FORMATION OF A SINGLE $\alpha$-Fe NANOPHASE DURING MECHANICALLY DRIVEN CRYSTALLIZATION OF AN FeMoSiB METALLIC GLASS

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Abstract — In this paper we report an investigation of the mechanically driven nanocrystallization of a Fe$_{77.2}$Mo$_{0.8}$Si$_{13}$ metallic glass during ball milling. TEM, XRD and DSC measurements indicated that after milling for 135 h, the amorphous sample crystallizes completely into a single $\alpha$-Fe supersaturated solid solution with a mean grain size of about 6 nm, which is fundamentally different from the thermally induced crystallization products, as well as those of the mechanical crystallization reported in the literature (an $\alpha$-Fe and borides). The as-crystallized nanophase sample milled for 262 h was found to exhibit an intrinsic thermal stability and no phase separation process was detected, even at 1173 K.

INTRODUCTION

Recently, it was found that some amorphous FeSiB-based alloys may crystallize completely when they are submitted to strong mechanical deformation like high energy ball milling (1-5). Trudeau et al. (1-3) found that the crystallization kinetics of the iron-based metallic glasses depends on the chemical composition of the amorphous alloys, and no intrinsic correlation in the structural stability exists between thermal and mechanical treatments. They suggested that the local chemical segregation induced by surface oxidation and internal strain under extensive deformation should be responsible for the structural changes of the amorphous phase. However, Bansal et al. (4) recently argued that the observed structural changes during ball milling might be attributed to the introduction of contaminations from the milling media, mainly of iron, and denied the concept of the mechanically driven crystallization. More recently, Huang et al. (5) found that the mechanically induced crystallization consists of both thermal and athermal characteristics. Nevertheless, in all cases above, similar crystallization products (an $\alpha$-Fe and borides) were obtained, which are identical to those of the conventional thermal induced crystallization of the same metallic glasses. In the present work, we investigate the crystallization process during ball milling in an FeSiB-based alloy with an addition of 0.8 at.% Mo. An unusual crystallization product of a single $\alpha$-Fe nanophase was formed, which exhibits an inherent thermal stability against phase separation.
EXPERIMENTAL

An amorphous alloy in the form of ribbon (25 μm thick and 8 mm wide) with a composition of Fe\text{77.2}Mo\text{0.8}Si\text{9}B\text{13} (at.%) was prepared by using a single roller melt-spinning machine. The ribbon was cut into small pieces (5 x 5 mm$^2$) and sealed in the milling vial under an argon gas. A stainless steel vial and hardened steel balls were used in this work with a ball-to-sample weight ratio of 40:1. The milling experiment was performed in a W1-1 planetary ball mill with a working voltage of 120 V. Thermal analysis of the samples was carried out on a Perkin-Elmer differential scanning calorimeter (DSC-7). Gold pans were used for both the sample holder and the reference one. The temperature (with an accuracy of ±0.02 K) and energy (±0.04 mJ/s) measurements were calibrated by means of standard In and Zn samples. Structural characterization was made by using a Rigaku X-ray diffractometer (D/Max-rA, 12 kW) and a Philips EM420 transmission electron microscope (TEM). The samples for TEM observation were prepared by collecting the milled powders after supersonic vibration in an alcohol solution onto a copper grid. Compositions of the samples were determined by use of the electron microprobe and chemical analysis.

RESULTS AND DISCUSSION

Figure 1 presents XRD patterns of the FeMoSiB metallic glass milled for different periods of time. Traces of diffraction peaks of an α-Fe solid solution with a bcc structure appear for the sample after 48 h of milling; meanwhile, the amorphous phase background obviously decreases.

Figure 1. XRD patterns of the samples milled for different periods of time (as indicated).
Figure 2. TEM images for the sample milled for 135 h, (a) bright-field image, (b) dark-field image, (c) corresponding SAED pattern and (d) a distribution histogram of the grain size.
With an increasing milling time, diffraction peaks of α-Fe sharpen and shift to lower 2θ angles, indicating a substantial increase of the grain size as well as the lattice parameter of the α-Fe phase. For the sample milled for 135 h, the XRD pattern can be simply indexed by a single α-Fe phase and the amorphous phase can be hardly distinguished. By means of the Scherrer equation, the mean grain size for the α-Fe phase was determined to be about 6 nm, according to the half maximum breadth of the XRD profiles. The lattice parameter was quantitatively measured from the (211) peak of the bcc solid solution, which shows a relative increment of about 0.21% with respect to that of the equilibrium pure Fe. With a further increase in milling time, the sample remains the α-Fe phase but the grain size increases, as shown in Figure 1.

