The influence of melt atomic structure on structure and properties of amorphous Fe-based alloys

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Abstract. The X-ray diffraction investigations of the melt structure (up to 1550°C) and the temperature dependence of its kinematic viscosity (up to 1650°C) under heating and cooling mode as well as the X-ray diffraction investigations of the amorphous Fe₈₀Si₁₆B₁₄ and Fe₇₇Si₈B₁₅ alloys structure obtained by rapid quenching of the melt from various temperatures were carried out. The direct and indirect data confirm the existence of the “critical” temperatures $T_{cr}$ (1420°C for Fe₈₀Si₁₆B₁₄ and 1440°C for Fe₇₇Si₈B₁₅) separating the low-temperature and high-temperature structural states of the melts. The high-temperature state is characterized by large relaxation times at $T<T_{cr}$ and can be inherited during melt amorphization. Preliminary temperature-time melt treatment at $T>T_{cr}$ results in increasing of the initial magnetic permeability and strength of amorphous Fe-Si-B ribbons by 45-50% and 25-30%, respectively.

1. Introduction
Amorphous and nanocrystalline Fe-Si-B-based alloys substitute successfully now many conventional crystalline soft magnetic materials at manufacturing of magnetic cores used in various products and devices of electronics, electrical and radio engineering [1,2].

Further possibilities for increasing the level of physical and mechanical properties of these materials can be related not only with an optimization of their chemical composition, but also with melt heat treatment before quenching. Anomalies in polytherms of viscosity, electric conductivity, surface tension, density [3-6] in the form of inflections of curves, as well as hysteresis of properties in “heating-cooling” cycles indicate that liquid alloys can undergo structural changes, that influence noticeably on performance capabilities of the alloys after their solidification. At the same time, the direct experimental data (in particular, the diffraction ones), which can directly confirm a presence of these structural changes under heating and cooling of melt, are very limited. This is also related to the problems of melt structure inheritance at glass forming during the process of rapid cooling of melt.

In this context, in the present work, the changes of kinematic viscosity ($v$) of the melts and structural changes occurred in them at different temperatures during the process of heating and subsequent cooling were studied for the same objects (Fe₈₀Si₁₆B₁₄ and Fe₇₇Si₈B₁₅ alloys). Besides, the X-ray diffraction study of structure of the amorphous ribbons made from these alloys by quenching of the melt subjected to different preliminary heat treatment and their magnetic and mechanical
characteristics were studied as well.

2. Experimental and results
Viscosity of the melts was measured using damped torsion oscillation method by Shvidkovsky variant [7]. The measurements were carried out in the protective atmosphere of purified helium under heating and subsequent cooling in the temperature range from liquidus $T_L$ up to $1600^\circC$ with the step $15-30^\circC$ after isothermal expositions during 20 min.

The X-ray diffraction (XRD) studies of the liquid samples were performed using a high-temperature $\theta\text{-}$diffractometer in helium atmosphere at temperature 1300-1550$^\circC$ in monochromatic Mo-$K\alpha$ radiation.

The alloys in amorphous state were produced by melt spinning (planar flow casting) method. The studies of strength (failure stress, $\sigma_f$) were carried out on amorphous ribbons with test working part $\sim 25$ mm at temperature 300 K by uniaxial tension at the testing machine with stiffness of 2.5 kN/mm. The magnetic properties of the toroidal cores made from the amorphous ribbons subjected to a preliminary heat treatment were studied by the standard induction-continuous measuring method.

The temperature dependences of viscosity of Fe$_{80}$Si$_6$B$_{14}$ (a) and Fe$_{77}$Si$_8$B$_{15}$ (b) melts obtained under heating and cooling mode in the range 1200 - 1600$^\circC$ are presented in figure 1. From the

Figure 1. Changes of the viscosity of Fe$_{80}$Si$_6$B$_{14}$ (a) and Fe$_{77}$Si$_8$B$_{15}$ (b) melts at heating and cooling.

