ISOTHERMAL CRYSTALLIZATION KINETICS IN $Fe_{73.1}Si_{15.5}B_{7.4}Nb_{3.0}Cu_{1.0}$ AMORPHOUS ALLOYS

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Abstract. The process of isothermal crystallization of $Fe_{73.1}Si_{15.5}B_{7.4}Nb_{3.0}Cu_{1.0}$ amorphous alloy at T=723K was studied by means of an X-ray diffraction method. The diffraction data were collected at various instants of the crystallization process, resulting in the time dependence of parameters determining the nanocrystaline structure (volume fraction, $X(t)$, mean size, $L(t)$ and concentration of nanocrystals, $N(t)$). The experimental data for analyzing the crystallization kinetics were employed using the Johnson- Mehl-Avrami approach.

1. INTRODUCTION

It is known that the crystallization process has been used for producing nanocrystals in amorphous matrices. This process significantly influences the main parameters of a nanocrystalline structure, viz. nanocrystal sizes, density and volume fraction in an alloy. Controlled changes of these parameters make it possible to improve the properties of nanocomposites which determine their application in many respects.

It should be noted that the formation of an α-Fe–based solution of a nanoscale size promotes significant improving of the magnetic characteristics in such alloys as FINEMET (Fe-Si-B-M-Cu) and NANOPERM (Fe-Co-B-M-Cu, M=Nb,Zr,Hf…) [1-3]. It has been shown [4,5] that an increase in the crystalline fraction volume is the reason for a significant increase in coercivity. The authors of [6-10] have concluded that α-Fe(Si)-based nanocrystals, randomly distributed in an Nb and B enriched residual amorphous matrix, are formed during the starting stage of crystallization in an Fe-Si-B-Nb-Cu amorphous alloy. It has been established by means of the small angle X-ray diffraction method and high resolution electron microscopy that Cu-nanoclusters, formed at the thermal treatment, promote the nucleation of a-Fe(Si) nanocrystals [11, 12].

No fundamental theory allowing the nanocomposite properties to be predicted on the basis of the alloy content and the thermodynamic and kinetic conditions of a crystallization process has been formulated to date. Thus, diffraction studies of the kinetics of isothermal crystallization of amorphous alloys are of large importance. In this work the structure changes in $Fe_{73.1}Si_{15.5}B_{7.4}Nb_{3.0}Cu_{1.0}$ amorphous alloy during isothermal crystallization at T=723K was studied using an X-ray diffraction method.

2. EXPERIMENTAL

An $Fe_{73.1}Si_{15.5}B_{7.4}Nb_{3.0}Cu_{1.0}$ amorphous alloy was prepared by pouring the melt onto the surface of a rotating cooper disk. The ribbons obtained in this way were 20 mm thick and 20 μm wide. The cooling rate was about 10^6 K/s. The chemical composition of the samples was checked by an X-ray fluorescence analysis. The diffraction data were obtained using a

