Structure and Magnetic Properties of Fe(Mn)–Si–B–Nb–Cu Alloys

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According to high energy X-ray diffraction measurements no significant changes were observed in a short range atomic order of amorphous ribbons Fe\textsubscript{x}Mn\textsubscript{1−x}Cu\textsubscript{1}Nb\textsubscript{3}Si\textsubscript{13.5}B\textsubscript{9} (x = 1 up to 15 at.%). Thermal stability of the as-prepared alloys was investigated by differential scanning calorimetry and by \textit{in situ} X-ray diffraction measurements. The two-step crystallization process was revealed, crystallization temperatures \(T_{c1}\) and \(T_{c2}\) were influenced by Mn content (thermal separation between \(T_{c1}\) and \(T_{c2}\) completely vanished for \(x = 9\)).

Nanocrystalline state of annealed samples was confirmed by electron transmission microscopy. The influence of Mn substitution on magnetic properties was confirmed by thermomagnetic measurements.

PACS numbers: 61.05.cp, 75.50.Tt, 77.80.Bh

1. Introduction

In 1988 nanocrystalline Fe–Si–B–Nb–Cu alloys named FINEMET were patented by Yoshizawa et al. [1]. Up to this day many modifications of FINEMET have been investigated with the aim to study the influence of different elements on its crystallization processes and soft magnetic properties [2–4]. In this work authors investigate the crystallization kinetics and magnetic properties of initially amorphous Fe(Mn)–Si–B–Nb–Cu precursor and identify the role of the partial iron substitution by manganese.

2. Experimental

Amorphous ribbons approximately 2 mm wide and 30 \(\mu\)m thick with nominal composition Fe\textsubscript{73.5-x}Mn\textsubscript{x}Cu\textsubscript{1}Nb\textsubscript{3}Si\textsubscript{13.5}B\textsubscript{9} (x = 1, 3, 5, … and 15) were prepared by single-roller melt spinning technique.

Thermal responses of samples were carried out by a NETZSCH STA 409 PC/PG differential scanning calorimeter at a heating rate of 20 K/min under a continuous nitrogen flow.

The glassy structure of as-quenched samples was investigated by high energy X-rays (100 keV, wavelength 0.12398 Å) in order to get higher magnitude of wave vector transfer \(Q\) necessary for calculation of atomic pair distribution functions \(g(r)\). Measurements were performed at HASYLAB at BW5 wiggler beamline.

The structural evolution during non-isothermal heating was investigated by \textit{in situ} X-ray diffraction (XRD) (wavelength 0.493 Å) at the B2 bending magnet beamline. The annealing was performed in the temperature range of 723–1073 K with 25 K step using STOE furnace.

Nanocrystalline character of the samples annealed at 823 K for one hour was detected by transmission electron microscopy (TEM) operating at 200 keV.

The coercivity of samples annealed gradually for one hour at different temperatures was determined from hysteresis loops measured by a DC fluxmeter. The dependence of the magnetic moment on the temperature (thermomagnetic curves) was measured in the constant magnetic field 300 mT in the temperature range 300–1073 K by vibrating sample magnetometer.

3. Results and discussion

Figure 1 shows the differential scanning calorimetry (DSC) curves of samples with \(x = 1, 5, 9\) and 15. It can be seen significant influence of Mn substitution on a crystallization process which evidently changes itself from the two-step process for \(x < 9\) to the one-step one for \(x \geq 9\). Increasing Mn content shifts onset of the first crystallization process to higher temperature \(T_{c1}\) and, on the other hand, onset \(T_{c2}\) of the second crystallization process decreases (see Table I).

The local atomic structure at the distance \(r\) from an average atom located at the origin is possible to investigate by means of a pair distribution function \(g(r)\). The pair distribution function is connected with a structural factor \(S(Q)\) by a Fourier transformation

\[
g(r) = 1 + \frac{1}{2\pi\rho_0} \int_{0}^{\infty} Q[S(Q) - 1] \sin(rQ) \, dQ, \quad (1)
\]

where \(\rho_0\) is an average atomic density. The total structural factor \(S(Q)\) is obtained from an elastic scattering intensity \(I(Q)\) by applying the Faber–Ziman formula [5].
TABLE I

| x [%] | T_{x1} [K] | T_{x2} [K] |
|-------|-----------|-----------|
|       | XRD      | DSC       | XRD      | DSC       |
| 1     | 798      | 803       | 948      | 951       |
| 5     | 823      | 818       | 898      | 907       |
| 9     | 848      | 847       | 873      | 847       |
| 15    | 873      | 869       | 873      | 869       |
to Fe₃Si phase but additional peaks prove a presence of other phases—borides. Temperatures $T_{x1}$ and $T_{x2}$ (temperatures in which first new Bragg peaks appeared) obtained from in situ XRD experiments are summarized and compared with results obtained from DSC in Table I. Very good coincidence can be seen between these both methods.

