VISCOSITY OF CuPb, CuPbSn, CuPbSnGa AND CuPbSnGaBi MELTS OF EQUIATOMIC COMPOSITIONS

Olga Chikova[1], Vladimir Tsepelev [2], Kseniya Shmakova[3]*
Ural federal university, Yekaterinburg, Russia

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**Corresponding author:e-mail:chik63@mail.ru, Department of Physics, Ural federal university, Mira str., 19, Yekaterinburg, Russia*

Abstract

We investigated the viscosity of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi melts of equiatomic compositions by the method of damped torsion vibrations of a crucible. We saw the melts of equiatomic composition as the melts high-entropy. All the investigated melts demonstrated the different temperature dependences of viscosity for heating and cooling. There is an anomalous reduction in viscosity resulted when the melt is heated to a specific temperature. The anomalous behaviour for viscosity we interpreted in terms of melt structure. This structural changes in the melt resulted when the melt is heated to a specific temperature. The microstructure of CuPbSnGaBi ingot of equiatomic composition we investigated using optical microscopy and measurement of microhardness. Collations data of the microstructures with of the microhardness gave three structural components: $CuGa_2$ dendrites, (Sn) + (Bi) + Bi_3Pb_7 ternary eutectic and rounded Pb inclusions having dimensions of ≈ 5 µm..

Keywords high-entropy melts, viscosity, Arrhenius law, microstructure of ingot, optical microscopy, microhardness

1 Introduction

It is known that most multicomponent liquid alloys are far from ideal solutions and reveal a microinhomogeneous atomic distribution. Various experimental methods are used to study inhomogeneities. Models of the inhomogeneous structure of liquid alloys have been developed [1–10]. The existence of inhomogeneous structure in liquid alloys within some temperature range is related to the anomalous temperature dependences of physicochemical properties. For example there are the anomalies of the temperature dependence of the viscosity within some temperature range after melting [1, 2, 6, 7]. However, literature data for multicomponent melts are scarce.

The results of viscosity measurements of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi equiatomic composition melts are presented in this work. We consider multicomponent melts as high-entropy melts. We discussed the laws of the existence of a microinhomogeneous distribution of atoms for a new group of multicomponent liquid alloys–high-entropy alloys (HEA) [11–15]. For destruction of microinhomogeneity in liquid alloy involves it heating to a temperature at which complete mixing of components and formation of a homogeneous solution come about, which substantially changes conditions of metal crystallization. It is known such this heating of liquid alloy at subsequent cooling and crystallization, even at relatively low cooling rates (1-10 K/s) enables getting a microstructure similar to microstructure, which is formed at high cooling rates [6]. The purpose of this study was to determine the temperature of

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heating, leads to the destruction of microinhomogeneities in the melts of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi equiatomic composition.

Current interest in studying of conditions of crystallization of high-entropy melts is increasing.. The high entropy of mixing stabilizes the formation of solid solutions and prevents the formation of intermetallic phases during solidification. High-entropy alloys possess high strength and thermal stability, combined with good resistance to oxidation and corrosion. An important factor in obtaining high-entropy alloys is high cooling rate of metal during crystallization, which makes it impossible to disintegrate of solid solution and formation of chemical compounds. High metal cooling rate, which is technically difficult to ensure, can be replaced by a destruction of the microinhomogeneity of chemical composition of liquid alloy before crystallization.

The high-entropy alloys can have either high strength or high ductility, and simultaneous achievement of both still constitutes a tough challenge. The inferior castability and the compositional segregation of high-entropy alloys are also obstacles for their technological applications. To tackle these problems for alloy CuPbSnGaBi, here we proposed a novel strategy to design high-entropy alloys using the eutectic alloy concept, i.e. to achieve a microstructure composed of alternating soft and hard phases. As a manifestation of this concept, a before AlCoCrFeNi eutectic high-entropy alloy was designed [16]. This high-entropy alloy possessed a fine lamellar microstructure, and showed an unprecedented combination of high tensile and high fracture strength at room temperature.

