

# TEMPERATURE DEPENDENCE OF STRUCTURE OF AMORPHOUS $\text{Fe}_{73.1}\text{Si}_{15.5}\text{B}_{7.4}\text{Nb}_3\text{Cu}_1$ ALLOY

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**Abstract.** The structure of amorphous  $\text{Fe}_{73.1}\text{Si}_{15.5}\text{B}_{7.4}\text{Nb}_3\text{Cu}_1$  alloy has been studied by means of X-ray diffraction at various temperatures. The atomic arrangement exhibited high stability within the 293K-678K temperature range. Diffraction data were used to calculate the crystalline grain size, found to be about 20 nm and increasing slightly with temperature.

## 1. INTRODUCTION

Amorphous alloys are well-known to have atomic arrangements sensitive to changes in temperature. Most of the structural data obtained by means of diffraction methods are available for room temperatures and are poor for higher ones. Therefore, structural studies at higher temperatures are of great importance both for fundamentals and for practical use connected with many interesting physical processes.

In recent years, there has been growing interest in studying multicomponent amorphous alloys possessing magnetic properties. Thermal treatment is commonly used in order to improve these properties. The heating of amorphous alloys is also used to obtain nanocrystalline structural units. The formation of this kind of structures significantly depends on crystallization kinetics. At first, Cu-atoms are commonly added in order to promote the nucleation process in the amorphous matrix. Then, inhibition of crystal growth process is required at nanocrystals' formation (cf. [1-3]). Elements with greater atomic diameters (Nb, Ta, Hf, W, etc.) can

be used as inhibitors of grain size increase. As has been demonstrated experimentally, niobium is the most effective of them in Fe-based amorphous alloys and the most commonly introduced into amorphous alloys.

A comparison of the XRD patterns of  $\text{Fe}_{77.5}\text{Si}_{15.5}\text{B}_7$  and  $\text{Fe}_{73.5}\text{Si}_{15.5}\text{B}_7\text{Cu}_1\text{Nb}_3$  amorphous alloys at varying annealing temperatures was carried out in [4]. It was shown that Cu atoms exist as clusters and promote a temperature increase in the region of coexisting crystalline  $\text{Fe}_3\text{Si}$  and amorphous matrix phases. Combined addition of Cu and Nb at a ratio of 1:3 was also noted to lead to broadening of lines in the diffraction patterns, indicating the small grain size of the  $\text{Fe}_3\text{Si}$  phase formed in this alloy.

The aim of the present work has been to study the structural change in the  $\text{Fe}_{73.1}\text{Si}_{15.5}\text{B}_{7.4}\text{Nb}_3\text{Cu}_1$  amorphous alloy with temperature, including the interval where nanocrystal formation occurs (see [4-7]). In recent years, amorphous alloys of the Fe-Si-B system doped with Cu and Nb have appeared to be the most attractive from the point of view of their magnetic properties.

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The effect of Cu and Nb on the crystallization of Fe-Si-B+Cu, Nb amorphous alloys was studied in [4,7-10]. For example, it was established in [4] that Cu atoms reduced the temperature of Fe<sub>3</sub>Si's primary formation and did not affect the nuclei density or the microstructure of Fe<sub>3</sub>Si crystallites. It was also shown that Nb was responsible for the increase in crystallite density and the formation of nanocrystalline Fe<sub>3</sub>Si, resulting from the diffusion barrier of Nb atoms. It was shown in these works that crystallization of such amorphous alloys significantly depends on their components' contents, influencing their main physical - especially magnetic - properties ones. It is therefore of importance to study the influence of compositional variation on the temperature dependence of the structure of Fe-Si-B-Cu-Nb amorphous alloys. It should be noted that above-mentioned papers dealt with annealed samples, while our studies were carried out at some temperatures only. This is important because the structure of annealed alloys is not always the same as that at above-room temperatures.

