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Influence of Cr, Zr and Nb on crystallization of amorphous alloys based on iron

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Abstract: In the present paper crystallization in amorphous alloys $Fe_{76}X_2B_{22}$ (X=Cr, Zr, Nb) was examined by applying resistivity measurements, differential scanning calorimetry and X ray diffraction analysis. It was shown that alloying additions cause a slowing down of diffusion processes which manifests as a shift of the nanocrystallization process into higher temperatures. From the DSC data the activation enthalpy of crystallization was determined as 2.1, 2.1, 2.7 and 4.0 eV for $Fe_{78}B_{22}$, $Fe_{76}Cr_2B_{22}$, $Fe_{76}Zr_2B_{22}$, $Fe_{76}Nb_2B_{22}$, alloys respectively. The crystallization phenomenon in examined alloys proceeds via formation of αFe nanograins (nanocrystallization for $Fe_{76}Zr_2B_{22}$ and $Fe_{76}Nb_2B_{22}$) and the growth of αFe nanograins plus formation of boride Fe_3B.

Keywords: Nanocrystallization; Amorphous alloys; DSC; XRD

1. INTODUCTION

Amorphous and nanocrystaline alloys based on iron obtained by melt spinning technique form one of the most widely studied group of modern soft magnetic materials [1]. These alloys are usually used as precursors of nanocrystalline materials for which magnetic anisotropy is drastically reduced by random distribution of nanograins [1, 2]. The key to the formation of nanocrystallites in an amorphous solid of an appropriate chemical composition is to control the annealing temperature and time to ensure relatively high nucleation rate and a small growth rate. It is already known that the crystallisation (nanocrystallisation) kinetic strongly depends on alloy chemistry. Different alloying additions (like Cr, Zr and Nb or metalloids as B or Si) can drastically change crystallisation temperatures and soft magnetic properties of the material as well [3-7].

The main idea of the present paper is to study the influence of alloying additions on crystallisation processes of the $Fe_{76}X_2B_{22}$ (X = Cr, Zr and Nb) group of amorphous alloys by applying different experimental techniques - resistivity measurements, differential scanning calorimetry and X ray diffraction.

2. MATERIAL, EXPERIMENTAL PROCEDURE AND RESULTS

The examined alloys were obtained by melt spinning technique in the form of strips with thickness and width of about 25 μm and 10 mm, respectively. As quenched samples were annealed for 1 h in the temperature range from 300 - 900 K.

For annealed samples X-ray patterns were measured at room temperature (Philips Diffractometer X'Pert PW 3040/60,). Kinetic of the crystallization process was examined by applying resistivity measurements $\rho(T)$ (four point probe method, heating rate 0.5 K/min), differential scanning calorimetry (DSC, Perkin-Elmer DSC-7, temperature range 300 to 850 K and heating rates ranged from 5 to 20 K/min). Fig. 1 shows normalized resistivity curves measured for all examined alloys. In all cases $\rho(T)$ varies linearly up to the crystallization temperature T_x. At this temperature $\rho(T)$ drastically decreases indicating formation of crystalline phases. For such measurements the so-called crystallization temperature T_x can be deduced from the condition $d\rho(T)/dT=0$. Fig. 2 shows DSC curves determined with heating rate 20 K/min. The crystallization phenomenon manifests as an exothermal peak of heat flow positioned at the crystallization temperature T_x. In both figures the influence of alloying additions is well demonstrated. For $Fe_{76}X_2B_{22}$ (X=Cr, Zr and Nb) alloys crystallization phenomenon shifts into higher temperatures in relation to the $Fe_{78}B_{22}$ alloy.

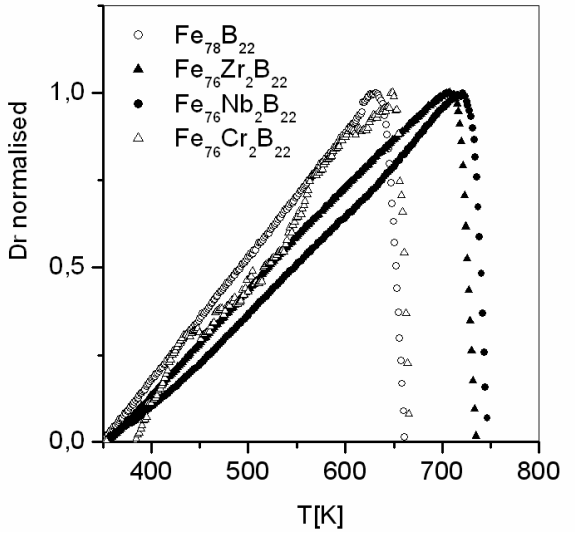

Figure 1. Normalized electrical resistivity curves (heating rate 0.5 K/min)

