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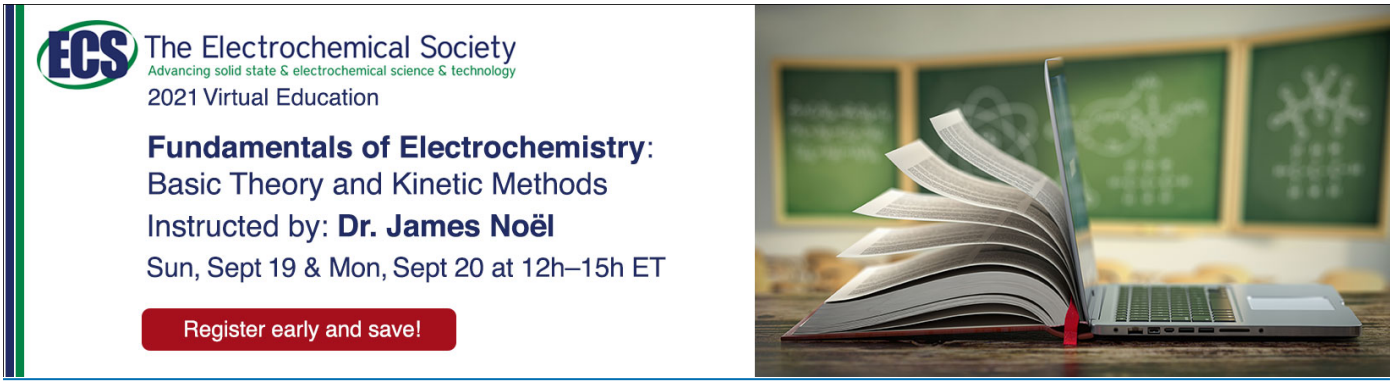

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Kinematic Viscosity of Melt Prepared from an Amorphous $Fe_{72.5}Cu_1Nb_2Mo_{1.5}Si_{14}B_9$ Ribbon

Ye A Kochetkova[1], Yu N Starodubtsev[1,2] and V S Tsepelev[1]

[1]Reserch Center for Physics of Metal Liquids, Ural Federal University, 19, Mira str., Ekaterinburg, 620002, Russia
[2]Gammamet Research and Production Enterprise, 92, Tatishcheva str., Ekaterinburg, 620028, Russia

E-mail: v.s.tsepelev@urfu.ru

Abstract. In this work, the viscosity of a melt prepared by melting an amorphous ribbon of $Fe_{72.5}Cu_1Nb_2Mo_{1.5}Si_{14}B_9$ alloy was studied. The amorphous ribbon was produced by rapid quenching of the melt, which was preheated at a temperature above (overheated mode) and below (not overheated mode) critical temperature T_k. A hysteresis loop was found in the temperature dependence of viscosity, the widest part of which falls on a temperature from 1670 K to T_k = 1760 K. In this temperature range, the melt has the highest activation energy and the largest cluster size. It has been proven that the melt viscosity increases with decreasing cluster size. In the low-temperature region, an overheated melt has the highest viscosity and the smallest cluster size comparable to the atomic size. It is shown that the heredity of the structure is preserved in the melt from the amorphous ribbon despite a number of structural transitions.

1. Introduction

The physical properties of liquid metals are characterized by various quantities, such as density, viscosity, diffusion, surface tension, thermal conductivity, electrical resistance, and others. Among these quantities, one can distinguish viscosity, which has a high structural sensitivity. The temperature dependences of the viscosity of multicomponent melts have a number of features that are not observed in pure liquid metals. Irreversible changes in the temperature dependence of viscosity at the stages of heating and cooling were detected, and the branch point corresponded to the critical temperature T_k [1]. During a long isothermal exposure of the melt, viscosity fluctuations occurred, and the amplitude of the oscillations significantly exceeded the random measurement error [2–5]. The largest amplitude of viscosity fluctuations was observed in the region of critical temperature [4].

The anomalous behavior of multicomponent melts is associated with a nonequilibrium state that occurs when the temperature changes. For rearrangement of the short range order and for approaching the equilibrium state, a certain time is required [1]. In turn, the relaxation time depends on the structure of the melt. At the melting stage, a short-range structure inherited from the multiphase solid state is retained in the melt. The structural component of the melt are clusters, the size of which depends on temperature [6]. With increasing temperature, the cluster size decreases, and at a temperature above T_k the melt structure becomes the most uniform.