TEM images and a corresponding selected area electron diffraction (SAED) pattern for the sample milled for 135 h are given in Figure 2. With many of the dark and bright field TEM images we found that the sample is completely crystallized into a single phase of α-Fe (with a bcc structure), which agrees with the XRD results. The α-Fe grains with an equiaxial morphology and random crystallography orientations exhibit a uniform distribution in their sizes. The histogram shows a lognormal distribution of the grain size for the bcc solid solution, as shown in Figure 2d, giving an average grain size of 5 nm, which coincides with the XRD result (6 nm) very well.

![Graph showing grain size variation with milling time](image-url)

**Figure 3.** Variation of the grain size with the milling time determined from both XRD and TEM.
In our TEM observations, extremely small grains, about 2 nm, were detected in the samples milled for a few hours. The grain size increases obviously when the sample was milled for a longer period of time, which agrees with the XRD results. The grain size of the α-Fe nanophase determined from both XRD and TEM was found to increase monotonically with an extension of milling, as shown in Figure 3, and tends to be about 8 nm when the sample was milled for 262 h.

Figure 4 shows the DSC curves of the samples after milling for different times at a heating rate of 20 K/min. For the as-quenched amorphous sample, two distinct exothermic peaks at 836 K and 855 K were observed, corresponding to a typical primary crystallization of α-Fe and borides (including Fe₂B, Fe₃B and Fe₂₃B₆) respectively. For the milled samples, these two exothermic peaks shift to lower temperatures and become overlapped together (see the sample milled for 87 h), indicating an evident depression of the thermal stability for the amorphous sample. The heat released during crystallization can be obtained by integrating the exothermic peaks. We noticed that the released heat decreases significantly with an increasing milling time and tends to be essentially zero (without any detectable exothermic peak in the DSC curve) after milling for 135 h. As we have known from the XRD experiments that a crystalline α-Fe phase crystallizes from the amorphous matrix during ball milling, the exothermal DSC peak for a milled sample can be...
attributed to crystallization of the residual amorphous phase during heating in the DSC experiment. A significant decrease in the released heat during DSC runs indicates that the amount of the residual amorphous phase becomes smaller with an extension of milling. For the sample milled for 135 h, the absence of detectable DSC peak implies that the amorphous sample has crystallized completely, without any residual amorphous phase during ball milling, which is consistent with XRD and TEM results.

From the results presented above, one may find that the amorphous FeMoSiB alloy crystallized into a single nanophase α-Fe solid solution when the sample was submitted to ball milling. The crystallization process and products are fundamentally different from those of the conventional thermally induced crystallization in the same amorphous alloy (6). The crystallization product is also apparently different from that of the mechanically driven crystallization in the Fe-based metallic glass with similar compositions (Fe78Si19B13), in which two phases (an α-Fe and borides) were formed during milling (1-5). Such a difference may result from different milling conditions (such as the milling intensity and milling time) and a small addition of Mo in our sample. In thermal crystallization, the addition of Mo enhances thermal stability of the glass by increasing the crystallization temperature of α-Fe and borides (6), but the final crystallization products seem to be independent of the Mo additions. The origin for the difference between the thermally and mechanically driven crystallizations might be attributed to their different crystallization micromechanisms and chemical contaminations during milling as well.

On considering the inevitable contamination during ball milling, we have determined the chemical compositions of the samples after milling for different periods of time. Table 1 lists the chemical composition analysis results of the as-quenched amorphous sample and the as-milled (262 h) nanocrystalline sample. We noticed that the concentration of Fe increases with the milling time, and meanwhile, more and more Cr was introduced into the sample due to contaminations from the milling media. Hence, the concentrations of other elements (Mo, B and Si) in the sample were relatively depressed (see Table 1).

It is known that the solid solubility of B in α-Fe is extremely small (< 0.05 at.% at room temperature), according to equilibrium phase diagram (7). Formation of a single α-Fe phase with such a high concentration of B indicated that B atoms are either supersaturated in the α-Fe nanophase or segregated at grain boundaries or triple junctions of the nanometer-sized grains. From a thermodynamic point of view, solid solubility in a nanophase might be much enhanced in terms of the well-known Gibbs-Thomson relation (8). It was found that the concentration of P in

