NUCLEATION CONTROLLED TRANSFORMATION IN BALL MILLED FeB

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Abstract—X-ray diffraction reveals the loss of sharp crystalline peaks, and differential scanning calorimetry shows nucleation controlled transformation besides grain growth in mechanically ground FeB intermetallic compound. On the other hand, the Mössbauer hyperfine parameters are close to the values of the disordered intermetallic compound (α-FeB) and different from those of the amorphous FeB produced by sputtering or evaporation. This controversy is attributed to the disordered interfacial phase existing at the grain boundaries.

INTRODUCTION

Amorphous alloy formation by mechanical grinding (MG) and by mechanical alloying (MA) is the subject of considerable interest in recent studies. Fe-B is a natural choice for these experiments since amorphous alloy formation was extensively investigated in it by many different methods like melt-quenching, evaporation, sputtering, implantation and laser surface melting (1-5). The results of some recent reports are, however, not unambiguous (6-8). Different milling parameters (impact, rate, material of ball and crucible, atmosphere etc.) yield significant differences. Usually, the distinction between amorphous and nanocrystalline phases is not easily made by commonly used methods. Besides X-ray diffraction, Mössbauer spectroscopy is very useful as a microscopic probe, and it can also be supported by magnetic investigations.

Beyond the usual differential scanning calorimetry measurements, further powerful calorimetric tests were suggested by Chen and Spaepen (9) to distinguish a crystalline from an amorphous structure. It was shown that the exothermal heat effect observed isothermally for simple grain growth is monotonously decreasing with increasing grain size (i.e. with time elapsed).

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Figure 1. XRD patterns of $\beta$-FeB samples ball milled in a vacuum tube mill for various times: (a) 40 min; (b) 22 h; (c) 62 h, (d) ball milled in normal atmosphere in "Pulverisette 7" for 6 h and (e) after 62 h ball milling heat treated in the DSC up to 800 K. Theoretical line positions for $\alpha$ and $\beta$-FeB are indicated on the top.

The crystallization of amorphous materials, on the other hand, is dominantly influenced by the nucleation of the new phase, and this is why the transformation rate is peaked at a definite, non-zero time. Besides this difference, it was also shown (9) that partial transformation influences the two processes oppositely. While it increases the starting grain size and thus shifts the peak temperature for grain growth to higher values in scanning measurements, a preannealing causes nucleation in the amorphous matrix, and the transformation peak temperature of crystallization is reduced.

The present work reports the results of the above mentioned experimental tests for the mechanical grinding of $\beta$-FeB. This phase is a high temperature form characterized by a (B27) type orthorhombic structure, with equivalent iron sites giving rise to one well defined set of hyperfine
parameters in the Mössbauer spectra and a Curie temperature ($T_c$) around 600 K. However, there exists a low temperature $\alpha$-FeB modification which is quite often overlooked in the literature. The X-ray diffraction pattern of $\alpha$-FeB is well described by random stacking of $\beta$-FeB (B27) type and CrB (Bf) type structures, leaving the coordination numbers and the interatomic distances unchanged (10). This $\alpha$-FeB phase has the same $T_c$ as $\beta$-FeB, but there is a broad distribution of the hyperfine fields with an average slightly lower than that of the $\beta$-FeB (10,11). The distribution was shown to originate from anisotropic hyperfine fields (11). Comparing the available data it seems that no unique, well-defined width can be attributed to the hyperfine field distribution of the disordered compound ($\alpha$), it is significantly influenced by preparation conditions which should be further studied. Because of this uncertainty, few percents of $\beta$ phase cannot be clearly defined from the $\alpha$ phase by Mössbauer spectroscopy. However, a few percents of $\alpha$ phase in a $\beta$ phase matrix can be well-identified by this method. In X-ray diffraction the situation is quite the opposite, and by combining the two methods one obtains reliable information on the ratio of the two phases. Mössbauer spectroscopy is an effective tool to detect the appearance of amorphous FeB, since the Curie temperature is substantially lower ($T_c = 550$ K) than that of crystalline FeB, and the quadrupole splitting and the isomer shift in the paramagnetic state are also significantly different (3).