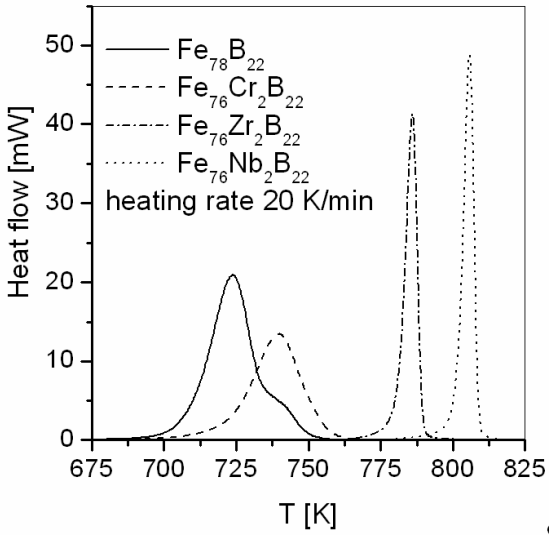

Figure 2. DSC curves for all examined alloys

Figs. 3a - 3d show X-ray patterns obtained for samples in the as quenched state, annealed for 1h at temperatures T_a close to the crystallization temperature (the lowest 1-h annealing temperature for which the first X-ray reflections of nanocrystallites were detected), and after crystallization. It is clear that for two alloys - i.e. $Fe_{78}B_{22}$ and $Fe_{76}Cr_2B_{22}$ αFe nanograins and boride Fe_3B are formed simultaneously (see Fig 3a and 3b). In contrary to this in $Fe_{76}Zr_2B_{22}$ and $Fe_{76}Nb_2B_{22}$ alloys the nanocrystallization (formation of αFe nanograins) and full crystallization (formation of boride Fe_3B) are well separated.

3. DISCUSSION AND CONCLUSIONS

Experimental results presented in this paper show that alloying additions Cr, Zr and Nb cause a slowing down of diffusion processes in amorphous material. For the $Fe_{78}B_{22}$ alloy the crystallization temperature is the lowest i.e. for the heating rate 20 K/min T_x =720 K. In relation to this value alloying additions shifts T_x into high temperature region by more than 15, 65 and 85 K for Cr, Zr and Nb, respectively. DSC measurements carried out with different heating rates allow determining activation enthalpy of the crystallization phenomenon [7, 8]. Using the well known Kissinger procedure [7] we have obtained: 2.1, 2.1, 2.7 and 4.0 eV for

