The lattice structure of nanocrystalline Fe–Cu–Si–B alloys

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Abstract

Nanocrystalline Fe–Cu–Si–B alloys with different grain sizes were synthesized by crystallization of an amorphous alloy. Two nanophases, α-Fe(Si) and Fe2B, were noticed in all samples. XRD results reveal that the lattice constant of the α-Fe(Si) phase increases; the a-axis is elongated and the c-axis is shortened in the Fe2B phase upon reducing the grain size. Based on the thermodynamic analysis, the changes in the lattice parameters were attributed to the solution of vacancies in the above two phases. Owing to the lattice distortion of the α-Fe(Si) and Fe2B phases, the crystallite with small size is found to exhibit a disordered character to some extent, which is manifested by large values of the half linewidth (HLW) and isomer shift (IS) of various Fe configurations in the Mössbauer parameters.

1. Introduction

There has been a growing research interest in the study of nanocrystalline material since it was first reported by Gleiter and others [1,2]. Up to now this special material has been structurally characterized by means of X-ray diffraction (XRD) [1,2], Mössbauer spectroscopy (MES) [3], positron annihilation (PA) [4] as well as high resolution electron microscopy (HREM). [5]. A common method to prepare nanocrystalline materials is called the ‘inert gas condensation’ [1], by use of which ultrafine powders can be prepared and an in-situ compaction procedure is required to obtain a bulk sample. It is inevitable to introduce defects, such as porosities or microvoids, in the bulk sample during the compaction process, which will more or less influence the structure and properties of the bulk sample. Crystallization of amorphous solids was recently introduced to synthesize nanocrystalline alloys...
[6,7], called ‘crystallization method’. An obvious advantage of this method over the inert gas condensation is in forming nanometer-sized grains and interfaces naturally within an amorphous matrix without any compaction process, so no defects would be introduced to the crystallized sample during the crystallization annealing. Furthermore, it can be applied to prepare a large variety of nanostructured alloys with various grain sizes by modifying the heat-treatment conditions. Clearly, it provides convenience to study both grain and interfacial structures in these alloys.

The nanocrystalline material was suggested to be composed of two components: nanometer-sized crystallites and interfaces, and the crystallites in the nanocrystalline material were generally supposed to be the same as those in the coarse-grained counterpart, but no experimental evidence was presented for it. Thomas et al. [8] found the interfaces in the nanocrystalline material to be in rather low energetic configurations showing flat facets interspersed with steps, rather than a random state without long- or short-range order as claimed by Gliefer et al. This interface structure is quite similar to that of the coarse-grained samples. It was found that several combinations of immiscible metals, immiscible even in the liquid state, could be formed in solid solutions through ball-milling when the grains are milled down to nanometer scale, such as Fe–Cu [9,10], Cu–Ag [9], Cu–W [11], Cu V [12]. Thus, it seems necessary to investigate the lattice structure of nanophases.

In this paper, we undertook an investigation on the lattice structure of the nanophases of α-Fe(Si) and Fe$_3$B in Fe–Cu–Si–B alloys by means of XRD (X-ray diffraction) and TMES (transmission Mössbauer spectroscopy). Experimental evidence was presented to show that the lattice structure of a nanophase is quite different from that of a perfect crystal.

2. Experimental procedures

Amorphous (Fe$_{0.9}$Cu$_{0.1}$)$_{78}$Si$_{3}$B$_{13}$ (at% ) ribbons were spun on a single copper roller. The amorphous nature of the as-quenched alloy was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The subsequent isothermal annealings to crystallize the amorphous ribbon samples were performed in a large tubular furnace under an argon stream. The temperature was controlled within ±3.0 K. The furnace was heated to the annealing temperature in advance of sample installation, and after finishing annealing the as-annealed samples were immediately extracted from the furnace. Different annealing temperatures (from 763 K to 913 K) were chosen to create different grain sizes in the crystallization products. The annealing time $t$ is 1 h for all samples. The lattice parameters and average grain sizes of the crystalline phases were determined from the peak positions and half maximum width of the X-ray diffraction lines, respectively. XRD experiments were carried out on a Rigaku X-ray diffractometer with a Cu Kα radiation. Transmission electron microscopy (TEM) experiments were performed on an EM420 microscope with an accelerating voltage of 120 kV.