Micrographs of as-quenched samples ($x = 1, 3, 5, 9, 15$) annealed at 823 K displayed in Fig. 4 document the influence of Mn substitution on the process of nanocrystallization. It can be seen that the increasing Mn content suppresses formation of a nanocrystalline phase. The sample with $x = 15$ is fully amorphous without any indication of nanocrystallites. These results are in accordance with above results from DSC and in situ XRD measurements. In the upper right corner of all micrographs there are shown corresponding diffractograms.

Table II shows thermomagnetic curves of selected specimens ($x = 1, 3, 5, 7$). Higher Mn content causes decrease in a magnetic moment in agreement with the fact regarding antiferromagnetic character of Mn atoms compared with ferromagnetic Fe atoms. With increasing temperature the magnetic moment of all samples sharply goes down to zero value, amorphous matrix is transformed from the ferromagnetic to the paramagnetic state. Maxima of the magnetic moment are formed (see inset in Fig. 5) about 850 K and 940 K, respectively, and they indicate the formation of a ferromagnetic phase during devitrification. According to our previous results the first maximum belongs to the crystallization of Fe₃Si phase and the second one could be explained as a result of borides’ formation. The Curie temperature $T_c$ of the amorphous matrix was determined from the inflection point of thermomagnetic curves. Crystallization temperatures $T_{x1}$ and $T_{x2}$ were estimated as the onset of maxima and together with $T_c$ they are listed in Table II.

Measurements of hysteresis loops did not prove any noteworthy dependence of a coercivity on the Mn concentration. Initial values of coercivity for as-quenched samples with $x = 0, 1, 3, 5, 7$ were about 4.1 up to 4.8 A/m and they slightly increased in process of annealing up to 7–8 A/m at 773 K.

### Table II

| $x$ [%] | $T_c$ [K] | $T_{x1}$ [K] | $T_{x2}$ [K] |
|--------|-----------|--------------|--------------|
| 1      | 585       | 798          | 956          |
| 3      | 540       | 808          | 941          |
| 5      | 494       | 814          | 916          |
| 7      | 452       | 827          | 900          |

Fig. 4. Micrographs together with diffractograms of Fe₇₃.₅₋ₓMnₓCu₁Nb₃Si₁₃.₅B₉ with $x = 1, 3, 5, 9$ and 15 (from the left to the right) alloys annealed at 823 K.

Fig. 5. Thermomagnetic curves of amorphous alloys Fe₇₃.₅₋ₓMnₓCu₁Nb₃Si₁₃.₅B₉. Inset shows their details in the temperature region of 750–1050 K.

4. Conclusion

The aim of the work was to identify the role of the partial iron substitution by manganese in initially amor-
phous Fe(Mn)–Si–B–Nb–Cu precursors. High energy XRD measurements enabled us to calculate atomic pair distribution functions. Analysis of $g(r)$s confirmed that no considerable changes were caused by Mn substitution in the short and middle range order. Both, DSC and \textit{in situ} XRD measurements revealed that $T_{x1}$ increased with higher Mn content whereas $T_{x2}$ showed an opposite tendency. Thus the temperature separation of the two crystallization events decreased with increasing Mn doping and completely vanished for 9% Mn content. Additionally, TEM confirmed the same Mn impact on the suppression of the process of nanocrystallization. Thermomagnetic measurements documented the decrement of the magnetic moment and $T_c$ with increasing Mn content. On the other hand, the coercivity did not change significantly with changes of Mn content.

Acknowledgments

HASYLAB is gratefully acknowledged for the support during synchrotron beam time. Paper was supported by Slovak Grant Agency for Science (VEGA) grants 1/4009/07.

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