Structure changes in Fe$_{73.1}$Si$_{15.5}$B$_{7.4}$Nb$_{3.0}$Cu$_{1.0}$ amorphous alloy with temperature

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Abstract. Structure of Fe$_{73.1}$Si$_{15.5}$B$_{7.4}$Nb$_{3.0}$Cu$_{1.0}$ amorphous alloy has been studied within 293–748K temperature range by means of high temperature X–ray diffraction method. Main structure parameters have been calculated from experimental data and then analysed. It was found a prepeak occurrence before principal maximum. Formation of nanocrystals with Fe$_3$Si like chemical short range order in amorphous matrix, is suggested to be responsible for that prepeak. It is shown also that heating of alloy is accompanied by increasing of inhomogeneities in short range order structure.

1. Introduction
It is well known that amorphous alloys, having a short range order structure in atomic arrangement, posses by some temperature interval where this structure persists with heating. It is of interest to study the structure behavior within this temperature range and upon phase transition from amorphous state to crystalline one. To present time the information on high temperature structure studies of amorphous alloys is scarce. Most of works consider quenched alloys, before annealed at different temperatures. It is clear that quenched alloys have a somewhat another structure than same alloys at elevated temperatures. The temperatures changes of structure are especially important for such amorphous alloys, in whose matrix growing nanocrystals are distributed [1-4]. Typical material, representing this group of alloys is Fe$_{73.1}$Si$_{15.5}$B$_{7.4}$Nb$_{3.0}$Cu$_{1.0}$ amorphous alloy whose structure at different temperatures has been studied in this work.

2. Experimental
Amorphous ribbons Fe$_{73.1}$Si$_{15.5}$B$_{7.4}$Nb$_{3.0}$Cu$_{1.0}$ of 30μm thickness were prepared by means of rapid quenching of molten alloy. Composition of samples was checked with using of X–ray microanalysis. X–ray diffractometer DRON–3, equipped with high temperature vacuum camera was used for diffraction studies. LiF single crystal, installed into initial beam allowed us to obtain monochromatized Co Kα– radiation. Diffraction patterns were recorded at isothermal conditions within temperature range 293-823 K. Upon accounting the corrections for absorption and polarization, the intensity curves $I(\theta)$ ($s = \frac{4\pi}{\lambda} \sin \theta$, $2\theta$- scattering angle; $\lambda$- wave length) were analyzed and used for calculation of structure factors and pair correlation functions, from which the main structure parameters have been directly obtained.
3. Results and discussion

Intensity curves for Fe$_{73.1}$Si$_{15.5}$B$_{7.4}$Nb$_{3.0}$Cu$_{1.0}$ alloy both in amorphous and amorphous–
crystalline state are shown in Fig.1. The main structure parameters, obtained from these functions are
listed in table 1. As is seen, such the parameters as principal peak position ($s_o$) and most probable
distance to nearest neighbors ($R$) are slightly changeable with temperature. At the same time the non-
monotonic temperature change of structure factor principal peak height $a(s_o)$ occurs. Namely, this
parameter shows the tendency to increasing within temperature range 293-563 K that is suggested to
be caused by local atomic ordering. On other hand, the topologic disordering of structure with
temperature is accompanied by decrease of $a(s_o)$, whereas at heating to pre-crystallization
temperatures this parameter increases up to 4,08, that is typical for pre-crystallization processes at
topologic and chemical ordering.

The important feature of intensity curves is the occurrence of prepeak, whose position changes
from. 18.5 up to 19.5 nm$^{-1}$ within temperature range, where amorphous phase is stable Appearance of
new maxima in diffractograms at $T=718$ K and corresponding to crystalline phase, indicates the
formation of nanocrystals in amorphous matrix on the base of $\alpha$-Fe(Si) solid solution, with DO$_3$
(Fm3m) ordering for Fe$_3$Si–phase. As follows from obtained experimental data, the range of thermal
stability for nanocrystalline structure is from 728 up to 823 K, (Fig.1).