If the melt is heated above the critical temperature and then transferred to the amorphous solid state using rapid quenching, it can be expected that a homogeneous structure will remain in the amorphous state.

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Heredity was studied on an amorphous ribbon obtained after the melt was held above and below the critical temperature [7–10]. It was proved that the amorphous ribbon after holding the melt above the critical temperature has a less ordered atomic structure [8], a larger molar volume [7], greater plasticity [8, 9], and the hardness and fracture toughness [9], higher crystallization enthalpy [7, 10]. After nanocrystallization of an amorphous ribbon obtained from $Fe_{72.5}Cu_1Nb_2Mo_{1.5}Si_{14}B_9$ melt with overheating above a critical temperature, an increased proportion of small nanocrystals 1–2 nm in size was discovered [10]. Thus, it was shown that the heredity of the structure is preserved not only in the amorphous solid state after melt quenching, but after crystallization of the amorphous ribbon.

In this work, we determined the depth of structural heredity that the material retains after melt preparation. For this purpose, the viscosity of the melt obtained by melting the amorphous $Fe_{72,5}Cu_1Nb_2Mo_{1,5}Si_{14}B_9$ ribbon was studied, and the amorphous ribbon was obtained by rapidly quenching the melt, which was heated above and below the critical temperature T_k.

2. Experimental

The $Fe_{72,5}Cu_1Nb_2Mo_{1,5}Si_{14}B_9$ alloy was melted in a vacuum induction furnace at temperature 1820 K and cooling in a flat mould. An amorphous ribbon 25 μm thick was produced by the planar flow casting process. When choosing the temperature regime, it was taken into account that in the samples after melting the alloy in a vacuum induction furnace, the critical temperature was 1760 K. Before the casting, the melt was prepared according to two modes. In the first mode, the melt was heated to 1750 K, kept at this temperature for 5 minutes, and then casting was carried out. The melt obtained from this amorphous ribbon will be called “not overheated” melt. In the second mode, the melt was heated to 1795 K with holding at this temperature for 5 minutes, then cooled to 1750, kept for 5 minutes, and casting was carried out. The melt obtained from this amorphous ribbon will be called “overheated” melt.

The crystallization temperature of the amorphous ribbon and the melting temperature were measured using differential thermal analysis. Kinematic viscosity of the melts is determined by torsional vibration method based on measuring the vibration damping factor [11]. The measurement error of the kinematic viscosity ν makes up ± 0.06 $m^2 \cdot s^{-1}$. In the first heating – cooling cycle, the amorphous ribbon was turned into a toroidal core and heated to 1720 K, followed by cooling to 1470 K. Then the second heating – cooling cycle from 1470 to 1870 K and back to 1470 followed, and immediately followed the third cycle, which completely repeated second cycle.

3. Results and discussion

Figure 1 shows the temperature dependences of the kinematic viscosity for the first heating – cooling cycle and for the heating stage of the second cycle in the melt obtained from the amorphous $Fe_{72.5}Cu_1Nb_2Mo_{1.5}Si_{14}B_9$ ribbon. From the figure it follows that immediately after the amorphous ribbon is melted, the melt viscosity is almost the same both in the overheated and not overheated melts. However, as the temperature rises to about 1540 K, the viscosity curves diverge noticeably. The viscosity of the overheated melt goes up sharply, and the viscosity of the not overheated melt changes slightly. At temperatures above 1540 K, the viscosity decreases due to an increase in the free volume of the liquid [12, 13].

Figure 1 also shows that in the overheated melt, the temperature dependence of viscosity goes to a stable trajectory, with the exception of a small loop in the temperature range 1670–1720 K. In the not overheated melt, the trajectory of the temperature dependence of viscosity gradually decreased. Thus, the melt obtained from the amorphous ribbon is nonequilibrium, and the not overheated melt has the greatest deviation from the equilibrium structure. The difference in the viscosity indicates a different structure of atomic groups participating in a viscous flow.

