The disaccommodation of the magnetic susceptibility and microstructure for the amorphous and nanocrystalline Fe₈₅Zr-B₆ and Fe₁₃.₅Cu₁Nb₃Si₃₃.₅B₉ alloys are investigated. It is found that the disaccommodation intensity decreases after annealing amorphous ribbons. It is due to the annealing out of some free volumes in these samples. The isochronal disaccommodation curves for the amorphous samples are analysed using a gaussian distribution in relaxation times and activation energies of relaxation processes are found. Moreover, it is stated that the relaxation processes occurring in the amorphous matrix are the main source of the magnetic disaccommodation in both investigated nanocrystalline alloys.

Key words: disaccommodation, gaussian distribution

1. Introduction

A structure of amorphous alloys produced by a rapid quenching method is metastable because of relaxation processes which involve the changes of the magnetic properties of these materials. The disaccommodation of the magnetic susceptibility, which is one of the magnetic after-effect phenomena, is very sensitive to these structural changes. The basic cause of the magnetic susceptibility disaccommodation is the presence of the lattice imperfections. In crystalline materials this effect results from rearrangements of anisotropic atomic defects within domain walls (e.g. hopping of C atoms between neighbouring octahedral interstitial sites in bcc α-Fe) 1). In amorphous alloys empty spaces, also called „free volumes“ act as vacancy-like defects and enable the reorientation of atom pairs 2).

The nanocrystalline alloys consist of the crystalline and amorphous phases. The investigations of the magnetic susceptibility disaccommodation for these materials allow also to determine the contribution of the relaxation processes occurring in particular phases to the observed effect.

The aim of this paper is to study the magnetic susceptibility disaccommodation and microstructure for both the amorphous and nanocrystalline Fe₇₅Cu₅Nb₃Si₃₃.₅B₉ and Fe₈₅Zr-B₆ alloys.

2. Experimental procedure

The amorphous ribbons were obtained by a melt quenching technique. The thickness of ribbons was 20 µm. The ribbon widths of the Fe₈₅Zr-B₆ and Fe₁₃.₅Cu₁Nb₃Si₃₃.₅B₉ alloys were 2 mm and 10 mm, respectively.

The disaccommodation of the initial magnetic susceptibility was investigated for toroidal samples of 30 mm inner diameter within the temperature range from 100 K up to 650 K. The experimental results are presented as isochronal disaccommodation curves

\[ \Delta \left( \frac{1}{\chi} \right) = \Delta \left( \frac{1}{\chi_0} \right) - \Delta \left( \frac{1}{\chi_1} \right) = f(T) \] (1)

where \(1/\chi_1\) and \(1/\chi_2\) are reciprocal magnetic susceptibilities at times \(t_1 = 2\) s and \(t_2 = 120\) s after demagnetization, respectively.

The microstructure of the samples was investigated by Mössbauer spectroscopy. From these studies the content of the crystalline phase in nanocrystalline alloys was determined. The investigations were performed for the Fe₈₅Zr-B₆ alloy in the as-quenched state and after annealing for 1 h at 700 K and 820 K. The microstructure and magnetic susceptibility disaccommodation for the Fe₁₃.₅Cu₁Nb₃Si₃₃.₅B₉ alloy were studied after annealing at 673 K for 1 h and at 823 K for 10 s and 1 h.

3. Results

The isochronal disaccommodation curves for the amorphous and nanocrystalline samples of the Fe₈₅Zr-B₆ and Fe₁₃.₅Cu₁Nb₃Si₃₃.₅B₉ alloys are shown in Fig. 1. The disaccommodation for the as-quenched amorphous samples of the Fe₈₅Zr-B₆ alloy was measured three times in the temperature range from 150 K up to 300 K (in order to avoid irreversible relaxations). The isochronal disaccommodation curve obtained during the third run (curve a) shows one pronounced maximum at about 215 K and the second one at 300 K. After annealing the sample at 700 K (curve b) the disaccommodation amplitude decreases and a very broad maximum between 150 K and 325 K in \(\Delta(1/\chi) = f(T)\) curve is observed. After the partial crystallization of this sample (after annealing at 820 K for 1 h) no relaxation processes are observed in the temperature range from 100 K up to 300 K apart from almost temperature independent background (curve c).

