On features in viscosity polytherms of Fe-B hypereutectic melts and their development in crystallization kinetics of rapidly quenched ribbons

V I Lad’yanov, A A Suslov, A L Bel’tyukov, A I Shishmarin, M A Eremina and V A Volkov

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

E-mail: las@pti.udm.ru

Abstract. An abnormal viscosity change (its decrease) has been revealed in the viscosity polytherms of the amorphysing Fe$_{81.5}$B$_{18.5}$ and Fe$_{79}$B$_{21}$ melts in the vicinity of 1420 – 1460 ºC and 1380 – 1420 ºC, respectively. They are caused by the change of the short-range order structure of the melts. The maintenance of the high-temperature state of the liquid phase down to solidification temperatures results in its viscosity hysteresis. It was found out that the quenching temperature rise results in an increase of the volume fraction of amorphous phase in rapidly quenched ribbons. It has been proven that crystallization of the ribbons obtained proceeds by the eutectic mechanism resulting in $\alpha$-Fe and tetragonal Fe$_3$B$_T$ formation. The kinetics of the process depends on the initial melt temperature and correlates with the anomalies in their viscosity temperature dependences.

1. Introduction

When investigating of metallic melts sharp changes of some properties such as density, viscosity and electrical resistance [1, 2] at certain temperatures (anomaly temperatures ($T_{anom}$)) have been found in the temperature dependences. Some authors consider them to be caused by relaxation of metastable heterogeneities in a melt; the others link them with changes in the short-range order of a melt. Taking into consideration structural heredity of amorphous ribbon and its liquid precursor it is of great interest to investigate properties and structures of amorphous alloys obtained by rapid quenching starting from the temperature lower and higher than $T_{anom}$. In this paper we demonstrate results of studying Fe$_{81.5}$B$_{18.5}$ and Fe$_{79}$B$_{21}$ melts viscosity and properties of rapidly quenched ribbons obtained after their quenching from various temperatures ($T_{quen}$).

2. Experimental

The alloys were prepared of carbonyl iron of 99.98 % purity and amorphous boron in a vacuum furnace. The iron and boron powder mixture was melted in a vacuum below 10$^{-5}$ mm Hg in an Al$_2$O$_3$ crucible. Then it was held at 1500 ºC for 30 minutes and cooled down to 1000 ºC at the rate of 10 ºC/min. After holding for 3 hours at the last temperature, it was cooled down to the room temperature. The chemical composition of the samples was tested before and after the viscometric experiments by means of the atom-emission spectrometer “Spectroflame Modula D”. The kinematic viscosity of the melts, $\nu$, was measured using the method of damped torsional vibrations of the crucible filled in with a
liquid under investigation [3]. The measurements were performed under protective atmosphere of purified helium. The samples were heated and then cooled in the temperature interval between liquidus and 1650 °C, the step being of 15 to 20 °C. Each measurement started after the isothermal exposition during 20 min. Cylindrical cups made of BeO were used as crucibles. The measurement procedure and statistic-stochastic evaluation of the experimental data have been described in [4]. The relative error of the viscosity measurement does not exceed 3 % at the accidental error of 1.5 %. Rapidly quenched ribbons were obtained by melt spinning on a copper disk from various $T_{\text{quen}}$ after isothermal exposition during 20 min. Afterwards, they were studied by the differential thermal analysis (DTA) using the STA-780 unit and by the differential scanning calorimetry (DSC) using the Perkin-Elmer DSC device. The flowing atmosphere of purified argon and the heating rate of 10 ºС/min were used in both experimental procedures. Besides, the ribbon structure was investigated by X-ray diffraction using the DRON-3M unit in Cu-K$_{α}$-radiation. The fraction of the amorphous component was estimated as the ratio of intensities of the amorphous halo and the crystalline phase reflection.

3. Results and discussion

The viscosity $ν$ temperature dependences of Fe$_{81.5}$B$_{18.5}$ and Fe$_{79}$B$_{21}$ melts are given in figure 1. An anomalous decrease of $ν$ within the intervals of 1420 to 1460 ºC (Fe$_{81.5}$B$_{18.5}$) and 1380 to 1420 ºC (Fe$_{79}$B$_{21}$) is observed while heating. During the following cooling, a distinct ramification of the heating and cooling curves (viscosity hysteresis) is observed below mentioned temperature intervals. We suppose that the anomalies in viscosity temperature dependences reflect some structural changes in liquid state at the temperature $T_{\text{anom}}$ specific of each composition. In this case the low-temperature ($T<T_{\text{anom}}$) and the high-temperature ($T>T_{\text{anom}}$) structural states of the melt can be considered and the high-temperature state is retained down to its crystallization. It results in the hysteresis of the viscosity polytherms. This point of view is confirmed by the results of diffraction experiment [5] which has shown that for Fe$_{82}$B$_{18}$ the curves of the structural factor and the radial distribution function obtained while heating up to 1550 ºC and following cooling down at a low rate are not identical.