In the model of hard spheres, the melt viscosity can be represented as [14]:

$$\nu \infty a\sqrt{\frac{k_B T}{m}} \tag{1}$$

where a is the atomic size, m, m is the atomic mass, kg, k_B is the Boltzmann constant, $J \cdot K^{-1}$. If clusters are involved in the viscous flow, it must be taken into account that the cluster mass increases

proportionally, and the cluster size is not proportional to the number of atoms [15]. Figure 2 shows the dependence of the relative melt viscosity ν_c/ν, where ν_c is the viscosity of a liquid consisting of clusters, on the number of atoms in a cluster n. From the figure it follows that the viscosity of the liquid should decrease with increasing cluster size.

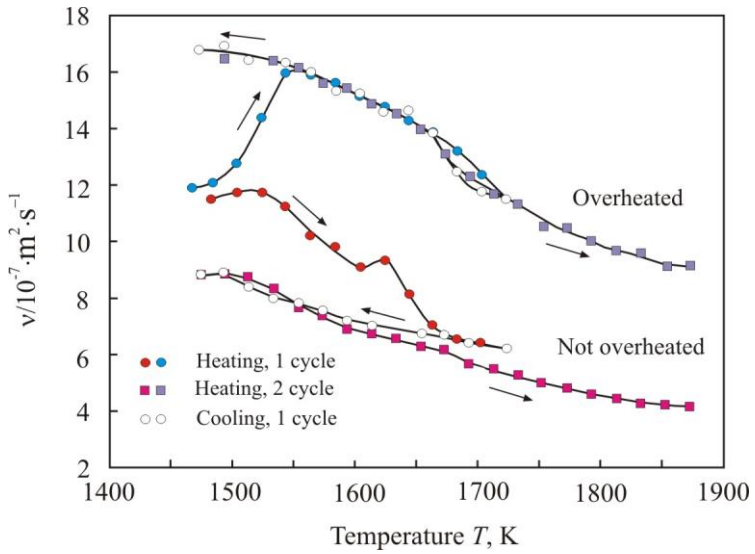

Figure 1. Temperature dependences of kinematic viscosity ν for the first heating – cooling cycle and for the heating stage of the second cycle in the overheated and not overheated melt prepared from the amorphous $Fe_{72.5}Cu_1Nb_2Mo_{1.5}Si_{14}B_9$ ribbon.

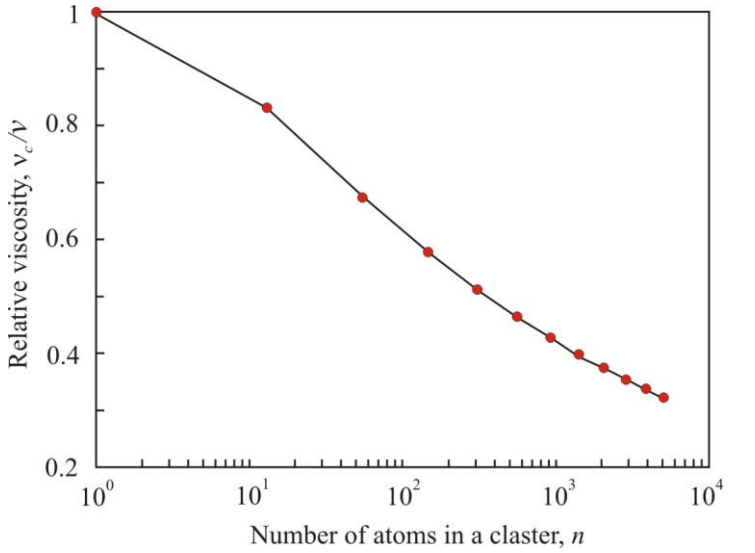

Figure 2. Relative melt viscosity ν_c/ν depending on the number of atoms in a cluster n.

Thus, in an overheated melt, increased viscosity can be associated with the small size of atomic groups in the equilibrium state of the liquid. The same conclusion can be drawn on the basis of general concepts [1], since the interaction energy increases with a decrease in cluster size, and this should lead to an increase in the melt viscosity.