It should be noted that positions of (110) and (200) superstructure reflexes in diffraction
patterns of partially crystallized samples are close to prepeak position in intensity curve for amorphous
phase (Fig.2b). It is known [5-9] that prepeak appearance is an evidence of correlation in atomic
distribution of medium scale due to formation of intermetallic–based nanoclusters. The correlation
interatomic distance $R_p$, can be calculated with using of Erenfest formula $s_p R_p = 7.73$ ($s_p$– prepeak
position). Experimental data, obtained here, allowed us to point out that within 293-653 K, temperature range the correlation distance varies within interval $R_p \approx 4.0-4.2$ Å. Analysis of crystalline
structure for Fe$_3$Si chemical compound shown that obtained values of $R_p$ are the same as interatomic
distances $R(\text{Si-Si})=4.01$ Å and $R(\text{Fe-Fe})=4.01$ Å in second coordination sphere. Therefore appearance
of prepeak in intensity curves for Fe$_{73.1}$Si$_{15.5}$B$_{7.4}$Nb$_{3.0}$Cu$_{1.0}$ amorphous alloy is caused by correlation of
Fe-Fe and Si-Si atomic pairs at distances ~4 Å and confirms the formation of nanoclusters with Fe$_3$Si
like chemical ordering. The size of such nanoclusters, determined from prepeak half-width, was found to be ~1-2 nm.

Table 1. Structure parameters of Fe$_{73.1}$Si$_{15.5}$B$_{7.4}$Nb$_{3.0}$Cu$_{1.0}$ amorphous alloy at different temperatures.

| $T$, K | $s_o$, nm$^{-1}$ | $s_c$, nm$^{-1}$ | $\Delta s/s_o$ | $a(s_o)$ | $r_\parallel$, nm |
|-------|-----------------|-----------------|----------------|----------|-----------------|
| 293   | 31.10           | 30.50           | 0.020          | 3.50     | 0.261           |
| 413   | 31.10           | 30.45           | 0.021          | 3.42     | 0.261           |
| 463   | 31.05           | 30.50           | 0.018          | 3.67     | 0.260           |
| 503   | 31.05           | 30.40           | 0.021          | 3.58     | 0.261           |
| 563   | 31.00           | 30.50           | 0.016          | 3.68     | 0.261           |
| 583   | 31.00           | 30.30           | 0.022          | 3.54     | 0.261           |
| 633   | 31.00           | 29.90           | 0.035          | 3.36     | 0.261           |
| 653   | 31.00           | 30.00           | 0.030          | 3.32     | 0.260           |
| 678   | 31.05           | 29.90           | 0.037          | 3.59     | 0.262           |
| 698   | 31.05           | 29.85           | 0.038          | 4.08     | 0.263           |

In order to determine the temperature change of structure inhomogeneities in amorphous alloy under investigation we have analyzed the angular distribution of scattered intensity in the region of principal maximum. For that purpose, along with determination of peak position as top point ($s_o$), the centroid of maximum was determined too according to formula:

$$S_c = \frac{\int_{s_1}^{s_2} I(s) ds}{(S_2 - S_1)}$$

where $(s_1,s_2)$- limits of integral ($s_1=9.8$ nm$^{-1}$, $s_2=45.0$ nm$^{-1}$), $I(s)$- scattered intensity distribution. Difference between both values (table 1) is evidence of asymmetric profile of principal diffraction maximum. Most probably that inhomogeneous short range order structure with Fe$_3$Si clusters is just the main reason of such scattered intensity distribution. One might could consider that $D_s = S_o - S_c$ parameter is the measure of inhomogeneity in structure of amorphous alloy.
Temperature dependence of such parameter reveals two individual regions of its change (Fig. 2). This parameter is in fact unchangeable within temperature range (293-583 K), whereas it increases significantly within pre-crystallization interval of temperatures (633-698 K). We suggest that increase of inhomogeneity is caused by increasing both of size and number of $\text{Fe}_3\text{Si}$ nanoclusters resulting the $\text{Nb}$-atoms enrichment of amorphous matrix. Shift of centroid diffraction maximum ($s_c$) to low $s$-values confirms such behavior. This conclusion is in agreement with results, obtained in [8], where the significant structure changes in $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_{9.0}\text{Nb}_{3.0}\text{Cu}_{1.0}$, amorphous alloy, annealed at $T=623-673$ K were revealed by means of small angle X-ray diffraction. The increasing of inhomogeneous regions of electron density fraction in amorphous alloy at low temperature annealing was suggested.