![Figure 1. The viscosity polytherms of the Fe$_{81.5}$B$_{18.5}$ and Fe$_{79}$B$_{21}$ melts.](image)

The rapidly quenched ribbons of Fe$_{79}$B$_{21}$ with the thickness of 21.8 to 28.2 μm were obtained from $T_{\text{quen}}$ of 1320, 1350, 1420, 1480, 1510, 1540, 1570, 1590 ºC (table 1). The phase composition has been identified by the X-ray diffraction analysis. It was shown that all the samples are in a mixed amorphous-crystalline state (table 1). The phase component analysis is rather hard to be performed due to a very small fraction of the crystals. So, to define the phases more properly, the initial ribbons were grounded in a ceramic mortar. This processing resulted in formation of almost fine crystalline powder, from one side, and larger fragments not including crystalline phase, from the other side. Studying the powder composition has discovered presence of $α$-Fe and tetragonal Fe$_3$B$^+$ boride. The
higher is the quenching temperature the more is volume fraction of the amorphous fragments in the ribbons obtained.

The rapidly quenched ribbons Fe\textsubscript{81.5}B\textsubscript{18.5} with the thickness shown in table 2 have been also obtained from the quenching temperatures between 1250 and 1600 °C. It has been shown by the X-ray diffraction analysis that they are either amorphous or amorphous-crystalline with a small fraction of a crystalline phase (table 2). The crystalline component consists of α-Fe, the tetragonal Fe\textsubscript{3}B\textsuperscript{T} boride, and γ-Fe as well.

It was interesting to compare the process of the amorphous component crystallization for the ribbons quenched from various temperatures to follow the influence of structural state of liquid precursor. For this purpose, we have performed DTA and DSC investigation of the samples obtained.

### Table 1. Data of the Fe\textsubscript{79}B\textsubscript{21} rapidly quenched ribbons.

| T\textsubscript{quen}, °C | d, μm    |
|-------------------------|---------|
|                         | 21,8±2  |
|                         | 23,4±1,7|
|                         | 25,5±4  |
|                         | 23,9±4,3|
|                         | 24,2±4  |
|                         | 26,6±2,7|
|                         | 28,2±4,8|
|                         | 25,1±3  |

| Phase analysis          | α-Fe    |
|                        | Fe\textsubscript{3}B |

### Table 2. Data of the Fe\textsubscript{81.5}B\textsubscript{18.5} rapidly quenched ribbons.

| T\textsubscript{quen}, °C | d, μm    | Phase analysis of the contact surface | Phase analysis of the free surface |
|-------------------------|---------|--------------------------------------|----------------------------------|
| 1250                    | 34,9±4  | α-Fe, γ-Fe                          | Fe\textsubscript{3}B, A          |
|                         | 1250    | α-Fe, γ-Fe                          | Fe\textsubscript{3}B, A          |
|                         | 1300    | α-Fe, γ-Fe                          | Fe\textsubscript{3}B, A          |
|                         | 1300    | α-Fe, γ-Fe                          | Fe\textsubscript{3}B, A          |
|                         | 1350    | α-Fe, Fe\textsubscript{3}B          | Fe\textsubscript{3}B, A          |
|                         | 1400    | α-Fe, γ-Fe                          | Fe\textsubscript{3}B, A          |
|                         | 1400    | α-Fe, γ-Fe                          | Fe\textsubscript{3}B, A          |
|                         | 1410    | γ-Fe, A                             | A                                |
|                         | 1410    | γ-Fe, A                             | A                                |
|                         | 1500    | α-Fe, γ-Fe                          | Fe\textsubscript{3}B, A          |
|                         | 1550    | α-Fe, Fe\textsubscript{3}B          | Fe\textsubscript{3}B, A          |
|                         | 1600    | α-Fe, γ-Fe                          | Fe\textsubscript{3}B, A          |