Figure 2. Time-dependences of viscosity of Fe$_{80}$B$_{14}$Si$_6$ (a) and Fe$_{77}$Si$_8$B$_{15}$ (b) melts under isothermal expositions at 1200$^\circC$, 1350$^\circC$ and 1500 $^\circC$ at heating and cooling with a rate of 100 degrees per minute.
obtained data it follows that the anomalous $\nu$ decrease is observed on the alloy melt polytherms near 1420°C ($\text{Fe}_{80}\text{Si}_6\text{B}_{14}$) and 1440°C ($\text{Fe}_{77}\text{Si}_6\text{B}_{15}$) under heating mode. After heating the sample $\text{Fe}_{80}\text{Si}_6\text{B}_{14}$ up to 1600°C and subsequent cooling below 1420°C the viscosity hysteresis (the values of $\nu$ obtained under cooling mode are lower than under heating) is observed. It exists till solidification of the specimen. The similar viscosity behavior is observed also for $\text{Fe}_{77}\text{Si}_6\text{B}_{15}$ alloy under cooling, however in contrast to the former alloy the hysteresis disappears at temperature about 1250°C and as a result the values of viscosity obtained under heating and cooling coincide over the range 1180-1250°C.

The anomalies of the temperature dependence of viscosity of the melts revealed in the present work are probably caused by structural transformations in liquid state at a certain critical (characteristic of every investigated alloy) temperature $T_{cr}$. Such a way, the low-temperature (from the melting temperature up to $T_{cr}$) and the high-temperature (from $T_{cr}$ up to 1600°C) melt structural states can be distinguished. Under cooling mode the high-temperature melt state can remain till crystallization ($\text{Fe}_{80}\text{Si}_6\text{B}_{14}$) or transition to the low-temperature one can occur at temperature below $T_{cr}$ ($\text{Fe}_{77}\text{Si}_6\text{B}_{15}$).

As it follows from comparison of figures 1a and 1b for $\text{Fe}_{80}\text{Si}_6\text{B}_{14}$ melt one can distinguish the two characteristic temperature ranges: 1200-1420°C and 1420-1600°C, while there are the three ranges for $\text{Fe}_{77}\text{Si}_6\text{B}_{15}$: 1200-1240°C (the low-temperature state under heating and cooling), 1240-1440°C (the region with the viscosity hysteresis, i.e. with the low-temperature state under heating mode and with the high-temperature one under cooling) and 1440-1600°C (the high-temperature state under heating and cooling). Taking into account this circumstance the measurements of the viscosity changes on time were carried out under isothermal conditions after heating and cooling with the rate 100 deg /min for the both alloys at temperatures 1200°C, 1350°C and 1500°C.

These investigations have shown that the values of $\text{Fe}_{80}\text{Si}_6\text{B}_{14}$ melt viscosity under heating up to 1200°C and 1350°C do not change with time (figure 2a). After heating up to 1500°C and the following isothermal holding the low-temperature melt state remains during five minutes only and then its transition to the high-temperature state occurs. This structural state remains for $\text{Fe}_{80}\text{Si}_6\text{B}_{14}$ melt under cooling to 1350°C and 1200°C and during holding at these temperatures for 120 min.

The similar results were obtained under isothermal holdings of $\text{Fe}_{77}\text{Si}_6\text{B}_{15}$ melt at 1350°C and 1500°C (figure 2b). However, the abrupt viscosity increase occurs after 40 min holding at temperature 1200°C indicating the transition of this melt from the high-temperature to low-temperature state.

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**Figure 3.** The changes of the height of the first maximum $i(S_1)$ of the XRD diffractograms for $\text{Fe}_{80}\text{Si}_6\text{B}_{14}$ melt at heating and subsequent cooling.

**Figure 4.** The changes of the area under the first RDF maximum for $\text{Fe}_{80}\text{Si}_6\text{B}_{14}$ melt at its separation by minimum, $A_{min}$ and the correlation length $R_k$ at heating and subsequent cooling.
During XRD investigations of the structure of liquid Fe-Si-B alloys the first exposure was carried out after melting and heating of the melt up to 1350°C, then subsequently at temperatures 1450, 1500, 1550°C. Then temperature decreased and X-ray diffraction exposures of the melt were carried out at 1450 and 1350°C. These studies have shown that all diffractions curves except the one obtained at the first heating up to 1350°C practically coincide. The main difference of this X-ray diffraction pattern is the appreciably lower height of the first intensity maximum (figure 3).