Transmission Mössbauer spectroscopy (TMES) experiments were made on an FH1-198 computerized Mössbauer spectrometer with a $^{57}$Co source. The Mössbauer spectra of the as-annealed samples were recorded at room temperature.

3. Results and discussion

The as-annealed samples were monitored by XRD, and the fully crystallized state was confirmed for all as-annealed samples with precipitation of α-Fe(Si) (BCC structure) and Fe$_3$B (BCT structure) phases throughout the whole heat-treatment conditions. No amorphous was detectable. The average grain sizes of α-Fe(Si) and Fe$_3$B phases were quantitatively determined from the half maximum width of XRD lines by using the Scherrer equation. Furthermore, the average grain size of the experimental samples was taken to be the mean value of the sizes of the two phases, as listed in Table 1. For example, XRD experiments of the half maximum
Table 1
Temperature dependence of the average grain size of nanocrystalline Fe-Cu-Si-B alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$, [K]</td>
<td>763</td>
<td>783</td>
<td>813</td>
<td>833</td>
<td>913</td>
</tr>
<tr>
<td>$\bar{d}$ [nm]</td>
<td>19</td>
<td>28</td>
<td>38</td>
<td>46</td>
<td>63</td>
</tr>
</tbody>
</table>

The linewidth of sample A lead to mean grain sizes of 27 nm from the (220) $\alpha$-Fe(Si) line and about 11 nm from the (332) Fe$_2$B line. The average grain size is 19 nm. Figure 1 describes a TEM image of sample A, annealed at 763 K for 1 h. The sample shows a homogeneous structure with an average grain size of about 25 nm, which is in reasonable agreement with the above XRD result.

3.1. Theoretical considerations

Let us consider a spherical grain with radius $r$, and let $\gamma$ be the surface energy. With respect to the infinite large crystal, the free energy of a grain with a radius $r$ is given by

$$\mu(T, r) = 3\gamma/r.$$  

Equation (1) suggests that with reduction of the grain size, the total free energy is enlarged proportional to $1/r$. Detailed analysis [13] revealed that an increase in the free energy of grains will result in two effects. One is an increase in the concentration of solute atoms in a solid solution. The increment is proportional to $1/r$, which will lead to a supersaturated solution structure. The other is an increase in the concentration of vacancies or point defects in a pure system or in a stoichiometric intermetallic compound, which has no solubility of other atoms. The enhancement of the vacancy or point defect concentration is also proportional to $1/r$. The increase in the solubility of vacancies in the small grains will give rise to either an increase in the lattice parameter [14] or a distorted crystal lattice. If both type and concentration of solute atoms show no change with decreasing of the grain size, the vacancy concentration in a nanophase will increase as mentioned above. That is to say, the smaller the phase, the higher the concentration of vacancies. The solution of vacancies in the lattice leads to a 'lattice distortion', which will result in an increased lattice parameter.

Due to the lattice distortion, the local atomic arrangement in a nanophase will exhibit a disordered character to some extent. It is well known that Mössbauer spectroscopy is a valuable tool in studying local atomic configurations and their electronic structures. Two Mössbauer parameters, the half linewidth HLV and isomer shift IS, are very important concerning the local configurations of iron atoms and their electronic structures. The former can reflect the distribution of iron atoms. A large value of HLV corresponds to a more disordered arrangement of Fe atoms. The relationship between IS and the s-electron density of an iron atom is given [15] by

$$IS = \frac{4\pi Ze^2}{h^2} \left| |\psi(0)|_A^2 - |\psi(0)|_S^2 \right| \frac{(\Delta R/R)R^2}{\Delta R/R}$$