The present study investigates the viscosity of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi equiatomic composition liquid alloys, with special attention given to the analysis of the temperature dependence of the viscosity coefficient using the theory of absolute reaction rates. The microstructure of the obtained sample CuPbSnGaBi of equiatomic composition after the viscosity measurement were researched additionally by means of optical microscopy and measurement of microhardness.

2 Experimental material(s) and methods

The sample alloys of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi equiatomic composition were produced in the laboratory in a resistance furnace in an inert gas atmosphere. The starting materials were Mk00 copper, tin brand “000”, lead brand “h”, bismuth granular mark “h”, gallium brand “0” and bismuth mark “h” ingots. The kinematic viscosity was measured using the oscillating cylinder method during heating and subsequent cooling. The measurements were carried out in the temperature range 600–1600 K with the isothermal delay no less than 30 min at relatively small (50 K) stepwise temperature changes. A given temperature was maintained to accuracy to 1 K using a high-precision controller. The vibration parameters were measured using an optical method with a system of photoregistration of vibrations. The experimental technique and the processing of experimental data have been described in detail [17, 18]. BeO crucibles were used in all experiments. All of the experiments were carried out in a high-purity helium atmosphere at a pressure of 10^5 Pa. The systematic error of measuring viscosity was 3wt% and including the random error no higher than 1.5% at a confidence level of 95%.

Metallographic investigation of the structure of the CuPbSnGaBi sample of the equiatomic composition was carried out using conventional methods. The cooling rate during the crystallization of the sample was 10 K/s. The study was conducted by means of optical on unetched and polished sections of etched alloy (etching carried out in an alcoholic solution of 3% HNO_3). A microhardness gage PMT-3 was used for the measurement of microhardness with a load of 0.1–0.5 H.

3 Results and discussion

Fig. 1 and **Table 2** show the results of a viscometric study of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi liquid alloys of equiatomic composition. All of the investigated melts demonstrate different heating and cooling temperature dependences of viscosity $\nu(T)$, i.e. hysteresis. The T^* temperature was measured by following the experience of the authors [8, 9, 10]. T^* is the temperature of the beginning of the matching portion of the temperature dependence of the viscosity, which is obtained by heating and cooling. Temperature T^* is 1410 K for alloy CuPb, 1180 K for alloy CuPbSn, 1230 K for alloy CuPbSnGa and 1460 K for alloy CuPbSnGaBi. Notice that there is a higher viscosity measured on heating than on cooling (**Fig. 1**). The most significant decrease in the viscosity at low temperatures (near the liquidus) is for melt CuPbSn. The temperature T^* value is increased with increasing number of components in the melt (**Table 1**). It is interesting to note that values of $\frac{d\nu}{dT}$ for all studied melts during cooling were equal to or lower than the corresponding values of $\frac{d\nu}{dT}$ recorded during heating (**Fig. 1**). Heating the liquid alloys CuPbSnGa and CuPbSnGaBi to 1100 K leads to an increase in the viscosity. The increase in the viscosity on heating can be explained by the quasi-gaseous state in the melt, which is retained during subsequent cooling of the metallic liquid. The quasi-gaseous behaviour of the melt, i.e. an increase in the viscosity with the temperature of the metallic liquid was earlier noted in Ref. 2 for the liquid metal and was associated with changes in the vacancy subsystem of the melt.