## 2. EXPERIMENTAL

Structural studies were carried out with the X-ray diffraction method. Diffraction patterns were obtained by means of a high-temperature diffractometer whose chamber was filled with pure helium in order to avoid sample oxidation. Co-K<sub>α</sub> radiation was used (λ=0.17902 nm), obtained by reflecting from a single LiF crystal. The penetration width for this radiation was calculated to be about ~7 nm (cf. [11]). Scattered intensities were recorded by an electronic system. The acquisition time was equal for various temperatures, what allowed us to conclude that this method was useful for studying structural changes in the bulk of a sample. Scattered intensities obtained at various angles of diffraction were corrected by polarization and absorption factors taking incoherent scattering into account [12]. The corrected intensity values were used in this procedure to calculate the structure factors (SF). The principal peak's position and height were the main parameters used in SF interpretation. Pair correlation functions (PCF) were calculated from SF's using the integral Fourier-transformation. The first peak position of this function was interpreted as the most probable interatomic distance,  $r_1$ . The accuracy of the obtained structure parameters was estimated according the following formulas:

$$\Delta s_i = s_i \operatorname{ctg} \theta \Delta \theta \quad \text{and} \quad \Delta r_i = \frac{r_i}{s_i} \Delta s_i. \quad (1)$$

The size of crystallites and its accuracy were determined as follows:

$$D = \frac{\lambda}{\beta \cos \theta}, \quad \beta = B - b, \quad \frac{\Delta D}{D} = \sqrt{\left(\frac{\Delta B}{B}\right)^2 + \left(\frac{\Delta b}{b}\right)^2 + (\operatorname{tg} \theta \cdot \Delta \theta)^2}, \quad (2)$$

where  $B$  and  $b$  were respectively the half-peak width for the investigated and referee samples. It was found that  $s_1$ ,  $s_2$  and  $r_1$ ,  $r_2$  were respectively determined with  $\pm 0.10 \text{ nm}^{-1}$  and  $0.001 \text{ nm}$  accuracy.

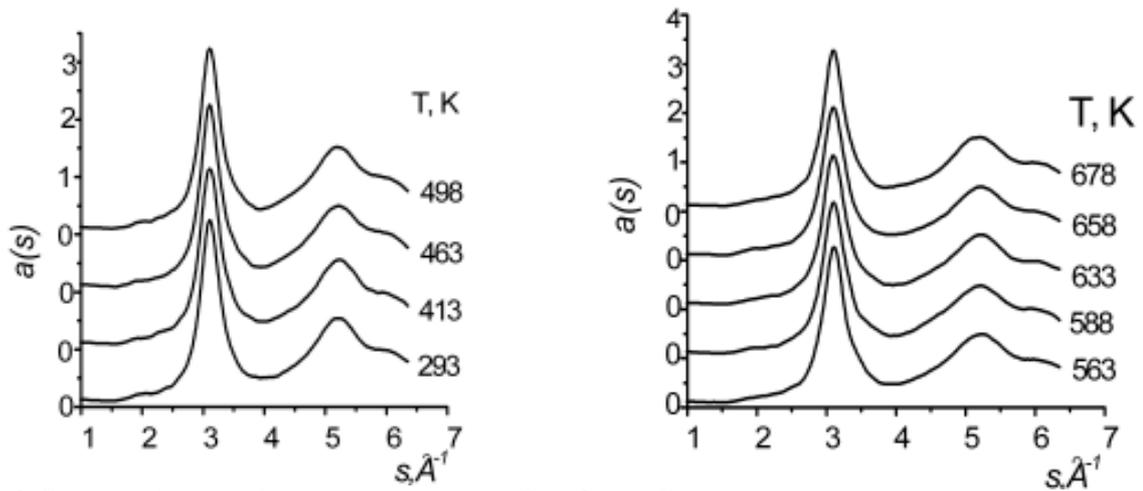
## 3. RESULTS AND DISCUSSION

The structure factors for the amorphous Fe<sub>73</sub>Si<sub>15.8</sub>B<sub>7.2</sub>Nb<sub>3</sub>Cu<sub>1</sub> alloy at various temperatures are presented in Fig. 1. The main features of SF are the existence of a small pre-peak before the principal maximum and the splitting of the second one. The pre-peak is more clearly visible in Fig. 2, where there is an  $\ln I(s)$  function instead of  $I(s)$ . The position of the principal maximum is close to the corresponding one of amorphous iron. Therefore, the influence of Fe-like topology on the atomic arrangement of the studied amorphous alloy can be assumed. The main features of SF observed at room temperature have also been exhibited at higher temperatures, which is evidence of high thermal stability of the alloy's structure.