When the amorphous ribbon is heated, crystallization and melting occur with the phase transition temperatures, which are shown in **Table 1**. At the first stage of crystallization (T_{x1} and T_{x2} are the temperatures of the beginning and the end), nanocrystalline grains are formed whose composition is close to $Fe_{80}Si_{20}$ and the average size is 10 nm [16]. It is important that in an amorphous ribbon prepared from a overheated melt, there are noticeably more small grains 1–2 nm in size [10]. At the second stage of crystallization (T_{x3} and T_{x4} are the temperatures of the beginning and end), metastable phases based on Fe-B and Fe-Si are formed [17]. The melting temperature of an amorphous ribbon with overheating (T_l and T_s are the liquidus and solidus temperatures) are slightly lower than in an amorphous ribbon without overheating. The Fe – B, Fe – Nb, and Nb – B clusters dominate in the melt [18]. Apparently,

the finer nanocrystalline structure of the amorphous ribbon obtained in the overheated mode became the basis for the formation of a finely dispersed melt structure.

Table 1. Phase transition temperature

Melt preparation regime	Crystallization temperature, K				Melting temperature, K	
	T_{x1}	T_{x2}	T_{x3}	T_{x4}	T_l	T_s
Overheated	770	800	940	965	1390	1455
Not overheated	782	805	950	970	1400	1460

Figure 3 shows the dependences of viscosity on temperature in the third heating – cooling cycle in the form convenient for analysis using the Arrhenius equation

$$\nu = \nu_0 \cdot e^{\frac{E_a}{RT}}, \tag{2}$$

where v_0 is a pre-exponential factor with the dimension of the kinematic viscosity $m^2 \cdot s^{-1}$, E_a is the activation energy of the viscous flow, $J \cdot mol^{-1}$, R is the gas constant, $J \cdot K^{-1} \cdot mol^{-1}$. After taking the logarithm we obtain

$$\ln \nu = \ln \nu_0 - \frac{E_a}{RT}. \tag{3}$$

Thus, the logarithm of the kinematic viscosity is a linear function of the inverse absolute temperature.

Figure 3 shows that despite the stabilization of the trajectories of the temperature curves of viscosity in the third heating – cooling cycle, viscosity is irreversible in the critical temperature region, which manifests itself in the form of a hysteresis loop. The branching of the curves begins at a temperature of 1670 K. Moreover, there is also an increased slope of the curves in this region, which indicates an increase in the activation energy of the viscous flow. The results of calculations of the activation energy E_a and pre-exponential factor ν_0 are presented in **Table 2**. The entire temperature region was divided into intervals that vary in the behavior of viscosity. The calculated values are obtained by linear fitting of the experimental points for each temperature range.

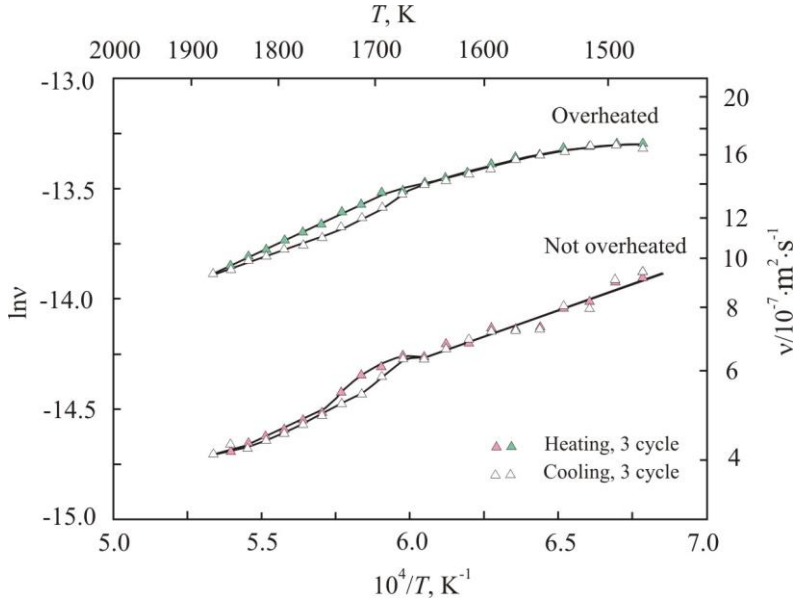

Figure 3. The logarithm of the kinematic viscosity lnν as a function of the reciprocal absolute temperature $10^4/T$ in the third heating – cooling cycle of the overheated and not overheated melt prepared from the amorphous ribbon.

Table 2. The activation energy E_a, cluster size d, and pre-exponential factor ν_0 in the overheated and not overheated melt obtained from the amorphous $Fe_{72.5}Cu_1Nb_2Mo_{1.5}Si_{14}B_9$ ribbon.