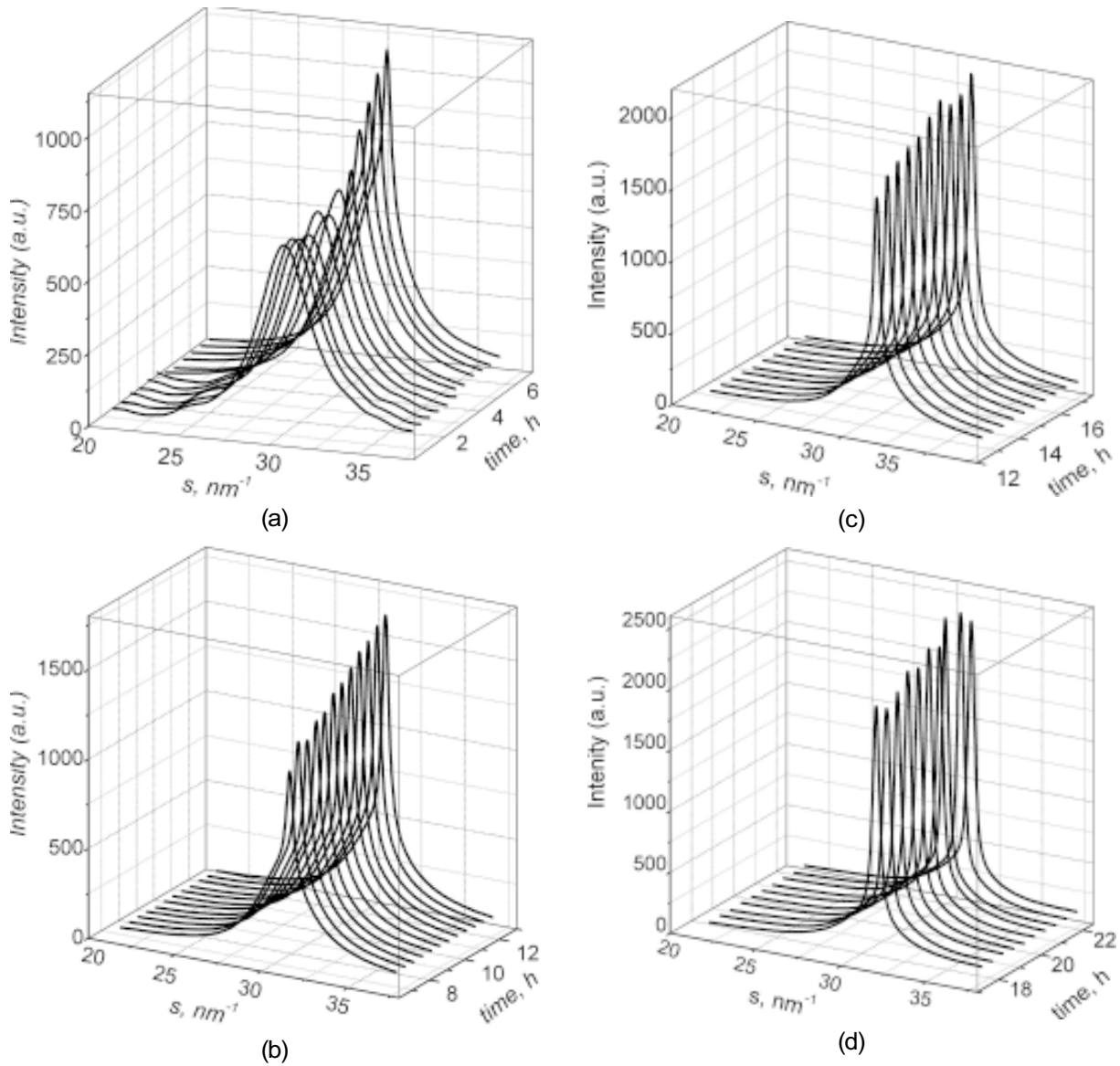Corresponding author: S.Mudry, e-mail: mudry@physics.wups.lviv

Fig. 1. Diffraction patterns of $Fe_{73.1}Si_{15.5}B_{7.4}Nb_{3.0}Cu_{1.0}$ amorphous alloys dependences on aging time at T=723K.

DRON-3 X-ray diffractometer with a high temperature camera attached. A LiF single crystal was installed in the primary beam in order to obtain Co K_a-radiation ($\lambda = 0.171$ nm). Scattered intensities were recorded by scanning with a small angular step (0.05°) within the $2\theta = 35$-65° range. The temperature of the sample was controlled with an accuracy of ±1K. The DHN_PDS software was used in order to carry out the experimental data processing. The crystalline phase volume fraction in an alloy was determined by separating the intensity curves into contributions corresponding to the scattering from the amorphous and crystalline phases: $X(t)=I_c/(I_a+I_c)$, where I_a, I_c were the integral intensities for

the crystalline and amorphous phases, respectively. The mean size of crystallites was calculated from the diffraction data by means of the Sherer formula: $L = 2\pi/\beta$, $\beta = (B - b + \sqrt{B(B-b)})/2$, where β- real half peak height width, B and b which were related to the half height width of the investigated sample and the etalon. Polycrystalline iron, annealed at $T = 973$K was chosen as the etalon.