Similar behavior has also been observed in the temperature dependence of the pair correlation function,  $g(r)$  (see Fig. 3). The main structural parameters obtained from SF and PCF are listed in Table 1. Most of them are almost independent of temperature within the  $T$  interval studied in this work. It should be noted that such structural parameters as second maxima positions,  $s_2$  and  $r_2$ , the second-to-first peak position ratio,  $s_2/s_1$  and  $r_2/r_1$ , and principal peak height,  $a(s_1)$ , are more sensitive to temperature for this alloy. The last structural parameter,  $c$ , is connected with the density of atomic packing and shows a small decrease with heating, most probably caused by topological disordering.

**Table 1.** Structural parameters of the amorphous  $\text{Fe}_{73.1}\text{Si}_{15.5}\text{B}_{7.4}\text{Nb}_3\text{Cu}_1$  alloy.  
 $s_1, s_2$ - positions of the first and second peaks of the structure factor  
 $r_1, r_2$ - the most probable distances  
 $a(s_1)$ - the structure factor principal peak height

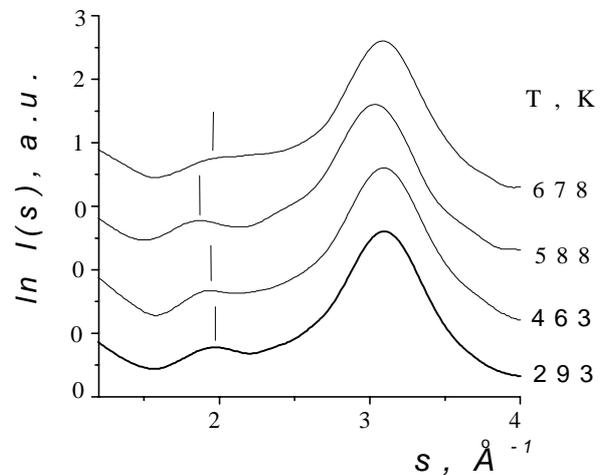
$T, \text{K}$	$s_1, \text{\AA}^{-1}$	$s_2, \text{\AA}^{-1}$	$a(s_1)$	$s_2/s_1$	$r_1, \text{\AA}$	$r_2, \text{\AA}$	$r_2/r_1$
293	3.10	5.17	3.285	1.668	2.60	4.16	1.600
413	3.10	5.24	3.161	1.690	2.60	4.13	1.588
463	3.11	5.24	3.292	1.685	2.60	4.23	1.627
508	3.10	5.18	3.267	1.671	2.60	4.17	1.604
563	3.10	5.23	3.301	1.687	2.60	4.17	1.604
588	3.10	5.18	3.219	1.671	2.60	4.23	1.627
633	3.11	5.22	3.160	1.684	2.60	4.17	1.604
658	3.10	5.24	3.132	1.685	2.60	4.20	1.615
678	3.10	5.23	3.296	1.687	2.60	4.18	1.608