The isochronal disaccommodation curve for the amorphous Fe₁₃.₅Cu₁Nb₃Si₃₃.₅B₉ alloy annealed at 673 K for 1 h (curve d) shows a very broad maximum at about 550 K.
Fig. 1 Isochronal disaccommodation curves for the Fe$_{87}$Zr$_{13}$B$_6$ alloy in the as-quenched state (third run) (a), annealed at 700 K for 1 h (b), annealed at 820 K for 1 h (c), and for the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.3}$B$_9$ alloy: annealed at 673 K for 1 h (d), annealed at 823 K for 10 s (e) and 1 h (f).

After annealing the sample at 823 K for 10 s the distinct decrease of the disaccommodation intensity is observed (curve e). The intensity of disaccommodation for the sample annealed at 823 K for 1 h almost drops to zero in the temperature range from 150 K to 400 K (curve f).

The results obtained from Mössbauer spectra analysis are shown in Table 1.

4. Discussion

The results obtained indicate that the magnetic disaccommodation in the investigated alloys depends on their microstructure (Fig. 1, Tables 1 and 2).

Table 1 The average hyperfine field ($<B>$) and volume fraction of the crystalline α-Fe ($V_1$) and α-FeSi ($V_2$) phases for the Fe$_{87}$Zr$_{13}$B$_6$ and Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.3}$B$_9$ alloys subjected to different heat treatments.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Heat treatment</th>
<th>$&lt;B&gt;$ [T]</th>
<th>$V_1$</th>
<th>$V_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{87}$Zr$</em>{13}$B$_6$</td>
<td>as-quenched (third run)</td>
<td>9.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>700 K for 1 h</td>
<td>10.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>820 K for 1 h</td>
<td>24.0</td>
<td>0.44</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>673 K for 1 h</td>
<td>22.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>823 K for 10 s</td>
<td>23.0</td>
<td>-</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>823 K for 1 h</td>
<td>23.2</td>
<td>-</td>
<td>0.49</td>
</tr>
</tbody>
</table>

| Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.3}$B$_9$ | 700 K for 1 h | 213 | 6.5 | 0.18 | 0.61 + 0.71 |
|                                          | 247 | 2.7 | 0.72 | 0.75 + 0.82 |
|                                          | 279 | 2.1 | 0.30 | 0.87 + 0.92 |
| 673 K for 1 h                            | 405 | 2.2 | 2.4 | 1.14 + 1.45 |
|                                          | 473 | 5.4 | 3.3 | 1.35 + 1.60 |
|                                          | 545 | 8.2 | 3.7 | 1.58 + 1.78 |
| 823 K for 10 s                           | 395 | 5.5 | 0.62 | 1.08 + 1.38 |
|                                          | 445 | 4.9 | 0.35 | 1.32 + 1.46 |
|                                          | 502 | 3.8 | 0.59 | 1.52 + 1.64 |

Table 2 The peak temperature ($T_p$), pre-exponential factor ($\tau_0$), intensity ($I_p$) and activation energy ($E$) of elementary processes for Fe$_{87}$Zr$_{13}$B$_6$ and Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.3}$B$_9$ alloys subjected to the different heat treatments.
The isochronal disaccommodation curves show very broad maxima which distinctly decrease after annealing the samples (Fig. 1, Table 2). This effect is connected with the annealing out of some free volumes in the amorphous ribbons. It is confirmed by Mössbauer spectroscopy investigations: the enhancement of the average hyperfine field \(<B>\) (Table 1) indicates that the packing density of atoms increases after annealing the samples.

For the analysis of the isochronal disaccommodation curves of amorphous materials the continuous spectrum of relaxation times is assumed. Up to now the box distribution was usually used \(2^{3}\). From the physical point of view, a gaussian distribution in \(ln\tau\) is more realistic than the box distribution and is defined by:

\[
P(\ln \tau) = \frac{1}{\sqrt{\pi} \beta} \exp \left[ - \left( \frac{\ln \tau / \tau_m}{\beta} \right)^2 \right]
\]

where \(\tau_m\) is an average value of relaxation times \((\tau)\) and \(\beta\) is a distribution parameter.

