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Kinetics of thermal devitrification (crystallization) of $Fe_xCr_yB_z$ glassy alloys

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Devitrification process of four glassy $Fe_xCr_yB_z$ alloys of different composition was investigated by both methods, differential-scanning-calorimetry and X-ray diffraction. It is shown that the crystallization process proceeds via one or two stages depending on the alloy composition. Kinetic parameters for the crystallization process (activation energy, rate constant, frequency factor) as well as the crystallization enthalpy are determined for all four alloys that are used. It is shown that exothermal maxima on DSC thermograms correspond to the crystallization process when polycrystalline Fe_2B and FeB phases are formed.

1. Introduction

Metallic glasses (MG) are considered as a new important class of disordered solid materials, so they have been the subject of a growing number of investigations. These investigations enable acquiring of more fundamental knowledge about the amorphous state of materials in general, as well as for important technology properties which originate from the absence of crystalline structure. Although a general theory of the disordered state of matter still has not been set up, it may be stated that some theoretical models do hold – the dense packing model [1], the microcrystalline model and random packing of an atomic cluster [2]. There are several developed methods for obtaining glassy metals and they are all based on the rapid cooling of liquid metals and alloys or on the vapors condensing (precipitating) on a cold support [3–6]. Depending on the chemical composition, various materials form glassy states with more or less difficulty. Some amorphous alloys are commercially manufactured, for example, iron based alloys ($Fe_{0.81}B_{0.135}Si_{0.033}C_{0.02}$, $Fe_{0.40}Ni_{0.38}Mo_{0.04}B_{0.18}$, etc.).

The crystallization of metallic glasses proceeds stepwise. Crystallization-theory indicates three types of the process [7] – (i) polymorphic crystallization, (ii) primary crystallization and, (iii) eutectic crystallization, which is proved by various methods. The most relevant ones are the measurements of electrical conductivity, mechanical and other properties in the course of heating. Thus it was shown that the amorphous alloy (Metglass 2826A) $Fe_{0.32}Ni_{0.36}Cr_{0.14}P_{0.12}B_{0.06}$ crystallizes in three steps. This is seen by the change in electrical resistance and DSC thermograms. The first step is primary and the second one is polymorphic-crystallization, while during the third step, a phase transition occurs upon completed crystallization. During the first step α-Fe phase is formed, while the amorphous phase is enriched with boron until the metastable equilibrium α-Fe + amorphous phase Fe-B is established, after this polymorphic crystallization with the forming of Fe_3B phase takes place.

The crystallization process of amorphous alloys $Fe_{0.80}Si_{0.10}B_{0.10}$ and $Fe_{0.83}B_{0.17}$ [8] was analyzed by measuring the volume changes during heating and by electronic microscopy. It was shown that in the first step α-Fe separates from the amorphous matrix which leads to the concentration changes, atom redistribution and formation of the Fe_3B phase. Investigations of the changes in mechanical properties of amorphous alloys $Fe_{0.40}Mo_{0.04}B_{0.18}Ni_{0.38}$, $Fe_{0.70}Si_{0.10}$-$B_{0.12}Ni_{0.08}$ and $Co_{0.60}Fe_{0.05}Ni_{0.10}B_{0.15}$ as a function of temperature indicate similar behaviour [9].

Science and technology research shows pronounced interest for electric transport in glass metals, as it is related to atomic and electronic structure of the material, so that electric conductivity of glass alloys is a nominal characteristic of those materials.

At the moment there are several theories which are attempting to explain electron transport. Ziman bases his theory on electronic properties of liquid metals [10]. The intentions of this theory go only as far as to explain the conductivity of simple metals. Güntherodt and Künzi [11] show that there exists a pronounced similarity between electric transport of liquid metals and that of metallic glass, stressing that, in the process of practical investigations, metallic glasses prove to be more favourable than liquid metals, as their structure remains unchanged in a wide temperature range.

Mooij [12] points out the great significance of the relation between the electric resistivity and the

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temperature resistance coefficient for a variety of different materials. He also establishes the correlation between the resistivity and the temperature coefficient (condition for a negative temperature coefficient being that the resistivity $\varrho \geqslant 150\,\mu$ohm cm). It seems that the phenomenon of the negative coefficient is general for materials which possess high resisitivity.

