13 alloy. From the above mentioned, it seems that until now no satisfactory explanation or model can be employed in the crystallization process induced by plastic deformation.

In our present case, the long-time mechanical attrition is believed to give rise to a large number of defects in the amorphous and to a temperature rise in the mill. The defects exist in the form of point defects or line defects, and they can become the nucleation sites for subsequent thermal crystallization. It was reported that the average temperature inside the mill is within 400–600 K. The presence of a large number of nucleation centers in the amorphous induced by mechanical deformation may cause the crystallization to occur at a low temperature, i.e., nucleation of bcc α–Fe phase in these regions. But the mechanical crystallization may occur in quite a different manner from that induced by thermal annealing. As we know, the crystallization induced by mechanical deformation occurs only in the amorphous region which is impacted by ball milling, and the crystallization stops once no impaction is acted on in this region. Since the collisions during ball milling are discontinuous and randomly occurring in the amorphous sample, the crystallization by mechanical deformation is discontinuous in comparison with the thermally induced continuous crystallization. Of course, several factors influence the kinetics of the mechanical crystallization process, such as the chemical composition as indicated by Trudeau et al. and in our present alloy system. Schultz et al. reported that oxidation affects the crystallization because the crystallization occurs rapidly in an oxygen atmosphere. Bansal et al. denied the concept of mechanical crystallization and argued that the observed phase transformation should be attributed to the introduction of contamination from the milling tool, mainly of iron. In our case, the contamination from oxygen and mill cannot be excluded. It seems further research work is required to have a better understanding of the mechanism of mechanical crystallization of amorphous alloys.

In the Fe–Mo–Si–B alloy only one crystalline phase, bcc–Fe, was observed throughout the whole milling process in the quaternary Fe–Mo–Si–B alloy system. Compared with experimental results on the Mo-free Fe–Si–B amorphous alloy by Grigoriew and Jachimowicz and Huang et al., one can see that the addition of a small amount of Mo (0.8 at. %) to the Fe–Si–B amorphous alloy exerts a considerable effect on its mechanical crystallization process because the mechanical milling of the present Fe–Mo–Si–B glass leads to the formation of a single bcc Fe phase, whereas in the case of the Mo free Fe–Si–B amorphous alloy, at least two crystalline phases have been observed during the milling process. Moreover, we reported in Ref. 3 that four crystalline phases, namely α–Fe, Fe3B, Fe23B6, and Fe3B, were observed during the thermal crystallization of the amorphous Fe–Mo–Si–B alloy examined in this paper. The significant difference in the crystallization products between by mechanical and by thermal crystallization reveals that a special structural change may occur in the nanocrystallization process driven by ball milling, which is the concern of the following study.

![Graph](image-url)
B. Structural changes during the nanocrystallization process induced by ball milling

It was shown in Sec. III.A that, as a consequence of the solubility of Si, B, Mo atoms in \( \alpha \)-Fe, the spectrum of \( \alpha \)-Fe is split into three sets of subspectra denoted by 8Fenn, 7Fenn, and 6Fenn, as in Tables I–III. In order to investigate the variations of the hyperfine parameters with milling time, Table V compares the relative area (AREA, %), isomer shift (IS), and half linewidth (HLW) of the subspectra of various Fe configurations in the Fe–Mo–Si–B samples milled for 65 h, 102 h, and 262 h, respectively. From Table V, one can conclude that the relative areas of both 8Fenn and 7Fenn, especially in the case of 8Fenn, increase significantly with the increasing milling time, whereas an inverse change was observed in the case of 6Fenn. When the milling time reaches 262 h, the percentage of 8Fenn occupies 63\% of all Fe configurations. Since only one crystalline phase precipitates throughout the entire ball-milling process, the above phenomenon can be ascribed only to the decreasing of the solubility of Si and B atoms in \( \alpha \)-Fe with milling. That is to say, the Si and B atoms will diffuse from the bcc Fe phase to the remaining amorphous phase and the \( \alpha \)-Fe/\( \alpha \)-Fe grain boundaries. Here, the influence of Mo atoms was omitted because of its relatively low content in the sample.

It is known that all the Mössbauer parameters the isomer shift (IS) and the half linewidth (HLW) are closely related to the electron structure and the arrangement of iron atoms in a material. According to the relationship between IS and the \( s \)-electron density, \(^{22}\)

\[
IS = \frac{4}{5} \pi Z e^2 (|\psi(0)|^2_A - |\psi(0)|^2_s) (\Delta R/R)^2,
\]

where \( Z \) is the atomic number, \( e \) is the electron charge, \( |\psi(0)|^2_A \) and \( |\psi(0)|^2_s \) are the densities of the \( s \) electrons at the nucleus of the absorber (specimen) and the source, respectively. \( R \) is the nucleus radius, \( \Delta R/R \) is the deviation in the nuclear radius in going from the excited to the ground state, and \( \Delta R/R < 0 \). Obviously, the increase in the density of \( s \) electrons will give rise to a decrease in IS. This conclusion has been proved by the smaller IS value of the compressed iron sample.\(^{23}\)

From Table V, one can see that with increasing the milling time the values of IS for all Fe configurations decrease, especially in the case of 6Fenn, indicating that the \( s \)-electron density of an iron atom increases with milling. This conclusion is in good agreement with the enhanced relative area of subspectra of 8Fenn and 7Fenn in Table V. That is to say, the diffusion of metalloid atoms of Si and B from the bcc \( \alpha \)-Fe phase to the remaining amorphous phase and the \( \alpha \)-Fe/\( \alpha \)-Fe grain boundaries will lead to an enhanced \( s \)-electron density of Fe atoms. Similarly, the arrangement of iron atoms in bcc Fe lattices will become more and more ordered with the decrease in the solubilities of metalloid atoms in it, which will lead to a decreased HLW. The above analysis can be confirmed by the half linewidth data of samples milled for different times, as illustrated in Table V.