3. RESULTS AND DISCUSSION

At first, the structure changes in an $Fe_{73.1}Si_{15.5}B_{7.4}Nb_{3.0}Cu_{1.0}$ amorphous alloy during isothermal crystallization at T=723K should be ana-
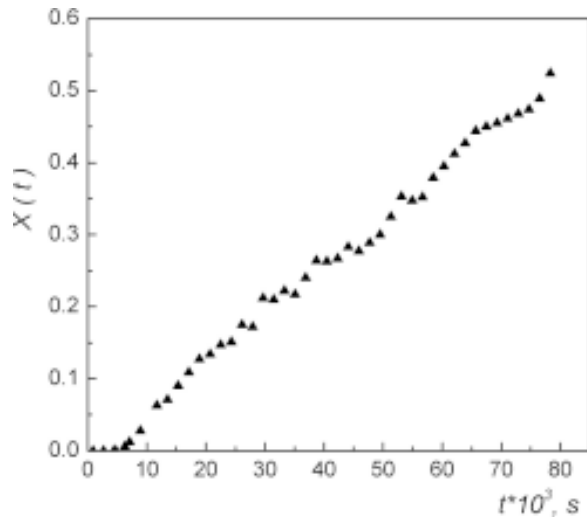
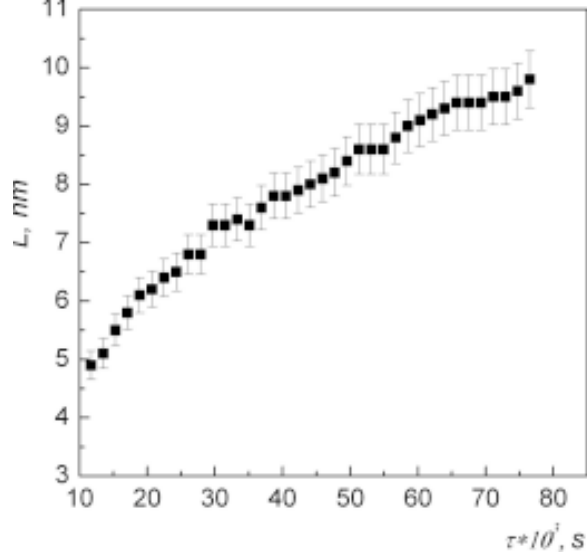**Fig. 2.** The time dependence of α-Fe(Si) nanocrystal volume fraction.

Fig. 3. The time dependence of α-Fe(Si) nanocrystal grain size.

Fig. 4. The volume fraction of α-Fe(Si) nanocrystals in double logarithmic coordinates.
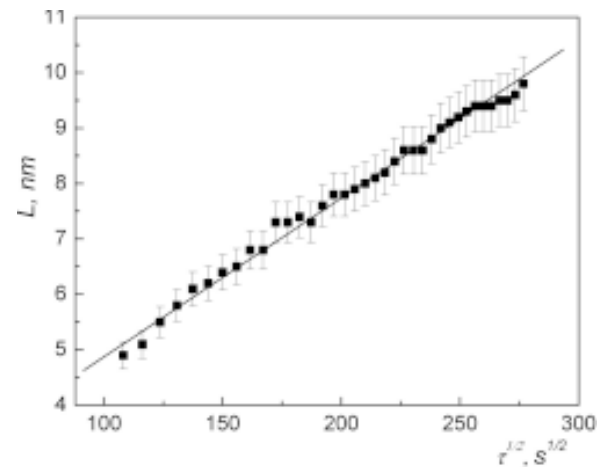
Fig. 5. The grain size α-Fe(Si) of nanocrystal dependences on $\sqrt{t}$.

lyzed (Figs. 1a-1d). As can be seen, significant changes occur in the scattered intensity upon annealing for t = 3.5 hours (Fig. 1a). The diffusive maximum becomes more asymmetric than is supposed to be caused by the formation of some amount of an α-Fe(Si) solution-based nanocrystalline phase of a DO$_3$ type structural ordering [6-8]. It is estimated that the mean size of nanocrystals at the starting stage of crystallization is about 5 nm and their volume fraction is 6%. Later, the intensity related to the crystalline phase increases as well as the size of nanocrystals, which equals 10 nm after 21 hours at fixed temperature (Figs. 2 and 3). It should be noted that the (110) maximum position for a-Fe(Si) is located at s_1 = 31.2 nm^{-1} and that in

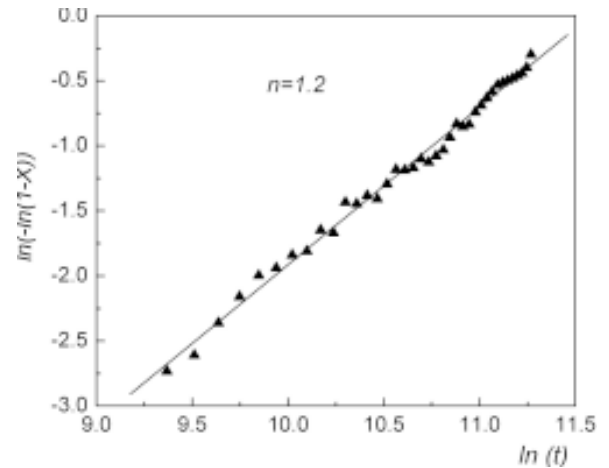fact it does not depend on the isothermal aging process duration. This is evidence that the chemical composition of a nanocrystalline phase during thermal treatment at this temperature is unchangeable. The first maximum position can be used to calculate the first neighbor distance r_1 according to the formula: $r_1 = (2\pi/s_1)\sqrt{3/2}$ (2p, which is commonly used for crystals of a volume centered cubic cell. It has been found that r_1 is equal to 0.245 nm for α-Fe(Si) nanocrystals. Comparing this value with the interatomic distances for pure α-Fe (r_1=0.248 nm) and stoichiometric Fe$_3$Si chemical compounds (r_1=0.244 nm) it is shown that the solubility of Si in initial α-Fe(Si) nanocrystals is about 23 at.%.