A typical DTA curve is presented in figure 2. According to the results, crystallization of the Fe\textsubscript{79}B\textsubscript{21} ribbons occurs in the temperature range of 380 to 480 °C. It has been proven by the presence of a high exothermic peak. According to [6] an amorphous matrix is dissociated into α-Fe and Fe\textsubscript{3}B\textsuperscript{T}. A small
An exothermic peak has been observed within 810 to 900 °C temperature interval. The presence of two exothermic peaks suggests that firstly, near 400°C, the ribbons crystallized into a metastable structure. Afterwards, being heated up to 900 °C they re-crystallize into the equilibrium state. According to [7], the second peak corresponds to the Fe2B phase formation. Figure 3 shows a dependence of the width of DTA main peak F, i.e. difference between temperatures corresponding to the peak maximum and to its onset, on the quenching temperature. It can be seen that low T_quen correspond to high F values, but at T_quen above T_anom the width of the peak decreases, the crystallization time becomes shorter, though the fraction of amorphous matrix increases and the peaks square does not change.

Figure 4 presents typical DSC curves of the Fe81.5B18.5 ribbons. At heating up to 500 °C a complex exothermic peak is observed in the range of 400 – 465 °C. As the quenching temperature increases it becomes more symmetrical. Moreover, at T_quen > T_anom the width of the peak (figure 5) decreases from 60 to 46 °C. According to [8], the peak corresponds to formation of α-Fe and Fe3B2 crystals. To analyze the crystallization process the ribbons have been heated up to 420, 440 and 460 °C, corresponding to onset, maximum and ending of the DSC peak. It was discovered that at identical ribbon thickness after heating up to 420 °C the fraction of amorphous phase in the samples quenched from T<T_anom is much higher than in the samples quenched from T>T_anom. After heating up to 460 °C all the ribbons are identical in phase composition. In other words, it takes more time for the ribbons quenched at lower temperatures to be crystallized, though their crystallization starts earlier.

We suppose that structure of ribbons quenched from T_quen>T_anom retains some features of short-range order of initial high-temperature melt. According to [9] this order is characterized by the existence of smaller microgroups of closer packing atoms in comparison to low-temperature melt. As a result, the process of crystallization starts at a later time and lasts during a shorter time interval. The low-temperature short range order of the melts is characterized by existence of larger microgroups of atoms packed similarly to corresponding crystals. At heating the samples obtained from the low T_quen the crystallization process starts at lower temperature and lasts during a longer time. It can be explained by the crystal nucleation on “quenching-in” centers. Thus, the rapidly quenched ribbons obtained from various quenching temperatures are crystallized through the mechanism of the α-Fe and Fe3B2 crystals formation but kinetics of the process depends on structural state of liquid precursor.

4. Conclusions

Anomalies in viscosity temperature dependences (sharp viscosity decrease) caused by the change of short-range order in the melt are observed in the Fe-B melts with 18.5 and 21 at. % B. Ramification of the curves obtained while heating and subsequent cooling the melts below the anomalies was linked with retaining of the high temperature structure of the short range order of the melt down to its
amorphization. The rapidly quenched ribbons \( \text{Fe}_{81.5}\text{B}_{18.5} \) and \( \text{Fe}_{79}\text{B}_{21} \) obtained from various quenching temperatures have been studied. It has been shown that their properties and structure depend on structural state of the liquid precursors. If the melt was quenched from the temperature below the anomaly, a larger fraction of crystalline component presents in the ribbon and its crystallization starts on “quenching-in” centers. If the quenching temperature was above the anomalies the ribbon structure and properties change together with kinetics of amorphous phase crystallization at heating.

References

[1] Kolotukhin E V, Baum B A, Tyagunov G V, Popel P S, Arkhangel’skiy E L 1988 Izvestiya vyshih uchebnyh zavedeniy, Chernaya metallurgiya 6 68
[2] Lad’yyanov V I, Bel’tukov A L, Shishmarin A I Rasplavy 4 34
[3] Shvidkovsky E G 1955 On some problems of viscosity of liquid metals (Moscow: Gostekhizdat)
[4] Logunov S V, Lad’yyanov V I 1996 Rasplavy 3 63
[5] Zelinskaya G M, Romanova A V, Nemoshkalenko V V et al. 1983 Ukrainskiy phizicheskiy zhurnal 28 1393
[6] Li Z, Li D, Li J 2005 Journal of Magnetism and Magnetic Materials 239 502
[7] Nemoshkalenko V V, Romanova A V, Il’inskiy A V et al. 1987 The amorphous metal alloys (Kiev: Naukova dumka)
[8] Kemeny T, Vincze I, Fogarassy B, Arajs S 1979 Physical Review B 20 476
[9] Mikhailova L E, Il’inskiy A V, Romanova A V, Khristenko T M 1990 Metallofizika 12 52