where $|\psi(0)|_A^2$ and $|\psi(0)|_S^2$ are the s-electron densities at the nucleus of the absorber and the source respectively. $\Delta R/R$ is the deviation in the nuclear radius in going from the excited to the ground state and $\Delta R/R < 0$. Obviously, the decrease in the s-electron density at the nucleus of the absorber gives rise to an increased isomer shift IS. An increase in the vacancy concentration in a phase will lead to a volume expansion, which is believed to decrease the s-electron density of iron atoms. Therefore, the isomer shift is expected to increase according to Eq. (2).
3.2. The lattice parameters of the $\alpha$-Fe(Si) and Fe$_2$B phase in Fe–Cu–Si–B alloys with different grain sizes

Table 2 summarizes the peak positions of (3 1 0) ($\alpha$-Fe(Si)) and (0 0 2) (Fe$_2$B) diffraction lines, determined from the broadened X-ray diffraction lines. It is clear from Table 2 that the peak positions of the diffraction lines of the $\alpha$-Fe(Si) and Fe$_2$B phases vary significantly with particle size of the above two phases, implying that the lattice parameters are changing during the grain growth. Figure 2 illustrates the lattice constant, $(a/a_0)/a_0$ of the $\alpha$-Fe(Si) phase and its change with average grain size. In Fig. 2, $a_{2 2 0}$, $a_{3 1 0}$ and $a_{2 2 2}$ are the lattice constants determined from 2 2 0, 3 1 0 and 2 2 2 diffraction lines; $a_0$ is the equilibrium value. Here, we took the lattice constant of the $\alpha$-Fe(Si) phase in sample E as $a_0$ because in sample E $a_{2 2 0} = a_{3 1 0} = a_{2 2 2} = 0.28475$ nm. It is of interest that with decreasing grain size, $a_{2 2 0}$, $a_{3 1 0}$ and $a_{2 2 2}$ increase significantly and $a_{2 2 0} > a_{3 1 0} > a_{2 2 2}$. When the average grain size decreases from 63 nm to 19 nm, the lattice constant of the $\alpha$-Fe(Si) phase, $a_{2 2 0}$, increases by 0.295%.

In the Fe–Cu–Si–B alloys, phases other than $\alpha$-Fe(Si) that contain Si atoms fail to be observed in the XRD profiles. Thereby we infer that all Si atoms are dissolved in the $\alpha$-Fe phase. Due to the negligible solubility of B atoms in the $\alpha$-Fe phase [16], both type and concentration of the solute atoms in the $\alpha$-Fe phase were not expected to change during the refinement of the $\alpha$-Fe(Si) phase. Or, in other words, with the grain size reduction an enhancement in the lattice constant of the $\alpha$-Fe(Si) phase does not mean a decrease in the concentration of Si atoms in the $\alpha$-Fe phase, though it was suggested that a decrease in the concentration of Si atoms might lead to a significant increase in the lattice constant because of a substitutional occupation of Si atoms in BCC Fe lattice points. Meanwhile, the pronounced difference in the lattice constant in Fig. 2 determined from different diffraction lines suggests that the lattice structure of the $\alpha$-Fe(Si) phase is not perfect but distorted when the average grain size is less than 63 nm.

Table 3 lists the variation of the reduced lattice parameters $(a/c, a_0/c_0)$, with the average grain size. The Fe$_2$B phase is of the body-centered tetragonal structure (BCT). The lattice parameters $(a$ and $c$) of the Fe$_2$B phase were calculated from the peak positions of 2 0 10 and 0 1 0 2 diffraction lines. In Table 3, $a_0$ and $c_0$ are taken from the ASTM card, which are 0.50919 nm and 0.42304 nm, respectively. It is obvious from Table 3 that with decreasing of the grain size the magnitude of $a/c$ increases, i.e. the $a$-axis of the Fe$_2$B phase is elongated while the $c$-axis is shortened simultaneously by reduction of the grain size. A similar result was also found in the Ni$_3$P phase by Lu and Sui [13]. Due to the fact that $a/c$ increases.