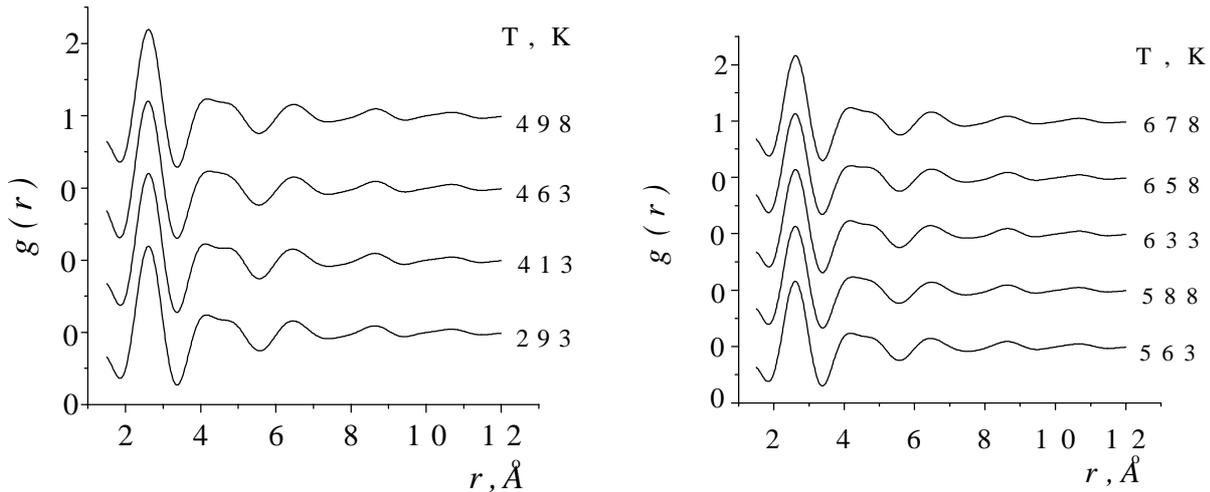
**Fig. 1.** Structure factors of the amorphous  $\text{Fe}_{73.1}\text{Si}_{15.5}\text{B}_{7.4}\text{Nb}_3\text{Cu}_1$  alloy at various temperatures.

We have also measured the half peak-height width, used to estimate the correlation radius. This characteristic feature of topologically disordered materials can be considered as the size of structural units. The value of correlation radius at room temperature has been found to be 15.3 Å. With heating, this parameter slightly increases and then decreases. The most significant increase is observed at the temperature of 678K (16.1 Å), possibly due to the amorphous alloy preparing for the crystallization process.

It should be also noted that the above-mentioned pre-peak in SF exists at all temperatures within the studied  $T$  interval, but it becomes broader at higher temperatures. The position of this peak



**Fig. 2.** Pre-peak profile change with temperature.

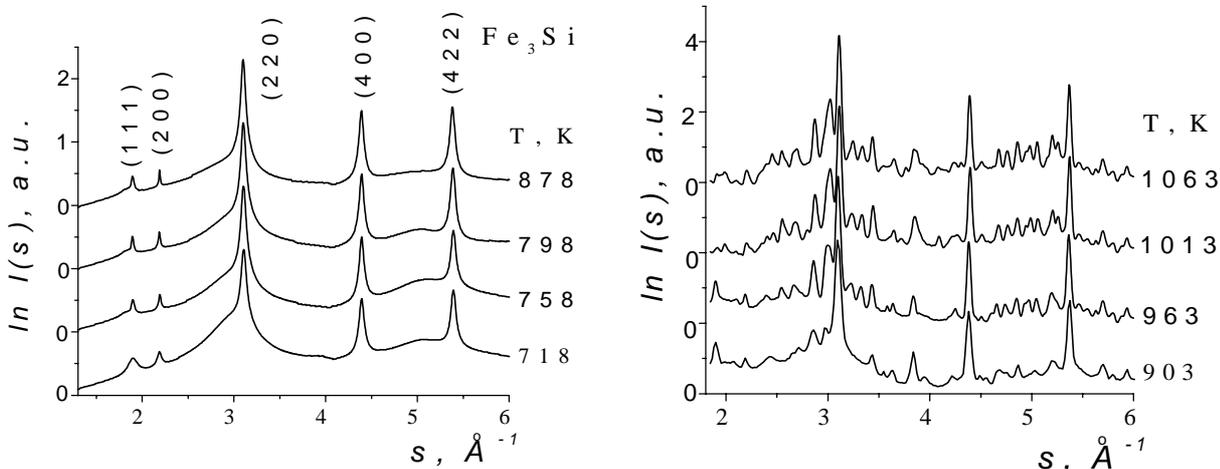


**Fig.3.** Pair correlation functions of the amorphous  $\text{Fe}_{73.1}\text{Si}_{15.5}\text{B}_{7.4}\text{Nb}_3\text{Cu}_1$  alloy at various temperatures.