Under the assumption that the observed relaxation spectra may be described by a superposition of individual processes \(4^{3}\), the isochronal disaccommodation curve may be expressed as:

\[
\Delta \left( \frac{1}{\chi} \right) = \sum_{i=1}^{n} \frac{1}{\sqrt{\pi} \beta_i} \int_{-3\beta_i}^{+3\beta_i} \frac{T_{p_i}}{T} \times \\
\times \left\{ \exp \left[ - \left( \frac{t_1}{\tau_{mi}} e^z \right)^2 \right] - \exp \left[ - \left( \frac{t_2}{\tau_{mi}} e^z \right)^2 \right] \right\} \times \\
\times \exp \left[ - \left( \frac{z}{\beta_i} \right)^2 \right] dz
\]

where \(z = ln \tau / \tau_{mi}\), \(T_{p_i}\) is the disaccommodation intensity at \(T_{p_i}\) (peak temperature) and \(\tau_{mi}\) is an average relaxation time of the individual process. The limit values for \(z\) are assumed to be equal to \(\pm 3\beta_i\), which approximately correspond to \(\pm \infty\).

From the numerical analysis of the relaxation spectrum the following parameters for individual processes are determined: the disaccommodation intensity \(I_{p_i}\) at \(T_{p_i}\), the average activation energy \((E_{mi})\) and distribution parameter \(\beta_i\).

Furthermore, the pre-exponential factor \(\tau_{omi}\) is given by the Arrhenius law:

\[
\tau_{omi} = \tau_p \exp \left( - \frac{E_{mi}}{kT_{p_i}} \right)
\]

where \(k\) is the Boltzmann constant and \(\tau_p\) - relaxation time at the peak temperature.

The distribution of relaxation times corresponds to the distribution of activation energies \(E_i\):

\[
E_{mi} = \beta_i kT_{p_i} \leq E_j \leq E_{mi} + \beta_i kT_{p_i}
\]

The results obtained from the decompositon of the isochronal disaccommodation curves into elementary processes for the investigated alloys are listed in Table 2. The experimental points and the fitted theoretical curve, being a sum of elementary processes, for the amorphous Fe\(_{73.5}\)Cu\(_{4}\)Nb\(_{3}\)Si\(_{13}\)B\(_{8}\) sample annealed at 673 K for 1 h, as an example, are shown in Fig. 2.

![Fig. 2 Experimental points and theoretical \(\Delta(1/\chi) = f(T)\) curve for the amorphous Fe\(_{73.5}\)Cu\(_{4}\)Nb\(_{3}\)Si\(_{13}\)B\(_{8}\) alloy annealed at 673 K for 1 h](image)

The fit of the theoretical curve to the experimental points yields the pre-exponential factor \(\tau_0\) of the order of \(10^{15}\) s. It indicates that the observed magnetic after-effect phenomenon in this alloy is due to the reorientation of mobile atom pairs in the vicinity of the "free volumes".

It is worth noticing that in the nanocrystalline alloys with the volume fraction of the crystalline phase of about 0.5, the contribution of the relaxation processes in this phase to the disaccommodation is not evident (Fig. 1, Table 1).

The increase of the disaccommodation intensity for the Fe\(_{80}\)Zr\(_{20}\)B\(_{8}\) alloy near 325 K (for the amorphous nanocrystalline samples, Fig. 1) is connected with the transition of the amorphous phase from ferro- to paramagnetic state (Hopkinson maximum). Similar effect is observed for the amorphous and nanocrystalline samples of the Fe\(_{73.5}\)Cu\(_{4}\)Nb\(_{3}\)Si\(_{13}\)B\(_{8}\) alloy near 600 K.

5. Conclusion

- The disaccommodation intensity distinctly decreases after annealing the samples.
- The gaussian distribution in \(ln\tau\) enables the determination of the pre-exponential factor of the Arrhenius law and the activation energy of relaxational processes responsible for the observed phenomena.
- The processes occurring in the amorphous matrix are the main source of the magnetic disaccommodation in the nanocrystalline alloys.

References