Thus, the results of X-ray diffraction research show that qualitative changes in Fe-Si-B melt structure under heating occur in the certain temperature ranges, and the low temperature structural state does not recover completely under following cooling of the melt. The areas under the first maximum of the radial distribution function (RDF), \(A_{\text{min}}\), (the characteristics of the coordination number) as well as the values of correlation length calculated from the experimental X-ray diffractograms are shown in figure 4. As can be seen both these parameters increase with temperature and remain practically unchanged at subsequent cooling.

The XRD investigations of structure of the amorphous Fe\(_{80}\)Si\(_6\)B\(_{14}\) and Fe\(_{77}\)Si\(_8\)B\(_{15}\) ribbons obtained by quenching the melt, preliminary heated to different temperatures, have revealed in particular that...
the height of the first maximum of structure factor (SF) \( i(s_1) \) for the amorphous ribbons obtained after heating the melt up to 1350, 1450 and 1550°C increases in the sequence of 3.68, 3.91 and 4.0 units (figure 5).

Besides, the value of \( i(s_1) \) at the XRD patterns of the ribbons has a tendency to increasing with time of the melt exposition before quenching (figure 5) and the coordination numbers for the amorphous ribbons determined from the RDF increase with an increase of the melt heating temperature before ejecting (figure 6). This behavior is quite similar to that observed at the XRD patterns of the melts, i.e. structure peculiarities of melts are substantially inherited during their amorphization.

The subsequent studies have shown that the preliminary heat treatment of the melt influences the properties of the amorphous alloys. In particular, increasing of both the melt temperature and time of exposition before quenching leads to enhancement of the failure stresses of the as-quenched ribbons (figure 7) and the initial magnetic permeability of the cores heat treated at 390°C for 1 h in He atmosphere (figure 8).

The maximum value of initial magnetic permeability (\( \mu_i \sim 7000 \)) has been reached for the amorphous Fe\(_{80}\)Si\(_6\)B\(_{14}\) alloy produced by ejection of the melt after exposure for 2 min at \( T = 1650°C \). It should be noted that this value not only essentially (> 50%) exceeds the values of \( \mu_i \) ribbons obtained from the melts treated for \( t_i \leq 12-14 \) min at \( T = 1350, 1450 \) and 1550°C, but it is superior to the \( \mu_i \) values of the ribbons quenched from the melts exposed at these temperatures from 12-15 to 20 min.

Thus, the clear tendency exists, which consists in that increasing of the Fe\(_{80}\)Si\(_6\)B\(_{14}\) melt superheat temperature as well as the melt exposure time at temperatures above 1350°C favor the essential enhancement of the properties of this amorphous alloy. There is obvious reason to suppose that the observed effect is resulted from inheritance of the structural features of the melt caused by its preliminary temperature-time treatment which to some extent are retained after the heat treatment of the amorphous core at temperatures below the onset of crystallization.

3. Discussion

At present various approaches to description of melt structure states and their changes with temperature exist. One of the possible explanations specified in the work and the effects described here can be connected with the theory of the long-range correlations of density fluctuations in glass forming melts (Fischer cluster [8]) developed in [9, 10]. The essence of the authors’ approach [9, 10] is that glass forming liquid has heterophase mesoscopic structure composed of solid-like (long-range) and fluid-like (short-range) species with different types of the short-range order. According to the theory the time interval of the long-range correlation formation in melt is about hundreds of seconds. These long-range correlations with dimension up to 300 nm include the short-range ~2 nm regions as “substructure” (the presence of the noncrystalline ordered microregions, which sizes significantly differ and are in the range from about 2 to more than 100 nm, was really observed during the experimental investigation of the glass forming melt structure by small angle neutron scattering method [11]). From these positions the temperature-time viscosity behavior revealed in this work can be explained by the assumption that the long-range correlations are destroyed under overheating the melts above the “critical” temperature and the more homogeneous short-range “substructure” is realized in the melt. The long-range correlations cannot develop under cooling due to long relaxation times that gives rise to a hysteresis of structure-sensitive properties of the melt.

In summary, the experimental results obtained have confirmed the existence of the interrelation between melt structure change at temperature-time melt treatment and inheritance of these structure changes during amorphization that finds manifestation in structure and physical properties of amorphous alloys.

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