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Mo</th>
<th>Si</th>
<th>B</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-quenched</td>
<td>77.70</td>
<td>0.77</td>
<td>8.79</td>
<td>12.74</td>
<td>0</td>
</tr>
<tr>
<td>As-milled</td>
<td>83.14</td>
<td>0.48</td>
<td>6.35</td>
<td>5.77</td>
<td>4.26</td>
</tr>
<tr>
<td>$T_a$ (K)</td>
<td>$t_a$ (min.)</td>
<td>Equilibrium phases at room temperature</td>
<td>Phases present after annealing</td>
<td>Grain size (nm)</td>
<td>Lattice parameter, a (nm)</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>as-milled</td>
<td>---</td>
<td>$\alpha$-Fe +Fe$_2$B</td>
<td>single $\alpha$-Fe solid solution</td>
<td>6</td>
<td>0.2870±0.0002</td>
</tr>
<tr>
<td>923</td>
<td>0</td>
<td>$\alpha$-Fe +Fe$_2$B</td>
<td>$\alpha$-Fe s.s.</td>
<td>16</td>
<td>0.2870±0.0002</td>
</tr>
<tr>
<td>953</td>
<td>10</td>
<td>$\alpha$-Fe +Fe$_2$B</td>
<td>$\alpha$-Fe s.s.</td>
<td>21</td>
<td>0.2869±0.0002</td>
</tr>
<tr>
<td>953</td>
<td>70</td>
<td>$\alpha$-Fe +Fe$_2$B</td>
<td>$\alpha$-Fe s.s.</td>
<td>25</td>
<td>0.2869±0.0002</td>
</tr>
<tr>
<td>1173</td>
<td>70</td>
<td>$\alpha$-Fe+Fe$_2$B</td>
<td>$\alpha$-Fe s.s.</td>
<td>26</td>
<td>0.2871±0.0002</td>
</tr>
</tbody>
</table>

A nanophase Ni solid solution is about 10 - 15 times higher than the equilibrium value (9), and similar phenomena were found in other nanophase samples (10,11). Hasegawa et al. (12) studied the formation of $\alpha$-Fe (B) solid solution during the melt-spinning. They pointed out the iron-based alloy with less than 12 at.% B is preferred to form an Fe (B) metastable supersaturated solid solution with a bcc structure during rapid quenching, while those with higher B concentration (> 12 at.%) to form an amorphous phase. According to Maurice (13) and Bhattacharya (14), one can imagine that there is an effective temperature rise for the sample at the impacting site during ball milling and this temperature rise will cool down to within 1 K of the initial ambient value at a high cooling rate of the order of $10^5$ K/sec, which is comparable to that attainable in the melt-spinning. Therefore, formation of the single bcc supersaturated solid solution during ball milling might be understandable.

Generally, solute atoms of Mo, Cr and Si occupy the substitutional sites in bcc $\alpha$-Fe nanophase. The larger atom radii of Mo and Cr (or the smaller atom radius of Si) with respect to that of Fe will result in an increase (or a decrease) of the lattice parameter of the bcc solid solution. Ray et al. (15) showed that the B atoms substitute iron atoms in bcc solid solution, replacing the average two Fe atoms by three B atoms, which will result in a decrease of the lattice parameter of the bcc solid solution. Qualitatively, the effect of these solute elements on the lattice parameter of the bcc solid solution will counteract to some extent, and as a result, the lattice distortion of the bcc solid solution is relatively insignificant (about 0.21% for the sample milled for 262 h). Even though it is possible to form an $\alpha$-Fe solid solution with such a high concentration of B, one cannot rule out the possibility of segregation of B and other elements at grain boundaries and triple junctions in the nanocrystalline materials. If all the B atoms are supersaturated in the bcc solid solution, occupying the substitutional sites, upon annealing the metastable supersaturated phase...
will tend to transfer into more stable state via phase separation and precipitation of borides. This may result in an increase of the lattice parameter of the bcc solid solution and the appearance of borides.

The thermal stability of the completely crystallized sample milled for 262 h was investigated by annealing it under different conditions, as listed in Table 2. Under all heat treatment conditions, it is surprising to note that the sample keeps the single nanophase structure and no phase separation was detected. The grain size increases markedly upon annealing and tends to a stable value of about 26 nm after annealing at 1173 K for 70 min, but no detectable changes in the lattice parameter for the bcc solid solution were obtained.

These observations imply that the as-milled single nanophase structure exhibits inherent thermal stability against phase separation and precipitation probably due to some kinetic constraints. Almost no detectable changes in the lattice parameter of the α-Fe nanophase upon annealing indicates that at least no remarkable diffusion of B (and other elements) out of the bcc nanophase lattice occurs upon grain growth. The kinetic constraints might originate from the segregation of B (and other elements) at grain boundaries or triple junctions, which significantly stabilizes the nanostructure. Further detailed investigations on the microstructure are in progress.

CONCLUSIONS

In summary, we have prepared a single supersaturated α-Fe nanophase by mechanically driven crystallization of a Fe77.2Mo9.8Si9B13 metallic glass during ball milling. The crystallization process has been completed after 135 h of milling, forming a nanophase with a mean grain size of 5 nm. The grain size increases with the milling time and tends to a stable value of about 8 nm. The as-crystallized nanostructure exhibits an intrinsic thermal stability against phase separation and precipitation even at 1173 K for 70 min.

ACKNOWLEDGMENT

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REFERENCES