The effect of melt temperature on the crystallization process of the rapidly quenched Fe$_{74}$B$_{16}$Si$_9$Ni$_1$ alloy

V I Lad’yanov, V V Muhgalin and M A Eremina

Physical-Technical Institute, Ural Branch of Russian Academy of Science, 132 Kirov Street, Izhevsk, 426000, Russia

E-mail: las@fti.udm.ru

Abstract. The crystallization process of amorphous Fe$_{74}$B$_{16}$Si$_9$Ni$_1$ was studied by means of X-ray diffraction, differential scanning calorimetry and resistivity measurements. It was found experimentally, that superheating the melt above liquidus results in a lowering of activation energy for crystallization and in a modification of the crystallization mechanism. On the first crystallization stage some orthorhombic Fe$_3$B formed additionally to Fe$_3$B (tetr) and bcc solid solution of silicon in iron. Second stage realized mainly by the formation of metastable Fe$_3$B (tetr) and \( \alpha \)-Fe(Si) instead of Fe$_2$B (tetr) and \( \alpha \)-Fe(Si). The observed changes in the crystallization behavior have been proposed as being linked with the structural transformation in the initial liquid alloy at 1400°C and structural inheritance during its rapid quenching.

1. Introduction

As materials with unusual physical properties, amorphous alloys based on Fe-B-Si system were studied extensively for a long time. For the recent years interest is supported by the possibility of operated nanocrystallization, which leads to additional improvement in mechanical and magnetic properties. At the same time, as it was shown in [1,2,3], nanocrystallization process is affected by the structure of amorphous alloys in as-quenched state as well as by their composition. It is known that amorphous alloy structure and process of their crystallization depend strongly on the structural state of initial melt and casting parameters [4,5]. Besides, the homogenization, i.e. thermally activated structural transformations in the short-range order can occur in the melts at heating [6,7,8]. These transformations are accompanied by changes in melt properties sensitive to its structure, such as viscosity and surface tension. Thus, investigation of effects of an initial melt superheating above liquidus before its quenching on the crystallization behavior of amorphous Fe$_{74}$B$_{16}$Si$_9$Ni$_1$ is physically attractive.

2. Experimental procedures

The Fe$_{74}$B$_{16}$Si$_9$Ni$_1$ glassy ribbons 5mm wide and 25\( \mu \)m thick were prepared by the planar-flow casting method after different heat treatments of the melt: the melt was initially heated up to the temperatures (\( T_L \)) of 1300 to 1600°C; then, after isothermal holding during 20 minutes, the temperature was decreased down to 1300°C and the melt was quenched.

Chemical analysis was performed using inductively coupled plasma spectroscopy. Differential scanning calorimetry (DSC) under argon stream was used to characterize the crystallization process and to determine suitable temperatures for the heat treatment. Electrical resistivity was measured by
the four-probe method in argon atmosphere at a heating rate of 20°C/min. The standard deviation of resistance was ±0.02%.

The samples for X-ray analysis were annealed in vacuum furnace in argon atmosphere. X-ray diffraction spectra were recorded using CuKα radiation and a graphite monochromation in the diffracted beam. The temperature dependence of viscosity of the alloy in liquid state was measured using an oscillating cup viscometer. Shvidkovskii’s equation [9] was applied to viscosity calculation from the measured damping data.

3. Results

Dynamic DSC curves for the samples prepared after different heat-treatment of the melt before its quenching presented in the Figure 1. Two overlapping exothermic reactions related to the different amorphous to crystalline transformations and small sharp endothermic peak due to ferromagnetic transition at the lower temperatures were observed.

![Figure 1. Dynamic DSC scans at 20°C/min of the samples prepared with the different melt superheat temperatures T_L before the quenching. In the upper-left corner: endothermic peak related to ferromagnetic transition.](image)

Both the Curie temperatures (T_c) and the temperatures at which crystallization starts (T_ons) were identical for all the specimens within the estimation error (Table 1). The enthalpies of the first and the second reactions ΔH_1 and ΔH_2 derived from the areas of the DSC peaks are 57 J g⁻¹ and 24 J g⁻¹ respectively for the ribbon prepared from the melt at 1300°C. At the same time the total enthalpy of transformation ΔH tends to decrease after the melt heating up to the temperatures above 1400°C before the quenching: ΔH_2 decreases at the expense of ΔH_1 with increasing T_L.