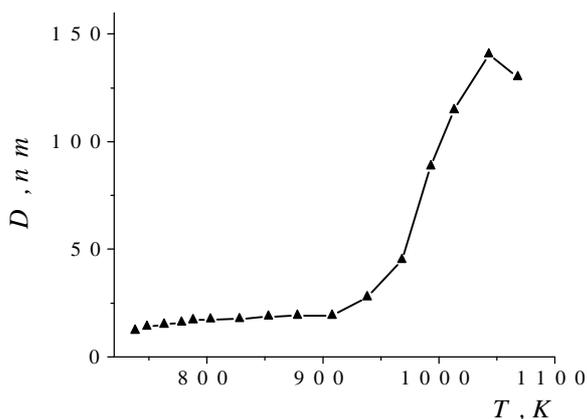
was found by resolution of the principal maximum with a computer method; its value equals  $1.90 \text{ \AA}^{-1}$  at 293K and slightly decreases with heating. Similar maxima were observed in other amorphous and liquid alloys and they were attributed to the intermediate range order [13]. We shall later compare it with peak positions for crystalline iron silicides.

Diffraction patterns at higher temperatures are shown in Fig. 4. There are significant changes in maxima profiles, which become very narrow with increasing temperature. Comparing the prepeak's position ( $\sim 1.96 \text{ \AA}^{-1}$ ) with diffraction patterns for the various phases that may exist upon crystallization,

peak positions for the  $\text{Fe}_3\text{Si}$  compound ( $s_{(111)}=1.90 \text{ \AA}^{-1}$ ,  $s_{(200)}=2.25 \text{ \AA}^{-1}$ ) were found to be in accordance (Fig. 4). Peak positions for other chemical compounds were distanced from the  $19.6 \text{ nm}^{-1}$  value. All these findings allowed us to suggest that the amorphous alloy is characterized by the existence of a hetero-coordinated structure formed by Fe and Si atoms, in which other atoms are distributed. We also suggest that the size of such chemically ordered microgroups slightly exceeds the nearest-neighbour distances. The dependence of crystalline grain size on temperature is shown in Fig. 5. As has been noted above, this parameter was de-



**Fig. 4.** X-ray diffraction patterns of the amorphous  $\text{Fe}_{73.1}\text{Si}_{15.5}\text{B}_{7.4}\text{Nb}_3\text{Cu}_1$  alloy at higher temperatures.



**Fig. 5.** Temperature dependence of grain size for the  $Fe_3Si$ -phase.

terminated by measuring the half-height width of SF's principal peak. The grain size is apparently invariant in a wide temperature range. It is less than 25 nm and increases rapidly when the temperature exceeds 903K. At these temperatures, the grains' tendency to grow cannot be inhibited by Nb atoms and the structural unit size rapidly increases as a result. The sudden lack of inhibiting ability is likely to be caused by two factors:

- Nb atoms are no longer a barrier for other atoms' diffusion due to increased atomic motion and
- with increasing crystallite size, the tendency to cooperate becomes dominant in the structure formation process.

Thus, the addition of Nb atoms to this amorphous alloy inhibits the crystallization process and there is no increase in crystalline grain size in a wide temperature interval. A similar behavior is likely to be observed in other Fe-based amorphous alloys.

#### 4. CONCLUSION

The structure of amorphous  $Fe_{73.1}Si_{15.5}B_{7.4}Nb_3Cu_1$  alloy is thermally stable within the 293-678K tem-

perature range due to the presence of Nb atoms which inhibit the crystallization process with heating. The hetero-coordinated distribution of Fe and Si atoms determines the features of total atomic distribution in the alloy. The size of  $Fe_3Si$  crystalline formations in the amorphous matrix is about 20 nm in a wide temperature range and rapidly increases at higher temperatures.

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