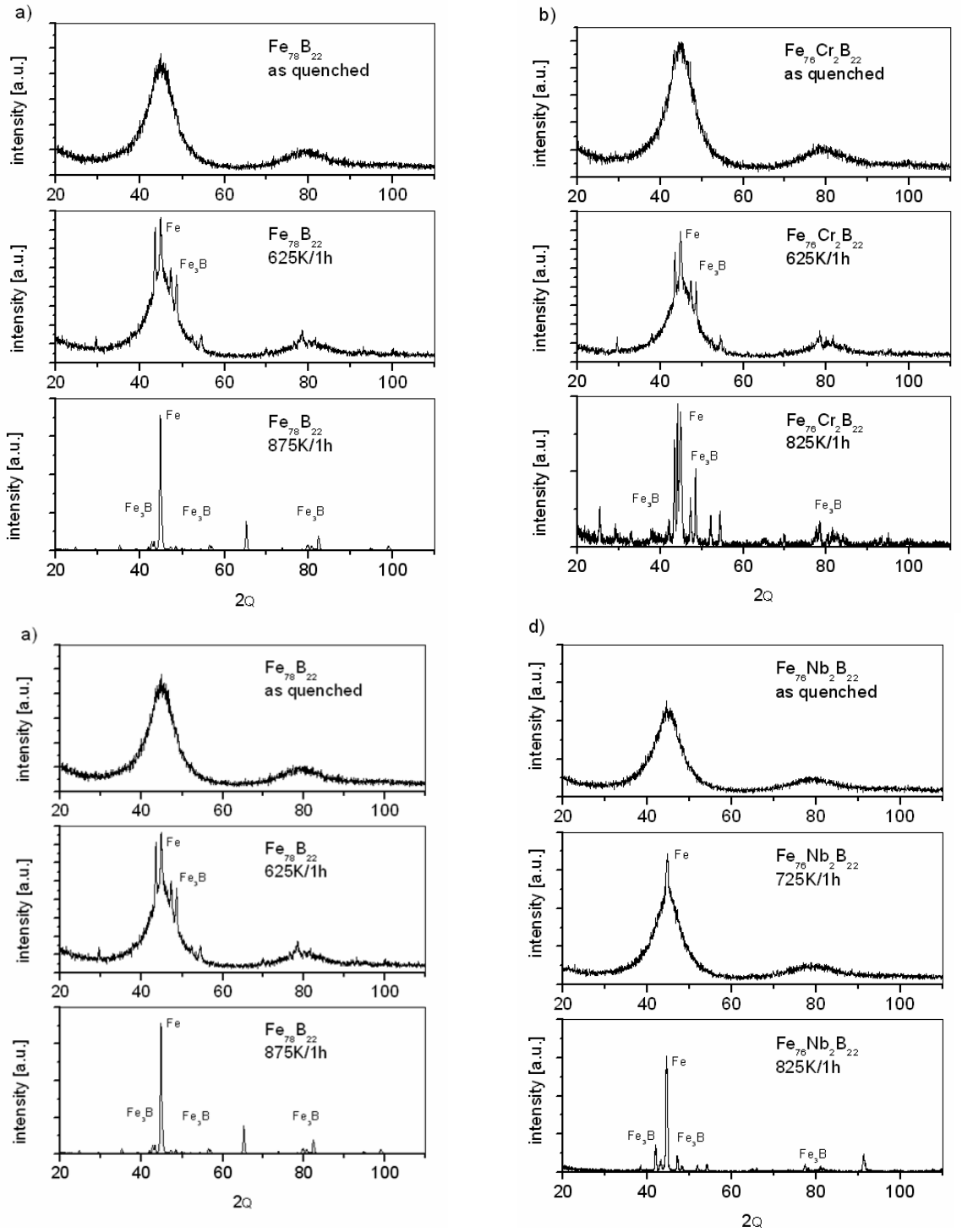

Figure 3. X-ray patterns obtain for a) $Fe_{78}B_{22}$, b) $Fe_{76}Cr_2B_{22}$, c) $Fe_{76}Zr_2B_{22}$, d) $Fe_{76}Nb_2B_{22}$ alloy

$Fe_{78}B_{22}$, $Fe_{76}Cr_2B_{22}$, $Fe_{76}Zr_2B_{22}$, $Fe_{76}Nb_2B_{22}$, alloys, respectively. These values obviously reflect the slowing down of diffusion processes in examined materials. Similar results were obtained in [4] for the same material using magnetic balance technique – i.e. 1.9, 2.0, 2.6 and 4.4 eV for $Fe_{78}B_{22}$, $Fe_{76}Cr_2B_{22}$, $Fe_{76}Zr_2B_{22}$, $Fe_{76}Nb_2B_{22}$, alloys respectively. These results obtained by different experimental techniques show that the influence of Cr atoms on

crystallization is the weakest as the Cr atomic radius does not differ to mach from Fe (R_{Fe}=1.24 Å, R_{Cr}=1.25 Å [9]). In contrary to this the highest influence on crystallization is observed for Nb atoms while Zr atomic radius is the greatest (R_{Nb}=1.43 Å, R_{Zr}=1.60 Å [9]). In any way we conclude that Nb atoms are the most effective in slowing down of diffusion processes in examined alloys. It makes possible that the nanocrystalization and annealing out of free volume in amorphous alloys with niobium do not overlap. As a consequence of it magnetic properties of these alloys can be optimised in the so-called relaxed amorphous structure which can give soft magnetic material essentially free of embrittlement - the main disadvantage of nanocristalline materials [10].

X ray studies for 1h annealed samples confirmed that Cr, Zr and Nb atoms shift the nanocrystallization process into higher temperatures and that this effect is the strongest for Nb. The crystallization in $Fe_{76}Zr_2B_{22}$, $Fe_{76}Nb_2B_{22}$ alloys goes via formation of αFe nanograins (nanocrystallization) and growth of αFe nanograins plus formation of boride Fe_3B,. For $Fe_{78}B_{22}$ and $Fe_{76}Cr_2B_{22}$ alloys αFe nanograins and boride Fe_3B are formed simultaneously.

The main conclusions of the present paper can be summarized as follows: i) alloying additions Cr, Zr and Nb cause the slowing down of the diffusion processes in the $Fe_{76}X_2B_{22}$ amorphous alloys (the crystallization temperature is successively shifted into higher temperatures), ii) activation enthalpies of the crystallization process determined from DSC measurements are: 2.1, 2.1, 2.7 and 4.0 eV for $Fe_{78}B_{22}$, $Fe_{76}Cr_2B_{22}$, $Fe_{76}Zr_2B_{22}$, $Fe_{76}Nb_2B_{22}$, alloys respectively, iii) the crystallization phenomenon in examined alloys proceeds via formation of αFe nanograins (nanocrystallization for $Fe_{76}Zr_2B_{22}$ and $Fe_{76}Nb_2B_{22}$) and the growth of αFe nanograins plus formation of boride Fe_3B.

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