Table 2

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>$D$ [nm]</td>
<td>19</td>
<td>28</td>
<td>38</td>
<td>46</td>
<td>63</td>
</tr>
<tr>
<td>$2\theta$ (3 1 0) [deg]</td>
<td>117.18</td>
<td>117.28</td>
<td>117.52</td>
<td>117.61</td>
<td>117.65</td>
</tr>
<tr>
<td>$2\theta$ (0 0 2) [deg]</td>
<td>43.00</td>
<td>42.95</td>
<td>42.80</td>
<td>42.73</td>
<td>42.70</td>
</tr>
</tbody>
</table>
The lattice parameters, $a$ and $c$, and $a/c - a_{\text{eq}}/c_{\text{eq}}$ of the Fe$_2$B phase as a function of average grain size of nanocrystalline Fe–Cu–Si–B alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ [nm]</td>
<td>19</td>
<td>28</td>
<td>38</td>
<td>46</td>
<td>63</td>
</tr>
<tr>
<td>$a$ [nm]</td>
<td>0.5110</td>
<td>0.5107</td>
<td>0.5105</td>
<td>0.5101</td>
<td>0.5100</td>
</tr>
<tr>
<td>$c$ [nm]</td>
<td>0.4230</td>
<td>0.4231</td>
<td>0.4232</td>
<td>0.4239</td>
<td>0.4239</td>
</tr>
<tr>
<td>$a/c - a_{\text{eq}}/c_{\text{eq}}$ [%]</td>
<td>0.544</td>
<td>0.433</td>
<td>0.363</td>
<td>0.078</td>
<td>0.046</td>
</tr>
</tbody>
</table>

Table 3

that atoms other than B atoms have no solubility in the Fe$_2$B phase, the result in Table 3 needs further investigation.

As mentioned in Section 3.1, if the type and concentration of solute atoms do not change during the grain size refinement, the vacancy concentration will increase, which would result in a supersaturation of vacancies in the lattice and consequently, an increase in the lattice constant. The smaller the grain size, the more serious the lattice distortion. The above analysis agrees with the data in Fig. 2 and Table 3. The lattice distortion will also produce a large difference in the magnitude of the lattice constant determined from different diffraction lines as in Fig. 2, and this difference is increased by decreasing of the grain size. On the contrary, after coarsening, the lattice distortion becomes weaker and weaker, which will decrease the magnitude of the lattice constant. From the above-mentioned, the variation of the lattice parameters with grain size exactly originates from the lattice distortion of nanophases. Or, in other words, the influence of the interfacial energy on the lattice structure of nanometer-sized phases particles cannot be ignored.

3.3. Mössbauer parameters of the $\alpha$-Fe(Si) and Fe$_2$B phases

As mentioned in Section 3.1, Mössbauer spectroscopy is a valuable tool in detecting the hyperfine structures in solids, such as local atomic configurations, electronic structure and s-electron density. Figure 3 is a Mössbauer spectrum of sample A, which can well be fitted by using five sets of subspectra, corresponding respectively to the $\alpha$-Fe(Si) and the Fe$_2$B phase. Some fitted results are summarized in Table 4 in reference to Ref. [17]. In Table 4, $H_{hf}$ is the hyperfine magnetic field, IS is the isomer shift, which is relative to the center of the $\alpha$-Fe spectrum, SQ is the quadrupole splitting and AREA the relative area of a subspectrum.

Table 5 lists the Mössbauer parameters, HLW and IS, of $^{57}$FeNN with the average grain size. It is clear that both HLW and IS, especially for HLW, increase rapidly with a decrease of the grain size. Since HLW reflects the distribution of iron atoms in a given Fe configuration, the larger HLW corresponds to a more disordered arrangement of iron atoms. The isomer shift IS shows the s-electron density at the nucleus of an iron atom in the sample according to Eq. (2). The drop in the s-electron density of the sample will result in a rapid rise in IS. The above analysis coincides with the lattice distortion observed in the $\alpha$-Fe(Si) phase, as in Fig. 2. Similar results were obtained for $^{55}$FeNN, $^{54}$FeNN and $^{53}$FeNN [18].