| Melt superheat T_L (°C) | 1300 | 1350 | 1400 | 1450 | 1500 | 1550 | 1600 |
|-------------------------|------|------|------|------|------|------|------|
| T_ons (°C)              | 548.5 ± 0.5 |
| T_curie (°C)            | 443.5 ± 0.5 |
| ΔH_1 (J g⁻¹)          | 57 | 57 | 57 | 57 | - | 63 | 61 |
| ΔH_2 (J g⁻¹)          | 24 | 26 | 18 | 19 | - | 14 | 14 |
| ΔH (J g⁻¹)            | 81 | 83 | 75 | 76 | - | 77 | 75 |
| E_a (J mol⁻¹)         | - | 555±10 | - | - | - | 473±10 | - |

*Estimation error ±2 J g⁻¹, separation of the peaks by a least square fitting of two Gaussian functions.
A series of isothermal DSC experiments were carried out on the as-quenched ribbons for the crystallization kinetics study. It was found that Johnson-Mellon-Avrami (JMA) activation energy for crystallization ($E_a$) and incubation period decreases with the melt superheat temperature $T_L$ increase: $E_a = 555 \text{ kJ/mol}$ for $1350^\circ C$, while $E_a = 473 \text{ kJ/mol}$ for $1550^\circ C$.

Additionally to the DSC the resistivity measurements were used for the dynamic study of the transformation during heating. Figure 2 shows the relative resistivity temperature dependence of the ribbons. Relative resistivity almost linearly increases up to $548^\circ C$ and then turns to decrease. The reduction in resistivity at this temperature comes from crystallization. But for all that, two stages of transformation observed on the DSC curves merged into one. This peculiarity is concerned with the second crystallization stage which starts at the temperatures near the maximum of the first stage. At the temperatures of $610$-$640^\circ C$ there is an additional reduction in resistivity, which indicative of significant structural transformations.

The percentage of the resistivity reduction at the first and the second stages $D_1+D_2$ as well as the third stage $D_3$ were estimated. Figure 3 illustrates the melt superheat $T_L$ dependence of the $D_1+D_2$ and $D_3$ values, which are not constant as can be seen. $D_1+D_2$ decreases steeply at $1400^\circ C$ whereas the $D_3$ increases. For the higher temperatures $D_1+D_2$ continuously decreases and reaches the minimum value at $1550$ and $1600^\circ C$. The resistivity reduction upon heating comes from the structural transformations. Taking it into account, the differences observed can be attributed to the different type, morphology or volume fraction of crystalline phases formed.

Figure 2. The temperature dependence of the relative electrical resistivity during continuous heating at $20^\circ C/\text{min}$ for the samples prepared with the different melt superheat $T_L$ before quenching.

Figure 3. The values of electrical resistivity reduction at the different crystallization stages as a function of the melt superheat temperature $T_L$ before the quenching.
In order to study the crystallization process all specimens were simultaneously heated up to the temperatures corresponding to a various stages of transformation. Figure 4a represents the x-ray diffractions spectra of the Fe$_{74}$B$_{16}$Si$_9$Ni$_1$ glassy ribbon prepared with the melt superheat temperature 1350°C in the as-quenched state and after heating up to 545, 585, 625°C.

It was found that the first peak of the DSC curve is caused by diffusion-controlled growth of α–Fe(Si) (bcc solid solution of silicon in iron) and tetrahedral Fe$_3$B formation. The α–Fe(Si) lattice parameter equals to 0.2855Å after heating up to 545°C. The second peak corresponds to the transformation of residual amorphous matrix via eutectic reaction with the formation of α–Fe(Si) and Fe$_2$B(tetr). This is indicated by increased reflexes of the latter phases on the X-ray diffraction spectra after the specimen heating up to 585°C. The α–Fe(Si) lattice parameter decreases to 0.2844Å. As a result, the ribbon is fully crystalline after the second crystallization stage.

![Figure 4. X-ray diffraction patterns of Fe$_{74}$B$_{16}$Si$_9$Ni$_1$ alloys: $T_L$=1350°C (a) and $T_L$=1550°C (b) in as-quenched state and after heating to the temperatures corresponding to the different stages of transformation.](image)

After the heating up to 625°C metastable Fe$_3$B(tetr) decomposes to α–Fe(Si) and Fe$_2$B(tetr), which is the reason for additional resistivity reduction at the temperatures of 610-640°C.

For the melt superheat higher than 1400°C the crystallization process of Fe$_{74}$B$_{16}$Si$_9$Ni$_1$ glassy ribbon deviates from described above. On the first stage some orthorhombic Fe$_3$B is formed simultaneously with the Fe$_3$B(tetr) and α–Fe(Si) (Figure 4(b)). Second stage, which is attributed to the residual amorphous matrix decomposition, realizes mainly by α–Fe(Si) and Fe$_3$B(tetr). It results in a higher fraction of metastable Fe$_3$B(tetr) formed after the heating to 585°C. This can be concluded from the much stronger Fe$_3$B(tetr) reflexes of the X-ray diffraction spectra and increased D$_3$ of the temperature dependence of resistivity (Figures 2 and 3).