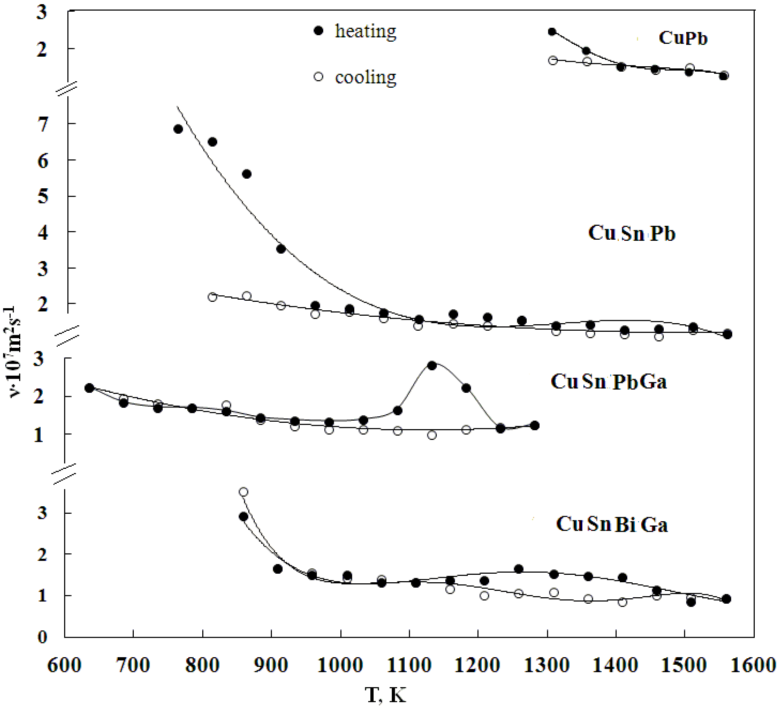

Fig. 1 Viscosity of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi melts of equiatomic compositions [8,9,10]

Our attention was focused on the changing characteristics of the viscous flow of the melts. The activation energy of viscous flow and the entropy factor in the Arrhenius equation $v = A\exp(E/RT)$ change when heating the liquid alloy to the temperature $T^{\#}$ ($T^{\#}$- is temperature of the beginning of structural transformations). The temperature dependences of viscosity of liquid CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi alloys of equiatomic compositions and deviation from the Arrhenius behaviour were found when the temperature was about 100–300 K higher than the melting point (**Fig. 2**).

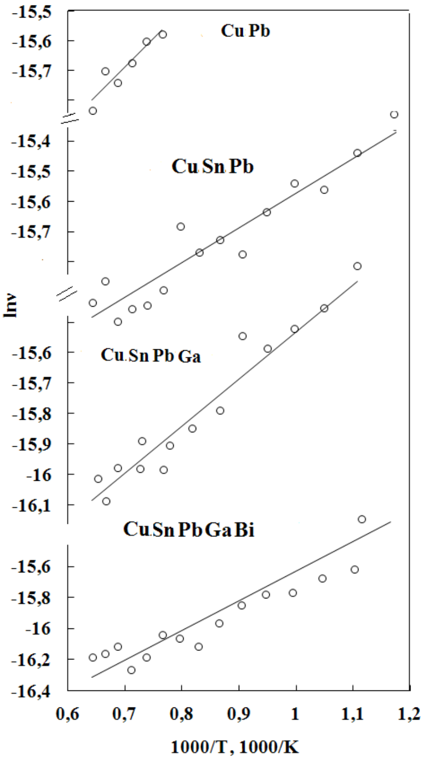

Fig. 2 The dependence of ln v on (1000/T) for melts upon cooling

The abnormal increasing of the viscosity and activation energy indicate changes of the melt structure during cooling. The temperature $T^{\#}$ for CuPb; CuPbSn; CuPbSnGa and CuPbSnGaBi melts is in the range of 900–1180 K. With increasing number of components in the melt, the value of $T^{\#}$ is reduced (**Table 1**).

