

**VISCOSITY AND ELECTRICAL RESISTIVITY OF LIQUID CuNiAl, CuNiAlCo, CuNiAlCoFe ALLOYS OF EQUIATOMIC COMPOSITIONS**

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Received: 25.09.2019

Accepted: 31.10.2019

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**Abstract**

The kinematic viscosity and electrical resistivity of equiatomic liquid alloys CuNiAl, CuNiAlCo, CuNiAlCoFe has measured during heating of the sample to 2070 K and subsequent cooling. We consider CuNiAl, CuNiAlCo, CuNiAlCoFe alloys of equiatomic compositions as the multi-principal element alloys (MPEAs), the complex concentrated alloys (CCAs), the high-entropy alloys (HEAs). The measuring results of the viscosity and the resistivity are discussed on base the available microheterogeneity concept. We searched the temperature  $T^*$  of the heating a melt for destroy of microheterogeneity.  $T^*$  is the temperature of the beginning of the matching portion of the temperature dependence of the viscosity and resistivity which is obtained by heating and cooling. All the investigated melts demonstrated different temperature dependence of viscosity for heating and cooling. The temperature  $T^*=1800$  K were determined only for liquid alloy CuNiAl of equiatomic composition. For alloys CuNiAlCo, CuNiAlCoFe the coinciding part of the temperature dependences of the viscosity which are obtained by heating and cooling is absent. The results of viscosity are discussed within the theory of absolute reaction rates. Entropy of activation of viscous flow and free activation energy of viscous flow were determined by analyzing the temperature dependences of kinematic viscosity. The increasing of components quantity in the alloy leads to the increasing of the free activation energy of viscous flow and the volume per structural unit of the melt (ion, atom, or cluster). The measuring results of resistivity were interpreted using the Nagel-Tauc model. The temperature coefficient of resistivity (characteristic of the structural state of the melt) was determined. The temperature dependences of the CuNiAl liquid alloy resistivity measured upon heating to 2070 K and subsequent cooling do not coincide. The value of  $T^*$  temperature for alloy CuNiAl of equiatomic composition is 1850 K. For CuNiAlCo, CuNiAlCoFe alloys the temperature dependences of the resistivity which are obtained by heating and cooling are coinciding. This means that destroy of microheterogeneity for melts after heating up to 2070K did not occur. The temperature coefficient of resistivity of the CuNiAl liquid alloy irreversibly decreases when it heated to a temperature of 1850 K. This is evidence of the destruction of microheterogeneity with the formation of a homogeneous solution at the atomic level. The increasing of components quantity in the alloy leads to a decreasing of the temperature coefficient of the resistivity (in cooling mode). According to the ideas of Nagel and Tauc, an irreversible decrease of the temperature coefficient of the specific resistance of the melt indicates an increase in the volume per structural unit of the melt (ion, atom, or cluster)

**Keywords:** multi-principal element alloys (MPEAs), complex concentrated alloys (CCAs), high-entropy alloys (HEAs), melts, microheterogeneity, viscosity, resistivity

## 1 Introduction

CuNiAl, CuNiAlCo, CuNiAlCoFe alloys of equiatomic compositions are the multi-principal element alloys (MPEAs), the complex concentrated alloys (CCAs), the high-entropy alloys (HEAs). The fields of MPEA, CCA, HEAs have expanded and now include microstructures with any number of phases and phases of any type. The scope of their application includes both structural and functional materials [1-6]. Regardless of classification, the researchers are based on the study of structure-properties and processing relations in these multicomponent alloys with the aim to surpass the physical properties of conventional materials [7]. Currently, two concepts HEA are being formulated: the 'entropy effect' and the 'sluggish diffusion' [1,2]. The effects of entropy on the structure and properties of alloys are summarized in terms of thermodynamics, kinetics, and size and position of atoms [1,3]. "The sluggish diffusion effect" of the HEA leads to the low coarsening rate of solid phase compared with other conventional alloys [2]. A rationale for the HEAs is that the configurational entropy contribution to the total free energy in alloys with five or more major elements can stabilize the solid-solution state relative to multiphase microstructures. It is important factor in the obtaining of high-entropy alloys is the high cooling rate of metal during crystallization which makes it impossible to disintegration of solid solution and formation of chemical compounds.

Most of the HEA research focused on alloy design, microstructural characterization, and mechanical testing rather than manufacturing, processing, and industrialization, although the properties, microstructures, and performance are strongly dependent on processing. The manufacturing process of HEAs can be classified into three main routes: liquid processing, mechanical alloying, and mixing elements of the vapour state [8]. In this article, we aim to describe the liquid of processing, the cast manufacturing processes applied to HEAs. High-entropy alloys (HEAs) can have either high strength or high ductility; a simultaneous achievement of both at the same time is still a difficult task. The inferior cast ability and compositional segregation of HEAs are also obstacles for their technological applications. To solve these problems we proposed a novel strategy to design HEAs using the microheterogeneity concept. This concept is based on numerous experimental data which indicate that at temperatures higher than the liquidus temperatures multicomponent metallic alloys can have microheterogeneities, the chemical composition of which differs from the composition of the surrounding melt for a long time [9]. To destroy of the microheterogeneity a liquid metal should be overheated to the temperature that is certain for each composition. After this action the melt irreversibly transforms into the state of the true solution which substantially changes the conditions of its solidification. The high cooling rate of metal which is technically difficult to ensure can be replaced by the destruction of the microinhomogeneity of the liquid HEA before crystallization. It is known that subsequent cooling and crystallization even at relatively low cooling rates (1-10 K/s) enables to obtain a microstructure similar to the microstructure that is formed at high cooling rates.