In order to study the phase transformations during isothermal annealing, the crystalline phase time dependence $X(t)$ volume was analysed by means of the Johnson-Mehl- Avrami formalism [13]:

$$X(t) = 1 - \exp\left(-\left(Kt\right)^n\right), \tag{1}$$

where n- the kinetic index, u- the crystal growth rate, I- the nucleation rate. Using a double logarithmic coordinates, Eq. (1) is transformed to:

$$\ln\left(-\ln\left(1-X\right)\right) = \ln K(T) + n\ln(t). \tag{2}$$

The time dependence of the nanocrystal volume fraction for the investigated sample is a linear function the slope of which corresponds to $n = 1.2$ (Fig. 4). At the same time, it is known from the published data [14] that at the initial crystallization which is characterized by both growth and nucleation mechanisms, the kinetic index is a sum of two partial indexes $n_G = 1.5$ and $n_N = 1$, corresponding to each of these mechanisms, respectively and equals $n = 2.5$. Taking into account the above data and the calculated value of the density of nanocrystals it can be supposed that the formation of a nanocrystalline structure in an amorphous matrix in our case is characterized by growth of α-Fe(Si) nanocrystals. In order to confirm this assumption the time dependence of a mean nanocrystal size was analysed. It is known that at the initial crystallization, controlled by volume diffusion, the change of the crystallite size with isothermal annealing duration can be determined according to the Zener equation [14]:

$$L(t) = \lambda\sqrt{D_v t}, \tag{3}$$

where λ- a parameter depending on the chemical composition of the nanocrystaline phase and the amorphous matrix, D_v – the effective diffusion coefficient value.

The dependence of $L(t)$ on $\sqrt{t}$ shows the linear dependence indicating the diffusive-controlled mechanism of nanocrystal formation over the whole isothermal aging period (Fig. 5). Assuming $\lambda \approx 1$ and using Eq. (3), the effective diffusion coefficient was calculated to be $D_v \approx 8*10^{-22}$ m²/s. Another parameter, nanocrystal density, was calculated according to the formula:

$$N(t) = \frac{6X(t)}{\pi L^3(t)}. \tag{4}$$

The error of this parameter estimation is related to that in determining the nanocrystal size, $\Delta N \approx (N\Delta L)/L$. The results of those calculations are shown in Fig. 6. As can be seen the nanocrystal density $N \approx 10^{24}$ m⁻³ is in fact unchangeable with the isother-
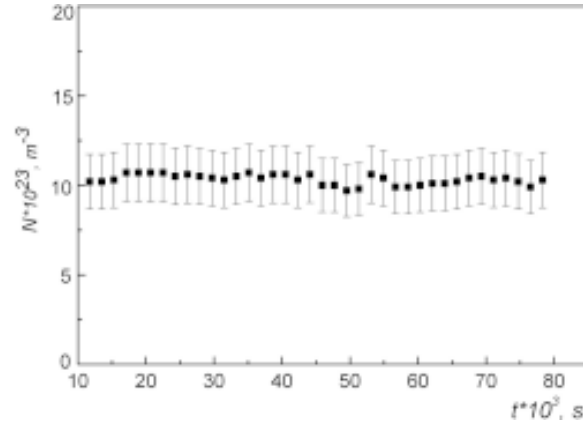

Fig. 6. The time dependence of α-Fe(Si) nanocrystal density.

mal aging duration. Thus, it can be stated that during isothermal crystallization of an $Fe_{73.1}Si_{15.5}B_{7.4}Nb_{3.0}Cu_{1.0}$ amorphous alloy at $T = 723K$ the diffusive-controlled mechanism of α-Fe(Si)-nanocrystal growth is the main factor, responsible for the increase in the crystalline phase volume fraction and the damping of further nucleation. These data confirm the conclusion of [15], where the structure evolution of an $Fe_{73.0}Si_{15.8}B_{7.2}Nb_{3.0}Cu_{1.0}$ amorphous alloy has been studied by means of a small angle X-ray diffraction method. The non-monotony behaviour of small angle intensity versus annealing temperature is considered by the authors of this work as evidence that the starting stages of a phase transformation are determined by the increasing nucleus number whereas it is the process of nanocrystal growth that is dominating at higher temperatures.