Table 1 The temperature of anomalous behaviour for viscosity of the melt, which is interpreted in terms of the characteristics of the structural state melts

The alloy of equiatomic compositions	T^*, K	$T^{\#}$, K
CuPb	1410	–
CuPbSn	1180	1180
CuPbSnGa	1230	1060
CuPbSnGaBi	1460	920

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The temperature dependence of the viscosity coefficient deviates from predictions of the classical theory of absolute reaction rates. According to the theory of absolute reaction rates [19], melt viscosity can be described by the equation $\nu = \frac{hN_A}{\mu}\exp(\Delta G^{\#}/RT) = \frac{hN_A}{\mu}\exp(-\frac{\Delta S^{\#}}{R})\exp(\frac{\Delta H^{\#}}{RT})$,

where h is the Planck constant, N_A is the Avogadro constant, $\Delta G^{\#}$ is the free energy of activation of viscous flow, μ is the molar mass, $\Delta H^{\#}$ is the enthalpy of activation of viscous flow, $\Delta S^{\#}$ is the entropy of activation of viscous flow, R is the universal gas constant and T is the temperature. The entropy factor in the Arrhenius equation $A = \frac{hN_A}{\mu}\exp(-\frac{\Delta S^{\#}}{R})$ depends on the entropy of viscous flow, $\Delta S^{\#}$. The activation energy ε and the entropy of activation of viscous flow $\Delta S^{\#}$ for CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi melts upon cooling were calculated (**Table 2**). With an increasing number of components in the melt, the absolute values of the activation energy ε and entropy of activation of viscous flow $\Delta S^{\#}$ are reduced.

Table 2 The activation energy ε and entropy of activation of viscous flow $\Delta S^{\#}$ for melts upon cooling

Alloy	**$-\Delta S^{\#}$, J·K^{-1}**	**Activation energy ε, kJ·mol^{-1}**
CuPb	31.3	14.9
CuPbSn	29.7	13.5
CuPbSnGa	28.8	12.5
CuPbSnGaBi	27.6	9.97

In experiments with liquid alloy CuPb, lower viscosity values than those specified in previous reports [20-22] were recorded, which the authors attribute to the equiatomic alloy composition (up to 0.01 g). The prevailing feature of the liquid Cu50Pb50 system is the existence of a monotectic turning.

The of viscosity results for alloys CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi equiatomic composition can be qualitatively interpreted using the concepts of microheterogeneity in liquid alloys [8, 9]. According to these concepts, when the liquidus line is reached, an atomically homogeneous solution does not form immediately and the heterogeneity state of the melt in the form of two phases differing in chemical composition is retained in the temperature range characteristic of each composition. In the region of states where a liquid metal contains microheterogeneities, the values of viscosity measured on heating and cooling a sample are different. At higher temperatures, the difference in the values of viscosity is within the random measurement error. The temperature T^* corresponding to branching curves ν (T) corresponds to the transition of the melt to the state of true solution. The increase in the melt viscosity during heating in microinhomogeneous condition can be explained by the process of dispersing the microheterogeneities. The temperature $T^{\#}$ corresponds to the beginning of the process of destroying microheterogeneities. Experiments in Ref. 6 show that for the destruction of microscopic inhomogeneities, enough liquid alloys needs to be heated to $T^{\#}$ and to stand for a while. The value $T^{\#}$ is always less than or equal to T^*. Differences between $T^{\#}$ and T^* values were detected for the alloys composed of four and five components (**Table 2**).

The main problem of production of the HEAs is related to the formation of a homogeneous structure of volumetric ingots. A separation by density in the gravitational field occurs on cooling of the multicomponent liquid alloys. The result is a heterogeneous ingot, the lower portion of which is enriched by the heavy components during curing. The separation of solidifying liquid metal can be suppressed by using a high cooling rate (10^3–10^6 K/s). The most promising method of suppressing the separation of HEAs and the production of a material with a homogeneous structure is a homogenization of metallic liquid, i.e. overheating above the certain temperature T^* [6]. This method makes it possible to produce bulk ingots with the required structure under conditions of natural gravitation even at fairly low cooling rates. After such an overheating, the melt changes irreversibly to the state of true solution, which substantially changes the conditions of metal solidification. We have the assumption that the heating of the liquid metal above the temperature T^* in the subsequent crystallization even at relatively low speeds will provide homogeneous structure volumetric ingots for the HEAs [14].