Table 6 compares the half linewidth HLW and the isomer shift IS of the subspectrum of the Fe$_2$B phase. Interestingly, both HLW and IS of Fe$_2$B, especially the isomer shift IS, increase with decreasing average grain size, which shows

Fig. 3. Mössbauer spectrum of sample A. Annealed at 763 K for 1 h. ●: experimental; ○: fitted.
the same trend as in Table 5. In view of the explanation on the lattice distortion of the \( \alpha \)-Fe(Si) phase, the results in Table 6 can be easily understood. So the Fe-B phase also shows a disordered character in the same way as \( \alpha \)-Fe(Si).

Usually a high vacancy content leads to a decrease of the lattice parameter because of an atomic relaxation around vacancies. A clear example is found in Ref. [19]. In the present investigation there is an increase in the lattice parameters. Apparently the reason of the increase is suggested by the Mössbauer effect to be a local atomic arrangement that is topologically somewhat disordered.

In addition to vacancies, grain boundaries also affect the solubility of elements in a phase. It is quite imaginable that the solid solubility in the bulk is different from that in the grain boundary. In nanocrystalline Fe-Cu-Si-B alloys, Cu atoms and some B atoms may be segregated to the interfaces. With decreasing grain size, the solubility of solute atoms in a nanophase increases significantly. These Cu and B atoms may diffuse to the nanophase, leading to a change of lattice parameters.

It is generally supposed that the grain size refinement exerts no influence on the lattice structure of crystallites, i.e. the major difference between a nanocrystalline material and a coarse one is the grain size. However, lattice distortion in nanophase was observed in nanocrystalline Fe-Cu-Si-B alloys, which is a challenge to the above idea. On the other hand, the phenomenon that the solid solubility can be significantly increased by refining grains to a nanometer-scale size is of practical significance because many metallic alloys are solution-hardened. There is no doubt that the appearance of nanostructured alloys is of great interest in designing new materials. Meanwhile, an increase in the vacancy concentration in nanophases may decrease the density of excess free volumes in the interface boundaries, which will lower the free energy of the interfacial component and therefore enhance the thermal stability of nanostructured alloys. That is to say, the total free energy of a nanocrystalline sample is lowered by lattice dis-

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### Table 5

Mössbauer parameters of \(^{57}\)FeNN in nanocrystalline Fe-Cu-Si-B alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D ) [nm]</td>
<td>19</td>
<td>28</td>
<td>38</td>
<td>46</td>
<td>63</td>
</tr>
<tr>
<td>HLW [mm s(^{-1})]</td>
<td>0.163</td>
<td>0.166</td>
<td>0.162</td>
<td>0.157</td>
<td>0.150</td>
</tr>
<tr>
<td>J [mm s(^{-1})]</td>
<td>0.088</td>
<td>0.110</td>
<td>0.107</td>
<td>0.080</td>
<td>0.083</td>
</tr>
</tbody>
</table>
tortion, which stabilizes the nanostructured material.

4. Conclusions

To sum up, variations of the lattice constants of $\alpha$-Fe(Si) and Fe$_2$B nanophases with the average grain size of nanocrystalline Fe-Cu-Si-B alloys were reported. Upon reducing the average grain size, the lattice spacing of the $\alpha$-Fe(Si) phase increases significantly, depending on the diffraction lines chosen for the lattice constant determination; the $a$-axis is elongated while the $c$-axis is shortened for the Fe$_2$B nanophase. The above results were attributed to the solution of vacancies in nanophases. The Mössbauer parameters indicate that the nanophase with smaller size exhibits a disordered character, which is manifested by larger values of the half linewidth $HLW$ and the isomer shift $IS$. When considering the grain size dependent properties of nanocrystalline alloys, lattice distortion characteristics should be taken into account.

References