In this paper we investigated the devitrification (crystallization) process of some of the $Fe_xCr_yB_z$ glassy alloys by both methods, DSC and X-ray diffraction, correlated with the thermal change of the electrical resistance.

2. Experimental

Investigations of thermal stability (devitrification) of glassy alloys, $Fe_xCr_yB_z$, with different composition in at% – (I) $Fe_{70}Cr_{15}B_{15}$, (II) $Fe_{75}Cr_{10}B_{15}$, (III) $Fe_{80}Cr_5B_{15}$ and (IV) $Fe_{83}B_{17}$, were done by thermal analyzer Du Pont 1090 using differential scanning calorimetry method (DSC) in hydrogen, nitrogen or argon atmosphere. Samples were in a ribbon-like form, about 0.001 cm thick, obtained by rapid quenching of a liquid alloy using cold rotating disc surface, i.e., by spinning method. Structure investigations before and after devitrification process were done by Philips PW 1051 diffractometer using CuK_α radiation and graphite monochromator. The samples of several milligrams were enough to show, on DSC thermograms at particular temperatures, characteristic exo-maxima of irreversible devitrification processes.

Kinetic analysis of the process was done on the basis of the change of heating rate of DSC cell, as shown in some previous papers [10, 11]. Namely, log (β/T^2) vs $1/T$ is a straight line with the slope $\Delta \log(\beta T^{-2})/\Delta T^{-1} = -ER^{-1}$, then $k = Z \exp[-E(RT)^{-1}]$ and $Z = \{\beta \exp[E(RT)^{-1}](RT)^{-2}\}$, where β is the heating rate in $K\,\mathrm{min}^{-1}$, T = peak temperature of the exo-maximum, k = rate constant of devitrification process, E = activation energy and Z = frequency factor of the process.

3. Results and discussion

DSC thermograms show that glassy alloys are transferred, in the flow atmosphere of mentioned gases and at the particular temperature, to crystalline state through one or two stages. Fig. 1 shows DSC thermograms for all four glassy alloys. It can be seen that only alloy IV crystallizes through one stage, while the other three crystallize via two stages which are clearly separated only at alloy III; the first crystallization stage of alloys I and II can be noticed only from the asymmetry at the beginning of the exo-maximum.

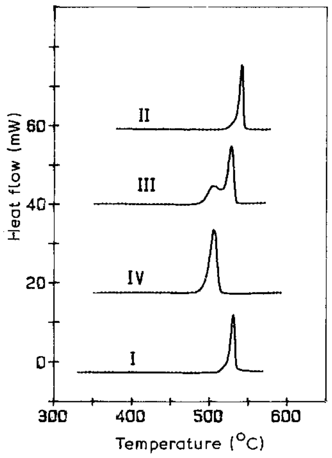

Figure 1 DSC thermograms of glassy alloys marked with I, II, III and IV according to the text, 25 K in hydrogen.

From the correlation of composition and number of crystallization stages no connection can be seen, same as from the crystallization temperature, i.e. stability, although all thermograms shown are obtained in the flow atmosphere of hydrogen.

Kinetics of the crystallization was investigated in the above described manner. Fig. 2 shows straight line dependence log (βT^{-2}) *vs* $1T^{-1}$ for all four alloys, and from the straight line slopes kinetic parameters of the crystallization for every alloy are determined and given in Table I. If the exo-maximum peak temperature, T_m, is taken as the measure of glassy alloy thermal stability, then from Table I, it can be seen that the most stable alloy is one marked I, and then alloy II, both of them containing higher and lower concentrations of Cr, B and Fe respectively, unlike to alloys III and IV.

Being that activation energies are quite high it follows that frequency factors are correspondingly also high. Crystallization rate constants are high for all alloys, but the constant for the most stable alloy I is quite higher than the constants for the other alloys. Crystallization enthalpies, which are determined by computer integration of the area under the maximum and on which accuracy only the subjective limit determinations for integration can influence, are of significant magnitude and there are no differences among them. Crystallization rate constant dependences on temperature are shown on Fig. 3. It can be seen that rate constants rise rapidly with the increase of temperature but specifically for every alloy.