EXPERIMENTAL

Mechanical grinding of $\beta$-FeB was carried out in a tube mill with 60 mm stainless steel ball (12) working in vacuum and in a Fritsch “Pulverisette 7” type planetary ball mill (at maximum setting, 700 rev/min) with four 12 mm diameter Cr-steel balls in normal atmosphere. X-ray diffraction (XRD) was made by Cu(Ka) radiation. Differential scanning calorimetry (DSC), as well as isothermal and preannealing experiments, were performed in a Perkin-Elmer type DSC-2 calorimeter. Mössbauer spectra (MS) were recorded on a standard constant acceleration spectrometer. Paramagnetic spectra were measured in a vacuum furnace of $10^{-3}$ Pa.

RESULTS AND DISCUSSION

XRD spectra of different time millings in the vacuum tube mill can be seen in Figure 1. Ball milling $\beta$-FeB (the high temperature phase in the phase diagram) results in the gradual appearance of $\alpha$-FeB in accordance with previous results (10). The sample ground in the tube mill for 40 minutes contains mainly the $\beta$ phase (Figure 1a), the one milled for 22 hours is a mixture of the $\alpha$ and $\beta$ phases (Figure 1b) and the one milled for 62 hours contains the $\alpha$ phase as main component (Figure 1c).

Grinding in the “Pulverisette 7” type mill yields the same result (Figure 1d), but on a shorter time scale, due to its larger energy impact. However, in case of longer grinding times (beyond two days) the formation of Fe$_2$B phase was observed followed by $\alpha$-Fe precipitation. This decomposition is attributed to the selective oxidation of boron. To check this idea we heat treated finely powdered $\beta$-FeB at 673 K for one day in normal atmosphere. According to our MS analysis, this resulted in partial decomposition, and about 14% of the iron atoms could be found in the newly formed Fe$_2$B phase. Selective oxidation was already reported in surface studies by conversion electron MS (13). Due to the increased surface fraction of the powder, the reaction rate is enhanced.
According to Figure 1c and 1d, a long time grinding causes the disappearance of the sharp crystalline peaks in the XRD, and the sample is either nanocrystalline or amorphous. The grain size estimated from the Debye-Scherrer formula is about 8 nm for Figure 1d. After heat treatment in the DSC up to 800 K the XRD pattern is not basically changed but the lines become narrower, as is shown in Figure 1e.

Figure 2 shows the transformation rate observed in 20 K/min heating rate DSC measurements. Two representative samples are shown; the first (dashed line) ground in the tube mill for 22 hours and the second (solid line) ground in "Pulverisette 7" for 6 hours. In the following they are referred to as sample A and B, respectively. It is evident that besides the extremely broad heat evolution, some other process is present which proceeds in a significantly narrower temperature range. The observed total heat effect is similar for the two probes: $60 \pm 10 \text{ J/g}$ in the 380-820 K temperature range. This value is close to that observed for mechanically alloyed Fe-Co (14) and for mechanically ground pure Fe (15). On this ground alone it would be very logical to assume that the observed heat effect is connected to recovery and grain growth only. Previous works also concluded that mechanical grinding of Fe$_2$B and FeB does not yield amorphous phase (6,8).

The shape of the calorimetric curve, on the other hand, suggests that besides the normal grain growth (380-750 K), a small fraction of the material undergoes some kind of sharp transformation, as well. When the heat effect is integrated for the 750-820 K temperature range, $10 \pm 1 \text{ J/g}$ exothermal heat effect is evaluated, which would indicate less than 10% amorphous fraction. Very
similar DSC curve was published for nanocrystalline pure Ni (16) where the sharp exothermic peak in the 600-700 K temperature range was attributed to the release of the increased energy stored in the grain boundaries.

The crystallization-type transformation is also confirmed both by isothermal measurements and by preannealing. Figure 3 shows the exothermal heat flux at 740 K. (No attempt was made to measure the transformation energy in isothermal mode, that is why heat flux is given in Figure 3 in arbitrary units. The instrumental sensitivity, 1 mcal/sec and the sample mass, 40 mg yields 0.1 W/g full amplitude). Beyond the monotonous decrease, a peak is also observed which is characteristic of nucleation effects.

The influence of heat treatment on the transformation temperature was also investigated. The probe, which had been ball milled in the planetary mill (Sample B), was heat treated at 700 K for 1000 s. The broad transformation is naturally eliminated by this pre-heating. The narrow heat evolution, on the other hand, is also observed after this treatment, and it is confirmed that the peak temperature is decreased by $3 \pm 0.5$ K. This small but significant decrease of the peak
temperature caused by pre-heating treatment further supports the view that, besides the grain growth processes, some kind of nucleation-controlled, i.e. crystallization-type transformation is also present.

