

CRYSTALLIZATION OF $\text{Fe}_{75}\text{Cr}_5\text{B}_{20}$ AMORPHOUS ALLOY

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The changes induced in chemical composition of Fe-TM-M amorphous alloys (TM = Cr, Mo, Zr., M = B, Si...) lead to short range order changes around Fe sites and, consequently, to large variations of magnetic properties (M_s , T_c , λ_s ,...).

The specific magnetic properties (e.g. low coercivity, high susceptibility) of the FINEMET alloys are obtained by controlling the crystallization process [1,2]. Small additions of Nd to the amorphous Fe-B alloys and the precipitation of α -Fe and NdFe_{14}B phases during the crystallization cause magnetic hardness [3,4].

Structural thermal stability of the amorphous alloys also depends on chemical composition; moderate temperature heating activates structural relaxation processes, while annealing at high temperatures leads to crystallization, as DTA, DSC, resistivity and magnetic measurements have proved [5].

Vavassori et al. [6] revealed a fairly good correlation between the variations of the coercive force and the crystalline volume fraction, as estimated from Mössbauer spectroscopy (MS) during the nucleation and growth stage of the crystallization process in $\text{Fe}_{80}\text{B}_{20}$ ribbons.

Brzozke et al. [7], using $M_s(T)$ measurements and MS, found different values of the volume fraction of the nanograins in partially crystallized FINEMET. The differences were attributed to the specific structural sensitivity of the conventional magnetic methods in comparison with the Mössbauer spectroscopy.

Mihalca et al., using magnetic methods (isothermal $M_s(t_a)$ [8], isothermal $H_c(t_a)$ [9] with t_a - the annealing time) have found close values of the crystallization energy for $\text{Fe}_{77}\text{Gd}_3\text{B}_{20}$ ribbons.

The aim of the present paper is to compare the results of $\text{Fe}_{75}\text{Cr}_5\text{B}_{20}$ amorphous alloy crystallization, as the process was either anisothermally (DTA) or isothermally (H_c modification) activated.

Amorphous ribbons of $\text{Fe}_{75}\text{Cr}_5\text{B}_{20}$ were manufactured by single-roller technique. Samples of 80 mm length, 30 μm thickness and 2.5 mm width were introduced in thin glass tubes under vacuum and were subjected to crystallization both anisothermally (DTA) and isothermally (flash-annealing below the DTA peak temperatures).

The crystallization kinetics were examined by measuring the changes in the room temperature (RT) values of H_c after subsequent isothermal annealing times. A very low frequency (24 s period) automatic hysteresisgraph was used.

Many investigations of the crystallization processes of amorphous alloys were carried out by non-isothermal experiments. For the $\text{Fe}_{75}\text{Cr}_5\text{B}_{20}$ alloy the crystallization takes place by a single exothermal process, whose temperature peak, T_m , shifts to higher values when increasing the heating rate (α). A set of three different heating rate DTA curves are shown in Fig. 1a. An activation energy $E_K = 1.98 \pm 0.37$ eV for the crystallization process was determined by the Kissinger's method [10] (Fig. 1b).

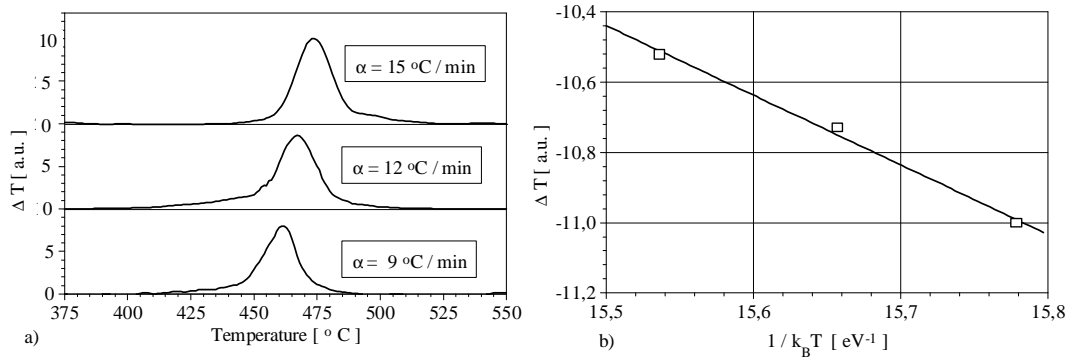


Fig. 1. DTA analysis of the crystallization process; a) DTA curves at $\alpha = 9\text{ }^{\circ}\text{C/min}$, $12\text{ }^{\circ}\text{C/min}$ and $15\text{ }^{\circ}\text{C/min}$, b) the corresponding Kissinger plot.

An isothermal method has been used, too, for the investigation of crystallization.

Assuming that the coercive force, H_c , represents a direct measure of the volume fraction of the crystallized phase [11,12], the kinetic process can be described by the dimensionless quantity:

$$X(t_a) = \frac{H_c(t_a) - H_c(0)}{H_c(\infty) - H_c(0)}$$

where $H_c(0)$, $H_c(t_a)$ and $H_c(\infty)$ correspond to the as-quenched (AQ), to the partially crystallized and, respectively, to the fully crystallized state. The evolution of X vs the cummulated annealing time t_a , is presented in figure 2a.