X-ray diffractograms of glassy and crystalline samples are shown on Fig. 4. It can be seen that alloys in glassy state contain no ordered phases detectable to X-rays (diffractogram 1). However, after heating

TABLE I Kinetic parameters of the crystallization process of investigated alloys in hydrogen atmosphere

Alloy	stage	slope	E kJ mol^{-1}	T_m, K	Z min^{-1}	k min^{-1}	ΔH J g^{-1}
I	1	-37.04×10^3	209.15	773.3	2.22×10^{48}	2.84	82
II	1	-23.81×10^3	455.87	763.2	4.87×10^{31}	1.90	92
III	1	-14.58×10^3	279.23	726.1	1.92×10^{20}	1.28	
	2	-17.50×10^3	335.07	749.7	3.12×10^{23}	1.43	95
IV	1	-10.00×10^3	191.48	728.3	5.73×10^{13}	0.88	80

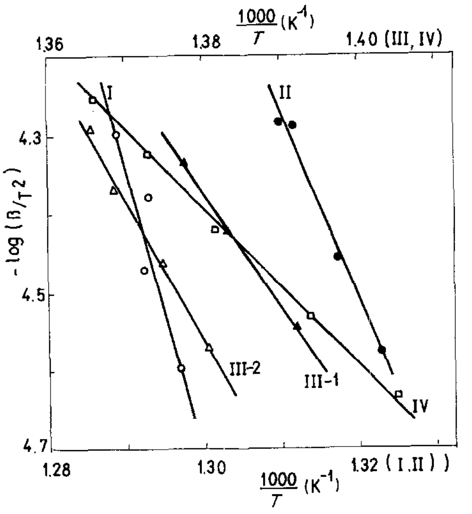

Figure 2 Energy activation plot of log (βT^{-2}) *vs* $1 \times T^{-1}$.

above crystallization temperature only one relatively poor reflection maximum at 44.5° 2θ appears at all alloys, and most probably corresponds to the primary crystallization during which polycrystalline phases α-Fe, FeB and Fe_2B are formed, as in some other cases of glassy alloy crystallization when alloy contains significant content of iron (12). In this case, it seems that only microcrystallites of mentioned phases are formed by crystallization, with quite small dimensions, and as a consequence reflection maxima of low intensity are obtained. Further, it is shown that reflection intensity does not become more intense even when the sample stays for longer time at the temperature above crystallization temperature. It seems that the presence of chromium is the consequence of such behaviour. Crystallization process of both stages takes place at 450° C (723 K) for alloy III, because the thermal processes are quite close one to another

Electric conductivity of the investigated alloys behaves rather irregularly in hydrogen atmosphere within the temperature range of the glass state stability, showing a nonlinear and very pronounced relative resistance rise, which is influenced by the alloy composition, too, Fig. 5. The maximum of the relative resistance is achieved at the temperature which precedes the process of crystallization. When crystallization ensues, the relative resistance steeply drops in

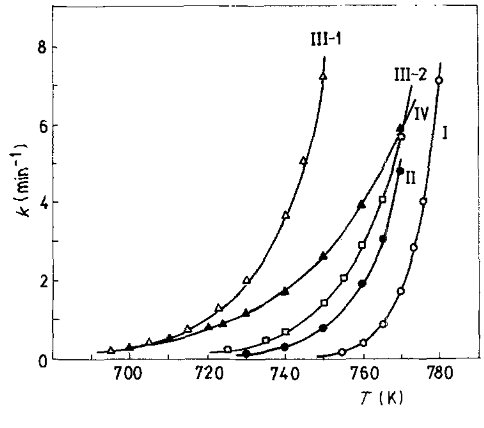

Figure 3 Rate constant dependence on temperature for devitrification process of glassy alloys I–IV.