To test this hypothesis, we conducted a metallographic study of the structure of the ingot CuPbSnGaBi alloy obtained after the viscosity measurement. Before crystallization, the ingot was heated to a temperature higher than T^*.

Images of the microstructure of CuPbSnGaBi sample of equiatomic alloy are shown in **Fig. 3**. The microstructure consists of multiple phases evenly spread over the section of the ingot.

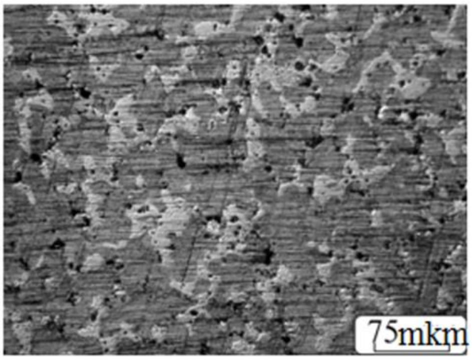

Fig. 3 The microstructure of the CuPbSnGaBi alloy [9]

After chemical etching, optical microscopy can distinguish the phase of the dendrites' origin, the dark phase of the small discharge and the interdendritic space consisting of plates, reflecting the morphology of the eutectic plate. The nature of the different phases also proves the sharp difference in the hardness of the structural components. The microhardness of the dendrites is about 2400 MPa, of the dark secretions is 180 MPa and for the eutectic phase is 150 MPa. The authors have suggested according to the data in Ref. 19, that the dendrites are $CuGa_2$. The data of the ternary eutectic (Sn) + (Bi) + Bi_3Pb_7 obtained from metallographic analysis and measurement of the microhardness also agree with the data in Ref. 20. The third component of the structure of the sample is clearly distinguished rounded inclusions of Pb having dimensions of ≈5 μm.

4 Conclusion

1. A viscometric studies of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi melts of equiatomic composition by heating and subsequent cooling were performed. Viscosity was measured using damping torsional vibrations of a crucible with a melt in the temperature range 600–1600 K.

2. The polythermals of the viscosity measured during heating and cooling are different from each other. For all alloys, we have identified specific temperatures at which an irreversible structural change in the state of the melt occurs: T^* and $T^\#$. The temperature T^* at the beginning of the matching portion of the temperature dependence of the viscosity, which is obtained by heating and cooling, was measured. The value of the temperature T^* is in the range 1180–1460 K. When heated to $T^\#$, the melts have a sharp change in the characteristics of viscous flow; the activation energy of viscous flow and the entropy factor in the Arrhenius equation are changed. The value of $T^\#$ is in the range 900–950 K.
3. For all of the studied melts, the values of viscosity during cooling were equal to or lower than the corresponding values recorded during heating. The most significant decrease in the melt viscosity near the liquidus temperature was for the melt CuPbSn.
4. A metallographic study of the structure of the ingot CuPbSnGaBi alloy obtained after the viscosity measurement was conducted. The microstructure consists of multiple phases evenly spread over the section of the ingot. The measurement of microhardness, showed $CuGa_2$ dendrites, a (Sn) + (Bi) + Bi_3Pb_7 triple eutectic, and Pb round inclusions, measuring about 5 microns. We showed that if the liquid metal is heated above the temperature T^*, then the subsequent crystallization even at relatively low speeds will provide homogeneous structure volumetric ingots for the high-entropy CuPbSnGaBi alloy.
5. The results of the viscosity of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi melts of equiatomic composition study can be qualitatively interpreted using the concepts of microheterogeneity in liquid alloys. The temperature T^* corresponding to branching curves $\nu(T)$ corresponds to the transition of the melt to the state of the true solution. The increase in the melt viscosity during heating in a microinhomogeneous condition can be explained by the process of dispersing microheterogeneities. The temperature $T^\#$ corresponds to the beginning of the process of destruction of microheterogeneities.

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