A Mössbauer Spectroscopy Study of Chemically Prepared Ultrafine Particles of Amorphous $\text{(Fe}_{1-x}\text{Co}_x)_{60}\text{B}_{40}$

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Ultrafine amorphous alloy particles of $\text{(Fe}_{1-x}\text{Co}_x)_{60}\text{B}_{40}$ with $x = 0.1, 0.3, 0.5, 0.7$, and 0.9 have been prepared by reduction of the metal ions using $\text{KBH}_4$ in aqueous solution. Electron microscopy shows that the particle size is of the order of 20 nm. Mössbauer spectroscopy has been used to elucidate the magnetic properties of the particles.

1. Introduction

Amorphous alloys are normally prepared as thin ribbons or films by the liquid quench technique or by vapor deposition. Recently, we have shown that ultrafine particles of amorphous alloys can be prepared by chemical reactions at a temperature below the glass transition temperature $T_g$ of the alloys /1,2/. Using the chemical techniques, we have earlier produced amorphous particles of $\text{Fe}_{89}\text{C}_{11}$ by thermal decomposition of $\text{Fe(CO)}_5$ in an organic liquid /1/ and $\text{Fe}_{62}\text{B}_{38}$, $\text{Fe}_{24}\text{Co}_{19}\text{B}_{37}$ and $\text{Fe}_{37}\text{Ni}_{28}\text{B}_{34}$ by reduction in aqueous solutions of appropriate mixtures of transition metal salts using $\text{KBH}_4$ /2/. Dragieva et al. /3,4/ have reported a similar procedure using $\text{NaBH}_4$.

When using the liquid quench technique, the material has to be cooled very rapidly ($\gtrsim 10^6$ K s$^{-1}$) from the liquid state to a temperature below the glass temperature, $T_g$. At a given cooling rate, formation of the amorphous phase is favored if the temperature interval $\Delta T$ between the liquidus curve $T_L$ and $T_g$ is small. This is probably one of the reasons that compositions near the eutectic are favorable for formation of an amorphous alloy, whereas compositions far from the eutectic may not lead to amorphous phases when using the presently available liquid quench technique. However, when the alloy is formed by a chemical method at a temperature well below $T_g$, it is in principle possible to form alloys with less restrictions to the composition compared to the quenching techniques.

An advantage of the chemical methods is that they can easily be used for production of ultrafine amorphous alloy particles instead of ribbons. Such small particles may have interesting applications for example in magnetic memory systems, ferrofluids, and catalysts.

2. Experimental

Ultrafine particles of amorphous Fe-Co-B alloys were prepared by adding dropwise an aqueous solution of $\text{FeSO}_4$ and $\text{CoCl}_2$, corresponding to the desired Fe-Co ratio, to a 1M aqueous solution of $\text{KBH}_4$. The chemical reaction was carried out under vigorous stirring. The black precipitate was washed in water and in acetone. Subsequently, it was dried in air. Electron microscopy studies revealed particle sizes in the range 10-100 nm.
Table 1
Chemical composition of the particles

<table>
<thead>
<tr>
<th>Fe:Co mixing ratio</th>
<th>% at. Fe</th>
<th>% at. Co</th>
<th>% at. B</th>
<th>Total</th>
<th>Fe:Co Final ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:90</td>
<td>6.8</td>
<td>54.5</td>
<td>38.7</td>
<td>100</td>
<td>11:89</td>
</tr>
<tr>
<td>30:70</td>
<td>18.6</td>
<td>43.2</td>
<td>38.2</td>
<td>100</td>
<td>30:70</td>
</tr>
<tr>
<td>50:50</td>
<td>28.8</td>
<td>29.0</td>
<td>42.2</td>
<td>100</td>
<td>50:50</td>
</tr>
<tr>
<td>70:30</td>
<td>47.6</td>
<td>18.9</td>
<td>38.5</td>
<td>100</td>
<td>70:30</td>
</tr>
<tr>
<td>90:10</td>
<td>54.1</td>
<td>6.3</td>
<td>39.6</td>
<td>100</td>
<td>89:11</td>
</tr>
</tbody>
</table>

Using atomic absorption spectrometry, the samples were analyzed chemically. The results are given in Table 1. It is clearly seen that there is good agreement between the original Fe:Co ratio in the metal salt solution and the resulting Fe:Co ratio in the metallic particles. Thus it is possible to choose any metal ion ratio and reproduce it in the final particles, i.e. there is no basic restriction on this ratio. A certain amount of boron is, however, necessary in order to stabilize the amorphous phase. In the present particles, boron atoms from KBH₄ have entered into the alloy particles as a stabilizing element during the chemical reaction. From the table it is seen that the final boron content in the particles is about 40% (at).

Mössbauer spectra were obtained using a conventional constant acceleration spectrometer with a source of ⁵⁷Co in a rhodium matrix. The spectrometer was calibrated by use of a 12.5 μm absorber foil of α-Fe at room temperature. Isomer shifts are given relative to the centroid of the calibration spectrum.

3. Results and Discussion

The five samples of Fe₅₋ₓCoₓ)₆₀B₄₀ with x = 0.1, 0.3, 0.5, 0.7, and 0.9 were studied with Mössbauer spectroscopy. Figure 1 shows the Mössbauer spectra obtained at 80 K of the different samples. The spectra show broadened lines due to the occurrence of hyperfine field distributions typical of amorphous alloys. Figure 2 shows the average hyperfine fields for the different samples deduced from the Mössbauer spectra of Figure 1. The average hyperfine field ranges from 15.2 T for the (Fe₀.₁Co₀.₉)₆₀B₄₀ sample up to 21.6 T for the (Fe₀.₅Co₀.₅)₆₀B₄₀ sample. The size of the hyperfine fields is considerably smaller than that of amorphous (Fe₅₋ₓCoₓ)₈₀B₂₀ /6/. This is due to the higher content of diamagnetic boron atoms which reduces the magnetic moment of the particles.

In all samples the isomer shift was 0.30 ± 0.03 mm/s⁻¹ at 80 K, and the average quadrupole shift was negligible. The value of the isomer shift is consistent with those found by Nakajima et al. /5/ in studies of boron-rich Fe-B amorphous alloys.

In the studies of (Fe₅₋ₓCoₓ)₈₀B₂₀ amorphous alloys /6/ the magnetic hyperfine field was found to vary only slightly with the composition, and the variation could be described by a linear relationship. In the present study of amorphous (Fe₅₋ₓCoₓ)₆₀B₄₀ alloys the variation in the magnetic hyperfine fields is much larger, and there is a non-linear relationship between the hyperfine field and the composition.

4. Conclusions

The present study has shown that amorphous Fe-Co-B can be produced by reduction of metal ions in an aqueous solution using KBH₄. It is found that the