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INFLUENCE OF ATOMIC SUBSTITUTION ON SHORT RANGE ORDER IN AMORPHOUS Fe$_{84}$B$_{16-x}$C$_x$ ALLOYS

J. Balogh, I. Dèssz, B. Fogarassy, L. Gránássy, D.L. Nagy, I. Vincze$^+$ and S. Arajs$^-$

Central Research Institute for Physics, Budapest, Hungary.

Solid State Physics Laboratory, Materials Sciences Center, University of Groningen, Groningen, The Netherlands.

Physics Department, Clarkson College, Potsdam, New York, U.S.A.

There is a considerable interest /1,2,3,4/ at present in the amorphous Fe-B-C alloys because of their relatively high room temperature saturation induction which makes the use of these alloys in power devices more attractive. This improvement in the magnetic properties has been achieved through the temperature dependence of magnetization which decreases slower in the Fe-B-C than in Fe-B glasses /2/. Another unusual effect of the carbon addition is the decrease of the thermal stability of these glasses /3/ contrary to the "confusion principle" according to which the stability of glasses is expected to increase with increased number of alloying elements. The study of the short-range order of these glasses can give important information to our understanding of their interesting and useful physical properties.

In this paper we report the preliminary results of Mössbauer and calorimetric (DSC) measurements on rapid quenched Fe$_{84}$B$_{16-x}$C$_x$ (0 $\leq$ x $\leq$ 10) alloys. The Mössbauer data were evaluated with the method of Ref. 5. The crystallization process was followed by differential scanning calorimetry and the crystalline samples were obtained by appropriate heat treatments in the calorimeter.

The crystallization takes place in two steps for x = 6, 8 and 10 similarly to the case of pure Fe$_{84}$B$_{16}$/6/. According to the Mössbauer measurements the first step is a precipitation of α-Fe and a shift in the composition of the remaining glass to the 25 at.% metalloid concentration. There is no substitutional or interstitial boron or carbon in the precipitated α-Fe on the base of the Mössbauer data (i.e. their amount is certainly less than 0.5%). In the second step this remaining glass transforms into crystalline Fe$_3$(B$_{1-y}$C$_y$) intermetallic compound.

$^+$On leave from the Central Research Institute for Physics, Budapest, Hungary.

![Fig. 1: Typical room temperature Mössbauer spectra of Fe$_{84}$B$_{16-x}$C$_x$ after different annealings: a) Fe$_{84}$B$_{16}$: after the first step of crystallization. The spectrum consists of α-Fe and am. Fe$_7$B$_{25}$. b) Fe$_{84}$B$_{16}$: after the second step of crystallization. The spectrum consists of α-Fe and cr. Fe$_3$B with the tetragonal structure. c) Fe$_{84}$B$_{14}$C$_2$: after the second crystallization peak. The spectrum consists of α-Fe, am. Fe$_7$(B$_{0.875}$C$_{0.125}$)$_{25}$ and a few percent of cr. Fe$_7$(B$_{0.875}$C$_{0.125}$)$_{25}$. d) Fe$_{84}$B$_{14}$C$_2$: after the third crystallization peak. The spectrum consists of α-Fe cr. Fe$_7$(B$_{0.875}$C$_{0.125}$)$_{25}$ with the orthorhombic structure.](image-url)
Fig. 2: Concentration dependence of the average iron hyperfine field.

Inequivalent iron sites which are coordinated by 2 and 3 C nearest neighbours, the relative occupation of these sites is $1:2$ [8]. The Mössbauer spectra of this two crystal structures are quite different as it can be seen in Fig. 1b and 1d. The spectra identified as boron substituted cementite were similar to those presented by Bernas et al. [9]. Electron diffraction measurements [10] supported the Mössbauer identifications of the crystalline phases.

For Fe$_{84}$B$_{14}$C$_{12}$ and Fe$_{84}$B$_{12}$C$_{4}$ three peaks appeared in the DSC curve, the new peak was between the peak corresponding to the $\alpha$-Fe precipitation and the final crystallization peak of the 25 at.% glass. This feature is not well understood at present but serious inhomogeneities in the samples can explain it. The presence of such inhomogeneities seems to be supported by in situ electronmicroscopic measurements [10] where some tetragonal Fe$_3$B was detected in the crystallization process.

The concentration dependence of the average iron hyperfine field is shown in Fig. 2. There is a slight increase in the hyperfine field at room temperature with increasing carbon content in agreement with average magnetization measurements [2,3]. The liquid nitrogen temperature values are nearly constant, thus the increasing carbon concentration results in a less flat reduced magnetization curve as it was shown by Hatta and Egami [2] from magnetic measurements (the Curie temperature: does increase dramatically).

The short-range order of the Fe$_{75}$B$_{25}$ glass was well approximated [11] with that of the metastable tetragonal Fe$_3$B compound which played a dominant role in the crystallization of Fe$_{1-x}$B$_x$ glasses (here tetragonal refers for the local neighbourhoods and not for the long-range symmetry of the structure). If we extrapolate these results for the Fe(BC) system we had to assume that the chemical short-range order of these glasses is orthorhombic, cementite like (again we refer for the local neighbourhoods).

That is the sudden changes in the physical properties of the Fe-B glasses for the carbon substitution are caused not only by chemical effect but an induced change in the short-range order of these glasses. Recent EDXD measurement of Egami [4] shows an indication of this supposed change in the atomic short-range order. The measured difference in the radial distribution function of Fe$_{85}$B$_{15}$ and Fe$_{85}$B$_{25}$ is characteristic for a supposed change from tetragonal to orthorhombic in the local order, namely the intensity of the second peak has decreased while that of the third peak has increased resulting in a tendency of reversing the intensity ratio of the "second splitted peak" [12]. The supposed change in the short-range order for carbon substitution should be reflected in the iron hyperfine field distribution. At the 25 at.% stoichiometric composition a narrowing of p(H) is expected due to the sharper distribution of local configurations in the orthorhombic than in the tetragonal structure. This narrowing of p(H) is absent at 16 at.% metalloid composition which is not surprising since the off-stoichiometry of these glasses will considerably broaden the distribution.

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References