Formation kinetics of nanocrystalline FeBSi alloy by crystallization of the metallic glass

State Key Lab of RSA, Institute of Metal Research, Academia Sinica, Shenyang 110015, People's Republic of China

(Received 13 August 1992; accepted for publication 11 August 1993)

In order to clarify the formation mechanism of extremely fine-grained microstructures by crystallization of the FeBSi metallic glass, the nucleation and crystal-growth rates have been determined. The results indicate that the parabolic growth rate increases with annealing temperature, showing a maximum nucleation rate at an intermediate temperature range. Obviously it is possible to obtain nanocrystalline structures by controlling crystallization of the metallic glass on annealing at temperatures near the maximum nucleation rate.

Materials with a nanocrystalline grain size, typically in the range of a few to a few tens of nanometers, have attracted growing interest in recent years from the viewpoints of material science and engineering materials. Much of the work has been done on the structures and physical properties of the nanocrystalline materials fabricated by the gas condensation method. However, there unavoidably exist many defects (from vacancy-sized defects to micrometer-sized voids) in the compacted bulk samples, which might modify some of the properties such as atomic diffusion and hinder full evaluation of the material.

To obtain nanocrystalline structure, different techniques are available, among which the “crystallization method” is an effective one. The basic idea of the method is to control the crystal nucleation and growth during the crystallization process by empirically adjusting the heat treatment conditions.

The devitrification occurs by both nucleation and growth, but the manipulation of the nucleation step which influences the number, type, and distribution of the forming crystals probably offers the best means. Nucleation processes occurring within a highly supercooled viscous liquid are often different from those within a normal metallic melt and may lead to the formation of metastable phases and microstructures that cannot be obtained by conventional processing. Moreover, the high nucleation rates during crystallization of metallic glasses at these large undercoolings result in the formation of fine-grained crystalline structure, especially nanocrystalline structure.

In this communication, the mechanism of the formation of the nanocrystalline was verified by elucidating the nucleation and growth process of the crystallization products in the FeBSi metallic glass over a wider temperature range.

The Fe$_{78}$B$_{12}$Si$_{9}$ amorphous alloy ribbons, approximately 10 mm wide and 20 µm thick, were melt spun in air using the planar flow casting technique on a copper wheel, then confirmed to be in an amorphous state by using x-ray diffraction (XRD).

In order to obtain comparatively shorter heat-up and cooldown times for the higher-temperature, short aging treatments, a specially designed vacuum furnace with an pressure of $2 \times 10^{-3}$ Pa was chosen. Specimens were prepared for transmission electron microscopy (TEM) using a twin-jet device at a voltage of 20 V with a 10% perchloric-acid–ethanol mixture and were examined in a Phillips EM420 transmission electron microscope with an accelerating voltage of 120 kV.

In the present study, the annealing temperature range 450–620 °C was chosen. It was possible to study such a wide range because of the relatively short heating or cooling times associated with the annealing technique used. Nevertheless, at temperatures above 580 °C, significant errors would be introduced due to these factors. When temperature was above 580 °C, a slight extrapolation was used, as follows.

In all cases, the transformation occurred by the continuous nucleation and growth as a function of time or temperature. At all temperatures, the previous XRD analysis has indicated that the phases were the same: body-centered cubic structures α-Fe(Si) solid solution and Fe$_3$B phase with a body-centered tetragonal structure. At temperatures below 540 °C, the recorded annealing times may be used directly because at lower temperatures the errors associated with heating and cooling times can be regarded as insignificant. However, at higher temperatures, there was some evidence of an effect of heating/cooling time on the recorded annealing times and corrections were made. For example, at 560 °C, a warm-up time $8 \pm 0.1$ s was included within the measured times. So, the removal of the warm-up time allows a correction of the finish time. A typical annealing response is shown in Fig. 1, which illustrates the sensitivity to the end of crystallization. Figure 2 and Table I show the isothermal transformation during final stage of amorphism. Because the errors are too small as compared to the units in Fig. 2, we did not show the error bars on the data points. Meanwhile, no significant effect can be found in the following discussion. The crystallization was determined by differential scanning calorimeters (DSC), selected-area electron-diffraction (SAED) patterns, and XRD. The results indicate that the Fe-based alloy has been crystallized completely, which is inconsistent with our previous work. As has been known, there are many factors resulting in the broadening of Bragg reflections such as instrument, internal strain, and fine...
FIG. 1. Transmission electron micrographs illustrating crystallization of the amorphous FeBSi alloy (a) as quenched and (b), (c) heated at 560 °C for 45 and 75 s, respectively.

grain size. In the present work, because the grain size is so small that the broadening effect would be very obvious, it can also explain the reason why the grain size is larger determined from TEM than that from XRD when ignoring the internal strain. In addition, the grain size distribution, which is almost uniform, with distance from the surface to the inner surface of the foil was also determined by the one-sided thinning technique.