Assuming that $X(t_a)$ obeys a Johnson-Mehl-Avrami law:

$$X(t_a) = 1 - \exp(-(Kt_a)^n)$$

with: K – the reaction rate and n – the reaction order, a fitting procedure of the experimental data was performed. The Arrhenius temperature dependence of the reaction rate was used in order to estimate the effective activation energy (Fig. 2b).

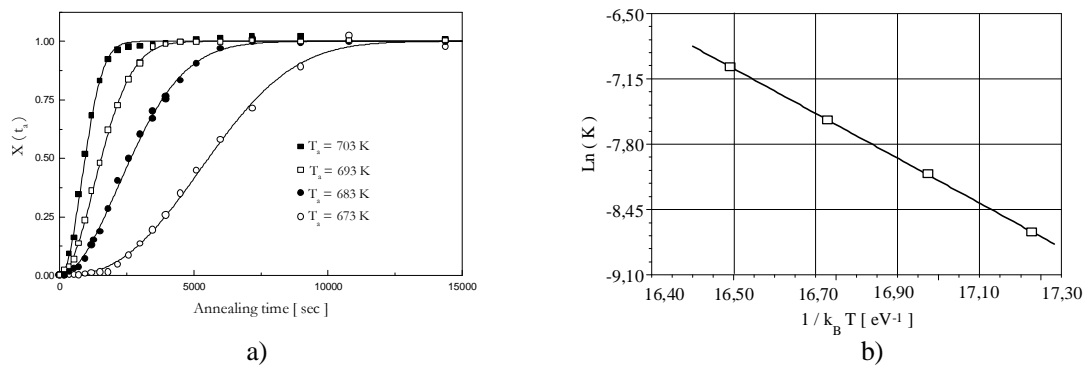


Fig. 2. Magnetic analysis of the crystallization process in amorphous $\text{Fe}_{75}\text{Cr}_5\text{B}_{20}$ alloy; a) - isothermal kinetics b) – the corresponding Arrhenius plot.

The results of the kinetic process analysis are presented in Table 1.

Table 1. Kinetics data on isothermally crystallized Fe₇₅Cr₅B₂₀ alloys.

T _a [K]	K [10 ⁻⁴ s ⁻¹]	K ₀ [s ⁻¹]	n	E _k [eV]
673	1.703		2.07	
683	3.041	7.97 10 ¹²	1.92	2.23±0.06
693	5.211		1.98	
703	8.778		2.01	

The crystallization process usually involves simultaneous nucleation and growth mechanisms. As the reaction order ranges from 1.92 to 2.07, the crystallization process can be attributed to nucleation with constant or decreasing nucleation rate and growth [13]. The estimated effective activation energy of crystallization process is E_k=2.23±0.06 eV.

Both RT and 80 K Mössbauer spectra were recorded using a constant acceleration spectrometer in transmission geometry with a ⁵⁷Co source in Rh matrix. Mössbauer spectrometry method has been, also, used in the characterization of the crystallized phases.

The RT Mössbauer spectra of isothermally crystallized samples have a complex structure showing many sextets with rather narrow lines (Fig. 3).

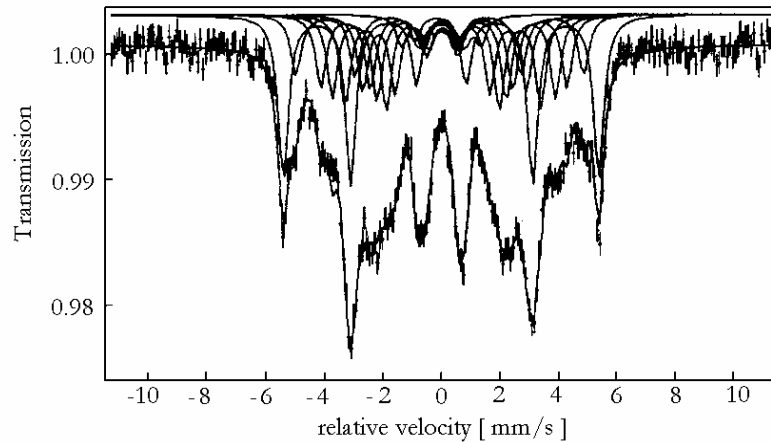


Fig. 3. Room temperature Mössbauer spectrum of crystallized (693 K, 14400 s) Fe₇₅Cr₅B₂₀ alloy.

They were fitted with an usual program for crystalline phases using Lorentzian lines; α-Fe (H_{hyp}=33.4T), α-Fe (Cr) (H_{hyp} =30.2T), (Fe, Cr)₂B (H_{hyp} =21T), (Fe, Cr)₃ (H_{hyp}=17.8T, 23.7T, 26.44T), and FeB (H_{hyp}=9.1T), crystalline phases were identified. XRD examination also revealed a low volume fraction of crystalline Cr₂B₅.

Comparable values of 1.98 eV (by DTA method) and 2.23 eV (by H_c method) were found for the effective activation energy of crystallization. The difference between the values of E_k can be attributed to the limited validity of the assumption that H_c is proportional to the volume fraction of the crystallized phase [12] and also to the specific DTA errors [14].

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