The hyperfine magnetic field, \( H_{hf} \), can be related to the saturation magnetization, \( M_S \), as\(^{24}\)

\[
H_{hf} = AM_S.
\]

In the above equation, \( A \) is a constant. As is well known, \( M_S \) is an intrinsic magnetic parameter, the value of which depends only upon the chemical composition of a ferromagnetic phase. The calculated average hyperfine magnetic fields of the \( \alpha \)-Fe phase in the three milled samples are 29.8 T (65 h), 30.8 T (102 h), and 32.2 T (262 h), respectively. The obvious increase of \( H_{hf} \) of the \( \alpha \)-Fe phase with increasing milling time confirms that the solubilities of metalloid atoms, Si and B, in \( \alpha \)-Fe decrease during the milling process.

Table V reveals that the ball milling exerts a great effect on the hyperfine parameters of the subspectra of various Fe configurations. As demonstrated by the previous x-ray diffraction, transmission electron microscope,\(^{10}\) and the current TMES experiments, only one crystalline phase is present throughout the whole ball-milling process. So the transportation of metalloid atoms from \( \alpha \)-Fe to the remaining amorphous phase and the \( \alpha \)-Fe/\( \alpha \)-Fe grain boundaries may be responsible for the changes in the fitted parameters of the subspectra of various Fe configurations.

The nanocrystalline material is structurally characterized by nanometer-sized grains and a large number of interfacial atoms. Quantitatively speaking, in a 5nm-

<table>
<thead>
<tr>
<th>Subspectrum</th>
<th>AREA, %</th>
<th>Milling time, h</th>
<th>IS, mm/s</th>
<th>Milling time, h</th>
<th>HLW, mm/s</th>
<th>Milling time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65</td>
<td>102</td>
<td>262</td>
<td>65</td>
<td>102</td>
<td>262</td>
</tr>
<tr>
<td>8Fenn</td>
<td>7.5</td>
<td>18.6</td>
<td>62.6</td>
<td>0.01</td>
<td>0.02</td>
<td>-0.01</td>
</tr>
<tr>
<td>7Fenn</td>
<td>15.8</td>
<td>27.8</td>
<td>30.8</td>
<td>0.05</td>
<td>0.05</td>
<td>-0.01</td>
</tr>
<tr>
<td>6Fenn</td>
<td>17.7</td>
<td>17.3</td>
<td>6.6</td>
<td>0.11</td>
<td>0.07</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Note: the error for both IS and HLW is ±0.01 mm/s.
grained material, the volume percentage of interfacial atoms can be as much as 50%. So these interfacial atoms can constitute a large volume fraction in the nanocrystalline material. A series of experiments demonstrate that the arrangement of interfacial atoms is disordered relative to that of the crystalline atoms. The typical boundary morphology observed in the HREM experiments is a large angle grain boundary or a noncoherent interface boundary. This kind of interface has a high free energy. From the above analysis, the segregation of metalloid atoms such as Si and B at the α–Fe/α–Fe grain boundaries can be easily understood. The segregation of B atoms in the interfaces was also reported in nanocrystalline Fe–Cu–Si–B alloys. Hoftier et al. reported that the diffusion of boron atoms is faster through the bulk than along the grain boundaries by a new type of diffusion kinetics in the nanocrystalline Fe sample. Several researchers have also observed the segregation of boron atoms to the grain boundaries at ambient temperatures in various materials. So the mechanical crystallization of the Fe–Mo–Si–B amorphous alloy is accompanied by complicated atomic diffusion.

The single-phase sample milled for 262 h is also found to exhibit inherent thermal stability against phase separation and precipitation. The powder sample milled for 262 h was subjected to thermal annealing at 1173 K for different periods of time up to 70 min. Under the above annealing conditions, the average grain size of the α–Fe phase increases from 8 nm (as-milled state) to 26 nm (annealing for 70 min). Interestingly, no other crystalline phase is detectable throughout the whole annealing process; i.e., the sample remains in the single-phase state upon heating. Quantitative measurements on the lattice constant of the α–Fe phase in different samples show no detectable change in the lattice parameter during the grain growth, indicating that at least no remarkable diffusion of B and Si atoms out of the bcc Fe phase occurs upon annealing.

The above experimental phenomenon observed upon annealing the as-milled sample can be ascribed to the segregation of B and Si atoms at the grain boundaries as concluded from the TMES experiments, which remarkably stabilizes the nanostructure. Traditionally, the methods used in order to keep the grain size small consist of the incorporation of inert, dispersed phases, or the production of a composite material in which grains of similar structures are isolated from each other. In our case, the segregation of B and Si atoms in the grain boundaries (or triple junctions) can be considered to be an effective drag to the displacement of grain boundaries and the atomic diffusion upon annealing, i.e., hinder the grain growth or phase separation in the sample. So the mechanical milling is an effective method to crystallize the amorphous Fe–Mo–Si–B alloy to produce a stable single nanophase.

IV. CONCLUSIONS

In view of the above TMES results, we can conclude that the amorphous phase will be gradually transformed into a bcc α–Fe phase and that the metalloid atoms will diffuse from the bcc α–Fe phase to the remaining amorphous phase and the α–Fe/α–Fe grain boundaries during milling the amorphous Fe–Mo–Si–B alloy, which gives rise to an increased relative area of the subspectrum of 8Fenn and 7Fenn, a decreased relative area of the subspectrum of 6Fenn, as well as decreased isomer shift (IS) and half linewidth (HLW) of various Fe configurations, especially in the case of 6Fenn.

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REFERENCES