Figure 3 shows the variation of mean grain size, which is obtained by TEM, as a function of annealing temperature. It can be seen that the grain size decreases as the temperature increases then passes through a minimum at about 510 °C, and subsequently continually increases. As is well known, the mode of crystallization of the FeBSi alloy is primarily crystallization. The growth of primary crystals, whether they are from liquid, glass, or crystalline solid solution, may be limited by either the rate of transfer of atoms across the advancing interface (interface control) or the rate of diffusion of atoms toward or away from the growing phase (diffusion control). All the evidence up to date is that the crystallization of metallic glasses is diffusion controlled. Under some circumstances, the growth of primary crystals depends on their morphology. In the absence of interfacial instabilities, the growth is parabolic with time, i.e., \( r = A(Dt)^{1/2} \), where \( D \) is the diffusion coefficient and \( A \) a constant of an order of magnitude.

For the case of steady nucleation, i.e., parabolic growth \( r = A(Dt)^{1/2} \), constant nucleation rate \( I_s > 0 \). If crystals are assumed to be spherical, ignoring impingement effects, the total volume \( V \) transformed at the time \( t \) can be described by

\[
V = \int_0^t I_s(\frac{r}{A}) \pi A^3 D^{3/2} t^{3/2} dt
\]

and after first derivation of Eq. (1) with respect to \( t \), yields

\[
g = \frac{(AD^{1/2})}{2t^{1/2}}
\]

where \( g \) is the growth rate.

On the substitution of Eq. (3) in Eq. (2), it gives

\[
V = I_s(\frac{r}{A}) \pi A^3 t^{4/3}
\]

Inclusion of impingement effects leads to the Johnson–Mehl–Avrami equation, which may be written as

\[
x = 1 - \exp\left[-(A \pi A^3 t^{4/3})\right].
\]

From Eq. (5) it can be seen that the virtually complete crystallization occurs when \( g'I_s t^{4/3} \approx 10 \). The nearness to full crystallization of the numerical value of this expansion can
TABLE I. Times for the finish crystallization of the amorphous FeBSi alloy.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>450</th>
<th>460</th>
<th>480</th>
<th>500</th>
<th>520</th>
<th>540</th>
<th>560</th>
<th>580</th>
<th>600</th>
<th>620</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured finish time (s)</td>
<td>$2.6 \times 10^3$</td>
<td>$1.1 \times 10^5$</td>
<td>$2.5 \times 10^4$</td>
<td>$3.9 \times 10^3$</td>
<td>$1.0 \times 10^2$</td>
<td>$2.1 \times 10^2$</td>
<td>$7.5 \times 10^1$</td>
<td>$2.4 \times 10^1$</td>
<td>Extrapolated values</td>
<td></td>
</tr>
<tr>
<td>Corrected finish time (s)</td>
<td>No correction made</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where $t$ is the time to reach this state, and then the growth rate can be obtained. Comparing Eq. (6) and supposing $g^3/\lambda^4 = 10$, the nucleation rate may then be deduced as

$$I_n = 189.63/[\langle d \rangle^3 t].$$

The growth rate and nucleation rate deduced are shown in Fig. 4. Because of the same reason as in Fig. 2, we did not show error bars on the data points except the two extrapolated ones. It can be shown that the growth rate increases with temperature and the nucleation rate has a maximum at an intermediate temperature range. At temperatures about 515 °C, the nucleation and crystal growth proceed at very fast rates and the maximum of the growth rate may occur at temperatures higher than the maximum of the nucleation rate. So, it is obvious that the microstructures with smallest grain size can be formed only at temperatures even slightly below the maximum of the nucleation rate at about 510 °C.

As mentioned above, the formation mechanism of FeBSi nanocrystalline alloy can be investigated by analyzing the nucleation and growth characteristics during crystallization. A detailed study of the transformation kinetics and microstructure has allowed a determination of the nucleation and growth rate. In the present work, the growth rate is shown increasing with the annealing temperature and the nucleation rate, which has a maximum near 520 °C. Therefore, it can be concluded that it is possible to obtain nanocrystalline structure by controlling the size of the crystallization products at appropriate annealing conditions.

This work is supported by National Science Foundation of China and the Chinese Academy of Sciences.