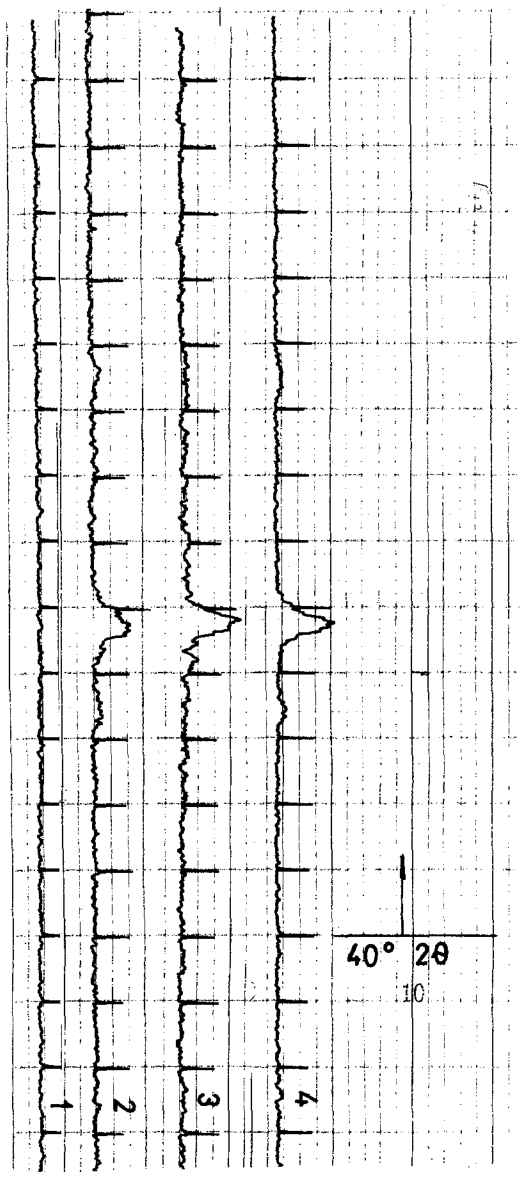

Figure 4 X-ray diffractograms for the alloys: 1. non-heated alloy I, 2. heated alloy II up to 530° C (803 K), 3. heated alloy III up to 450° C (723 K), 4. heated alloy III up to 530° C (803 K).

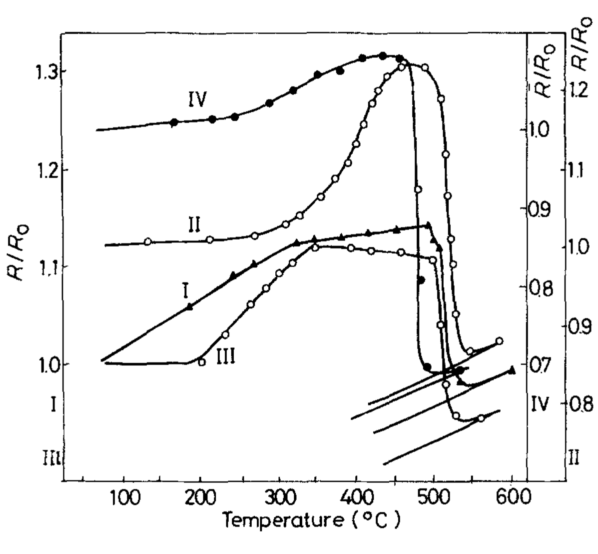

Figure 5 Temperature dependence of the relative resistance for the glassy alloys I–IV.

or or two steps, following the step process of crystallization. After crystallization, the relative resistance changes with temperature almost linearly, having a positive temperature coefficient. The irregular rise of the resistance of these glass alloys with temperature is unusual with respect to the usual behaviour of the glass alloys, which, to a smaller or greater extent, agree with theoretically predicted behaviours. The steep rise of the conductivity at the temperature of crystallization is a consequence of structure arranging, which enables extension of the electron mean free path and the increase of the number of ionic, at the expense of covalent bonds, as we have shown in the previous paper [16].

4. Conclusions

Thermal behaviour (stability) of some glassy alloys of type $Fe_xCr_yB_z$ is shown by both methods, DSC calorimetry and X-ray diffraction. Transition of glassy to crystalline state takes place at different temperatures and the process itself performs via two stages, except for alloy IV (which contains no Cr), as can be seen from the asymmetry of DSC thermograms. The thermal stability increases with the rise of Cr and B content and with lowering Fe content. Crystallization rate constants are significant and increase rapidly by temperature rise. Crystallization activation energies are quite high and depend on the alloy composition; it seems that the main contribution to the high activation energy values is the content of Fe, Cr and B, which is the most favourable for alloy II. According to X-ray analysis during crystallization microcrystalline α-Fe, FeB and Fe_2B phases of low reflection are formed.

Relative resistances of amorphous samples show irregular behaviour with a positive temperature coefficient of resistivity within the temperature range of glass-state stability. At crystallization temperature the resistance drops abruptly, following completely the process of crystallization as it goes on. The rise of conductivity (drop of resistance) is attributed to the extension of the electron mean free path and to the increase of the number of ionic at the expense of covalent bonds, due to arranging (crystallization) of the alloys.

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