Temperature range	Heating			Cooling		
	E_a/kJ·mol^{-1}	$\nu_0/10^{-8}$·m^2·s^{-1}	d/nm	E_a/kJ·mol^{-1}	$\nu_0/10^{-8}$·m^2·s^{-1}	d/nm
Overheated melt 1790 K → 1750 K						
1470 – 1670 K	23.2	26.3	0.05	26.0	21.1	0.05
1670 – 1870 K	51.4	3.47	2.5	45.7	4.8	1.5
Not overheated melt 1750 K						
1470 – 1670 K	37.6	7.6	0.4	38.2	4.0	1.5
1670 – 1750 K	83.1	0.27	380	76.1	0.26	410
1750 – 1870 K	44.1	2.31	6	38.4	3.47	2.5

Table 2 also shows the calculated cluster size d. The calculation was performed using the Eyring model based on the transition state theory [13]. In this model, the pre-exponential factor ν_0 depends on the cluster size clusters d participating in the viscous fluid flow and this relationship can be transformed in the relation [19]:

$$d = \left(\frac{2\pi k_B T}{\rho}\right) \cdot \left(\frac{v_f}{v}\right)^{\frac{2}{3}} \cdot \nu_0^{-2}, \quad (4)$$

where ρ is the melt density, kg·m^{-3}, v_f/v is the relative free volume. To calculate the cluster size, typical values of the melt density and the relative free volume of nanocrystalline alloys were used [20]. For a temperature of 1600, 1700, and 1800 K, we used the densities of 6550, 6500, and 6450 kg·m^{-3} and the relative free volumes of 0.035, 0.043, and 0.05, respectively.

From the **Table 2** it follows that the activation energy is higher in the overheated melt. In addition, in the region of the hysteresis loop (see Figure 3), the activation energy is approximately two times higher.

When discussing cluster size data, it must be taken into account that model representations differ from real liquid. For example, atoms and clusters of different composition and size coexist in a real liquid. The model selects the cluster size in a homogeneous fluid, which should correspond to the experimental value of the kinematic viscosity. **Table 2** shows that the cluster size is higher in the melt obtained from the not overheated ribbon. Moreover, the largest cluster size falls on the hysteresis loop of kinematic viscosity, where there is also the highest activation energy of the viscous flow.

For the low-temperature region in the overheated melt, an effective cluster size of 0.05 nm was obtained, which can well be taken as the atomic size, taking into account the accuracy of the model approximation. Thus, in this temperature range, the melt viscosity is associated with the vibration of individual atoms, which are mainly located near their equilibrium positions. With increasing temperature, the mobility of atoms increases, but the strong bonds Fe-B, Fe-Nb(Mo) and Nb(Mo)-B inhibit the decomposition into individual atoms and ensure the formation of clusters.

4. Conclusions

In the work, the viscosity of the melt prepared by melting an amorphous ribbon from an $Fe_{72.5}Cu_1Nb_2Mo_{1.5}Si_{14}B_9$ alloy was studied. An amorphous ribbon was produced by rapid quenching of the melt, which was prepared before casting at a temperature above (overheated mode) and below (not overheated mode) critical temperature T_k. The activation energy E_a and pre-exponential factor ν_0 were calculated from the Arrhenius equation for different temperature ranges. Cluster size was determined

from the Eyring model based on the transition state theory. The results of the study allow us to draw the following conclusions.

1. Immediately after melting the amorphous ribbon, the melts have close kinematic viscosity, however, with increasing temperature, the viscosity of the overheated melt becomes much higher than the viscosity of the not overheated melt. The transition to an equilibrium state occurs faster in an overheated melt.
2. After repeated thermal cycling, a hysteresis loop is retained in the temperature dependence of viscosity, the widest part of which is between 1670 K and T_k = 1760 K. In this temperature range, the melt has the highest activation energy and the largest cluster size.
3. In the low-temperature region, an overheated melt has the highest viscosity and the smallest cluster size comparable to the atomic size. The melt viscosity increases with decreasing cluster size.
4. Structural heredity recorded in an amorphous ribbon after rapid quenching of the melt remains in the melt obtained after heating and melting the ribbon, despite a number of structural transitions.

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