A decrease in the kinetic index ($n = 1.2$) in comparison with the typical value ($n_G = 1.5$) is characteristic for nanocrystallization of multicomponent amorphous alloys and it indicates the damping of nanocrystal growth processes. It may be that the formation of initial α-Fe(Si)- nanocrystals which causes the change of the chemical content of the residual amorphous matrix due to an increase in both the Nb and B atom content, is the reason for the kinetic index reduction. As the atomic radius R_{Nb} in that case is larger than R_{Fe} (R_{Nb}=1.50 Å, R_{Fe}=1.27 Å), the presence of Nb-atoms slows down the diffusion from the interface boundaries nanocrystal-amorphous phase and promotes the formation of diffusive shells, enriched with these components.

5. CONCLUSIONS

1. Isothermal crystallization of an Fe$_{73.1}$Si$_{15.5}$B$_{7.4}$Nb$_{3.0}$Cu$_{1.0}$ amorphous alloy is accompanied by formation of α-Fe(Si) nanocrystals randomly distributed in a residual amorphous matrix. The mean size of α-Fe(Si) nanocrystals at isothermal aging at T = 723K changes within a range of 5-10 nm, whereas the density of nanocrystals is about 10^{24} m^{-3}.

2. The growth of α-Fe(Si) nanocrystals at T = 723K reveals a diffusive-controlled mechanism and is characterized by a parabolic dependence of a nanocrystal size on the crystallization process duration. The growth process of these nanocrystals dominates at the formation of a total nanocrystalline structure of an Fe$_{73.1}$Si$_{15.5}$B$_{7.4}$Nb$_{3.0}$Cu$_{1.0}$ amorphous alloy. The formation of diffusive shells, enriched with Nb and B-atoms around the nanograins, is the most probable reason for the nanocrystal growth damping.

REFERENCES

[1] M. E. McHenry, M. A. Willard and D. E. // *Prog. in Mat. Sci.* **44** (1999) 291.

[2] Y. Q. Wu, T. Bitoh, K. Hono, A. Makino and A. Inoue // *Acta Mater.* **49** (2001) 4069.

[3] Y. Yoshizawa, S. Fujii, D. H. Ping, M. Ohnuma and K. Hono // *Scripta Mater.* **48** (2003) 863.

[4] J.S. Blazquez, V. Franco, C.F. Conde and A. Conde // *Journal of magnetism and Magnetic Materials* **254-255** (2003) 460.

[5] B Majumbar and D Akhtar // *Bull. Mater. Sci.* **28** (2005) 395.

[6] S. Mudry, Yu. Kulyk, A. Korolyshyn and Yu. Plevatchuk // *Rev.Adv.Mater.Sci.* **14** (2007) 41.

[7] N. Mattern, A. Danzig and M. Muller // *Mat. Sci. Eng. A* **194** (1995) 77.

[8] Won Tae Kim, Pyung Woo Jang and Seong Cho Yu // *Materials science & engineering* **179-180** (1994) 309.

[9] W. Z. Chen and P. L. Ryder // ***Mat. Sci. Eng.*** 34 (1995) 204.

[10] Pavol Sovák, Gabriel Pavlik, Vladimir Kolesar, Karel Saksl and Jan Fuzer // *Rev. Adv. Mater. Sci.* **18** (2008) 518.

[11] M. Ohnuma, K. Hono, S. Linderoth, J. S. Pendersen, Y. Yoshizawa and H. Onodera // *Acta mater.* **48** (2000) 4783.

[12] M. Ohnuma, K. Hono, H. Onodera, J. S. Pedersen and S. Linderoth // *Nanostruc. Mater.* **12** (1999) 693.

[13] W.A. Johnson and R.F. Mehl // *Transactions of the Metallurgical Society of AIME* **135** (1939) 416.

[14] J. Christian, *The Theory of Phase Transformation in Metals and Alloys.- Part 1, Equilibrum and general kinetic theory, 2nded.* (Pergamon Press, Oxford,1975).

[15] V.V. Maslov, V.K. Nosenko, L.E. Taranenko and A.P. Brovko // *The Physics of Metalls and Metallography* **91** (2001) 47.