4. Discussion

Different crystallization behavior seems to be the consequence of different structure of the ribbons in as-quenched state. It has been shown experimentally [10] and theoretically [11] that real melts and amorphous alloys are characterized by the presence of short-range ordered structural units (clusters). Their existence is related to the strong bonding energy between the atoms of different kinds: Fe-Si, Fe-B. It may be assumed, these aggregates attempt to form a crystalline structure during cooling and make up the amorphous matrix with the set of Fe-Si and Fe-B clusters in the case of rapid quenching. Cluster sizes, their local stoichiometric composition and short-range order changes with the increasing of the melt temperature. Most likely the strongest changes take place in Fe$_{74}$B$_{16}$Si$_9$Ni$_1$ melt in the...
temperature region of 1380-1410°C, which can be confirmed by the viscosity steep decrease (Figure 5).

At the same time, formation of crystalline phase critical nuclei in the amorphous matrix upon heating is determined by the short-range order, sizes and the number of clusters retained in the amorphous structure [12].

In the context outlined above the changes in crystallization behavior of the Fe$_{74}$B$_{16}$Si$_{9}$Ni$_{1}$ glassy alloy prepared from the melt overheated above 1400°C may be explained in the following way. Subcritically sized clusters close to Fe$_3$B local stoichiometric composition are preserved in amorphous matrix. During heating these clusters reach soon the critical size for growth. It provides a higher fraction of the metastable Fe$_3$B(ort) formed after the first crystallization stage. Taking into account a smaller volume fraction of the solid solution formed, the latter is the reason for the residual amorphous matrix depletion in boron and enrichment in silicon (in comparison with the ribbons prepared at $T_L<$1400°C). As a result crystallization at the second stage is realized mainly by Fe$_3$B(tetr) and α–Fe(Si) formation.

5. Conclusions
The crystallization process of amorphous Fe$_{74}$B$_{16}$Si$_{9}$Ni$_{1}$ was studied by means of X-ray diffraction, differential scanning calorimetry and resistivity measurements. It was found two possible crystallization mechanisms:

1) the first crystallization stage is characterized by simultaneous formation of α–Fe(Si) solid solution and tetrahedral Fe$_3$B; at the second stage eutectic crystallization of α–Fe(Si) and Fe$_3$B appeared;

2) at the first stage some orthorhombic Fe$_3$B is formed simultaneously with α–Fe(Si) and Fe$_3$B(tetr); the second stage realizes mainly by formation of metastable eutectic α–Fe and Fe$_3$B(tetr).

The third stage of crystallization at a higher temperature for both the cases is related to metastable Fe$_3$B to Fe$_3$B and α–Fe transformation. It is shown that ribbons prepared at melt superheat temperature above 1400°C crystallize predominantly by the second type. It is assumed that the crystallization behavior modification is caused by the structural transformation in the initial liquid alloy at 1400°C and structural inheritance at rapid quenching.

References
[1] Kane S N, Sarabhai S, Gupta A, Varga L K and Kulik T 2000 JMMM. 215-216 372
[2] Haslar V, Kraus L, Jankovic D, Svec P and Duhaj P 1997 Mater. Sci. Eng. A227-228 331
[3] Kulik T and Kopcewicz M 2000, JMMM 215-216 455
[4] Lu K. 1996 *Mater. Sci. Eng.* v. *R16* 161
[5] Lovas A, Kisdi-Koszo E, Potocky L and Novak L 1987 *J. of Mater. Sci.* v. 22 1535
[6] Lad’yanov V I, Volkov V A, Harlamov D N and Mokrushina M I 2004 *Metally* v. 5 99
[7] Supov A Y and Ivanova I M 2000 *Materials Science and Heat Treatment* v. 43, N. 11-12
[8] Manov V P, Popel S I, Buler P I, Manukhin A I and Komlev D G 1991 *Mater. Sci. Eng.* v. *A133* 535
[9] Vertman A A and Samarin A M 1969 *Metody issledovaniya svoistv metallicheskih rasplavov* (Moskva: Nauka)
[10] Hirotsu Y, Akada R and Onishi A 1985 *J. Non-Crystalline Solids* v. 74 97
[11] Hodgkinson R J 1971 *Philos. Mag* v. 23 673
[12] Duhaj P and Svec P 1997 *Mater. Sci. Eng.* v. A *226-228* 245