To check the possibility that this nucleation-controlled transformation could be associated with some kind of impurities from the ball and the crucible, we prepared samples in the planetary mill with agate and tungsten carbide crucibles and balls, as well. The DSC curve of these samples also showed the sharp transformation feature in the 750-820 K temperature range, which makes this explanation unlikely.

Mössbauer spectroscopy and magnetic measurements do not support the presence of an amorphous fraction, which might yield the observed sharp transformation. In Figure 4a,b,c MS spectra of the original powder and that of the two ball milled samples are shown. Sample A can be well described by three six-line patterns with equal isomer shifts. The isomer shift and the average hyperfine field agree well with the values given in (10) (IS = 0.29 mm/s, H_{av} = 10.0 T) and the spectra is well described as a mixture of the α and β phases. Sample B, however, better resembles the one in (11), having a broader distribution of fields. When fitting the spectra with independent six-line patterns, this significantly broadened component has a fraction of approximately 40%. To decide whether this broadening might also be due to an amorphous fraction, we investigated the temperature dependence in both samples. We could only find a single Curie temperature in both samples around 580 ± 3 K. This was also confirmed by thermomagnetic measurements on both sample A and B (17).

MS spectra of sample A and B above the Curie temperature are shown in Figure 4 d,e. The symmetrical structure of the paramagnetic spectra is further evidence against the presence of a significant amount of amorphous FeB. The isomer shift of β-FeB is higher than that of amorphous FeB by 0.05 mm/s at this temperature (3). The quadrupole splitting (e^2qQ/2) for β-FeB and for amorphous FeB are 0.43 ± 0.01 and 0.55 ± 0.01 mm/s, respectively (3). We are not aware of any data on the paramagnetic MS parameters of α-FeB, but in any case, for sample A, which is a mixture of the α and β phases, one expects that the presence of the amorphous phase in the amount indicated by calorimetry would cause an appreciable asymmetry.

The paramagnetic MS parameters are summarized in Table 1. In the paramagnetic state both samples show a symmetric quadrupole doublet, but the parameters are slightly different, which should be due to the different amount of the α-phase in the samples. One can see that the quadrupole splitting is slightly larger in the α phase than in β-FeB and probably this phase should be described by a quadrupolar distribution, which results in a larger linewidth when the spectra is fitted with one doublet. This can be attributed to the disordered structure of the α phase.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isomer Shift</th>
<th>Quadrupole Splitting</th>
<th>Linewidth</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.07 ± 0.01</td>
<td>0.46 ± 0.01</td>
<td>0.37 ± 0.01</td>
</tr>
<tr>
<td>B</td>
<td>0.05 ± 0.01</td>
<td>0.50 ± 0.01</td>
<td>0.46 ± 0.02</td>
</tr>
</tbody>
</table>
Figure 4. Mössbauer spectra at 293 K: powdered $\beta$-FeB (a); sample A (b); and sample B (c), and at 593 K; sample A (d), and sample B (e).
Samples heat treated in the DSC in argon atmosphere above the temperature of the sharp DSC peak were also checked by MS, as well as samples heat treated in the vacuum furnace. The MS parameters show no significant change upon this heat treatment, neither in the ferromagnetic nor in the paramagnetic temperature range. This also proves that the sharp DSC peak cannot be connected to structural changes. (However, there is a small change in the Curie temperature shifting to $T_c = 600$ K. This might indicate a slight change in the interatomic distances.) Upon heat treating the samples in a vacuum furnace for two days at 823 K (well above the DSC peak) no Fe$_2$B or $\alpha$-Fe formation could be found. These observations, in accordance with the XRD result (Figure 1e), exclude the possibility that the sharp DSC peak could be interpreted as crystallization, decomposition, or as transformation of the $\alpha$-phase to $\beta$-FeB.

In conclusion, it is established by calorimetry that a fraction of the ball milled probe transforms by nucleation, while Mössbauer spectroscopy and magnetic studies exclude the possibility of a separate amorphous phase with a different Curie point. Since all other possible nucleation-controlled processes (impurity segregation, decomposition, $\alpha$ - $\beta$ transformation) can be excluded, we suggest an interpretation based on the extremely small grain size of the samples. We suggest that the highly distorted phase, existing at the grain boundaries cannot simply grow into the existing $\alpha$-phase, but nucleation plays an important role, as well.

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**REFERENCES**

17. L. Kiss, private communication.