4. Conclusions
1. It is shown that prepeak in intensity curve of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_{9.0}\text{Nb}_{3.0}\text{Cu}_{1.0}$, amorphous alloy is related with correlation in distribution of Si-Si and Fe-Fe atomic pairs in $\text{Fe}_3\text{Si}$ like clusters.
2. Increase of inhomogeneity fraction in short range order structure at near crystallization temperatures is supposed to be caused by increasing both of size and number of $\text{Fe}_3\text{Si}$ clusters as well as Nb-atoms enrichment of amorphous matrix.
3. At initial crystallization the formation of nanocrystals on the base of $\alpha$-Fe(Si) ordered solid solution occurs. The structure of such nanocrystals is unchangeable within 713-823 K temperature range.

References
[1] Hono K, Ping D H, Ohnuma M and Onodera H 1999 Cu clustering and Si partitioning in the early crystallization stage of an $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_{9.0}\text{Nb}_{3.0}\text{Cu}_{1.0}$ amorphous alloys. Acta Mater. 47, 997-1006.
[2] Chen W Z and Ryder P L 1995. X-ray and differential scanning calorimetry study of the crystallization of amorphous $\text{Fe}_{73.5}\text{Cu}_{3}\text{Ni}_{3}\text{Nb}_{1.0}$ alloy. Mat. Sci. Eng. 34 204-209.
[3] Mudry S, Bednarska L, Kulyk Yu, Kovbuz AND M, Herstyk O. 2004 Temperatures changes of structure in $\text{Al}_{87}\text{Ni}_{8}\text{Y}_{5}$ amorphous alloy. Archives of Materials Science 25 373-379.
[4] Mattern N, Danzig A and Muller M 1995 Effect of Cu and Nb on crystallization and magnetic properties of amorphous $\text{Fe}_{77.5}\text{Si}_{15.5}\text{B}_{7}$ alloys. Mat. Sci. Eng. 194 77-85.
[5] Ruppersberg H, Lee D and Wagner C N J 1980 Observation of chemical short range order in an amorphous Ni$_{40}$Ti$_{60}$ alloy. J. Phys. F: Metal Phys. 10 1645-52.
[6] Sakata M, Cowlam N and Davies H A 1981 Chemical short-range order in liquid and amorphous Cu$_{65}$Ti$_{34}$ alloys. J. Phys. F: Metal Phys. 11 157-162.
[7] Jergel M and Mražko P 1984. The temperature dependence of the prepeak in the diffraction pattern of the amorphous $\text{Ti}_{60}\text{Cu}_{16}\text{Ni}_{23}$ and $\text{Ti}_{62.5}\text{Cu}_{12}\text{Ni}_{25}\text{Si}_{2.5}$ alloys. Phys. Stat. Sol. 83A 113-121.
[8] Xu. R, Verkerk P, Howell W S at al. 1993 Nanometre superstructure in liquid alkali-thallium alloys J. Phys.:Condens. Mater 5 50 9254-9260.
[9] Zhang Lin, Wu Youshi, Bian Xinfang at al. Origin of the prepeak in the structure factors of liquid and amorphous Al-Fe-Ce alloys J.Phys.: Condens. Mater 11 50 7959-69
[10] Maslov V V, Il’inski A G, Nosenko V K, Brovko A P and Evlash I K 2000 Roentgenografic study of structural transformation in a thermotreated amorphous Finemet-type alloys. Metallofizika i novelishie tekhnologii 22 3 43-55.