Alloys of the Cu – Ni – Al – Co – Fe system are the subject of extensive structural studies [10-11], nevertheless, the properties of the liquid state of these alloys [12-14] associated with their processing are little studied. For example, the density of the liquid equiatomic AlCoCrCuFeNi alloy as well as the quaternary AlCoCuFe alloy was determined over a wide temperature range [12]. The viscosity of CuNiAl liquid alloys was studied using the oscillating crucible method [13] and the enthalpy of mixing  $\Delta H$  of liquid ternary CuNiAl alloys at 1700 K was measured using a high-temperature mixing calorimeter [14]. The values the electrical resistivity and viscosity of liquid Cu-Ni binary alloys were measured [15-16]. Similar results for the ternary system Cu-Ni-Al are not known to the authors.

In this work we based on the available microheterogeneity concept. The liquid AlCuNi, AlCuNiCo, AlCuNiCoFe alloys have been qualitatively studied by measuring the viscosity and resistivity during the heating/cooling process. The results of viscosity and resistivity measurements of the CuNiAl, CuNiAlCo, CuNiAlCoFe melts equiatomic composition are important for cast industry also.

## 2 Experimental material(s) and methods

The samples CuNiAl, CuNiAlCo and CuNiAlCoFe alloys equiatomic composition were obtained by vacuum arc melting at laboratory. High purity metals, i.e., aluminum of A999 special purity grade, 99.9%, copper of the Mk00 brand (99.98%) and carbonyl iron (special purity grade, 99.98%) were applied as initial materials.

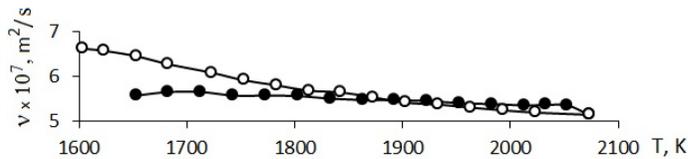
The kinematic viscosity was measured using by the oscillating cylinder method during heating and subsequent cooling. The measurements were carried out in the liquidus temperature range up to 2070 K with an isothermal delay at least 30 min with relatively small (50 K) stepwise temperature changes. A set temperature was maintained accurate to 1K using a high-precision controller. The vibration parameters were measured optically using a photo recording system of vibrations. We used BeO crucibles in all experiments. All the experiments were carried out in a high-purity helium atmosphere at a pressure of  $10^5$  Pa. We did not observe signs of melt evaporation and a decrease in the sample mass. The kinematic viscosity was measured using the unit described in [17]. The systematic error of measuring viscosity was 3%, including a random error of no higher 1.5% at a confidence level 95%.

The resistivity  $\rho$  of liquid CuNiAl, CuNiAlCo and CuNiAlCoFe alloys equiatomic composition were measured using the rotating magnetic field method during heating to 1830K and subsequent cooling. A working chamber was initially evacuated to 0,001 Pa, and then filled with helium to a pressure of  $10^5$  Pa. Samples were kept in the chamber with an inert atmosphere for 5-8 min at the melting temperature and then heated to 1830K at a step of 30-50K. Isothermal holding at the measurement points was at least 15 minutes. The electrical resistivity was measured using the unit described in [18]. The estimation of the error in the measurement of resistivity by the technique described in [1] showed that the total relative error was about 3% when using BeO crucibles. The systematic error in the resistivity measurement was 5%, including the random error no higher 2% at a confidence level of 95%.

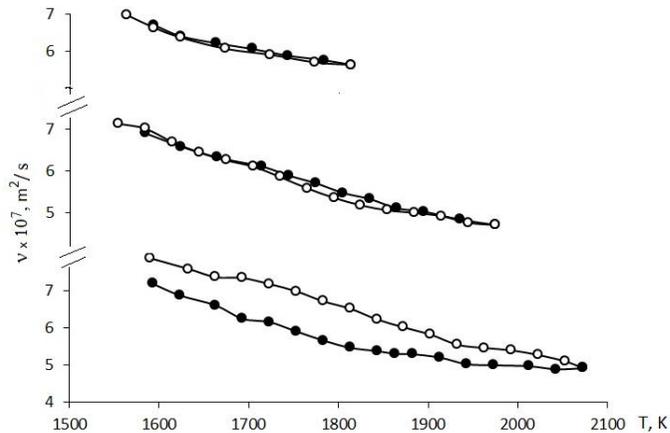
## 3 Results and discussion

Figures 1-3 show the results of a viscosimetric study of liquid alloys CuNiAl, CuNiAlCo, CuNiAlCoFe of equiatomic composition. All the studied melts demonstrate different temperature dependences of viscosity when heated to 2070 K and cooled, i.e., a hysteresis. The temperature  $T^*$  is the temperature of the beginning of the coinciding part of the temperature dependence of the viscosity which is obtained by heating and cooling. The value of temperature  $T^*$  for alloy CuNiAl of equiatomic composition is 1800 K (**Fig. 1**). For CuNiAlCo, CuNiAlCoFe alloys, the coinciding part of the temperature dependences of the viscosity obtained during heating and cooling is absent (**Fig. 2-3**). We showed that the hysteresis appears only when the CuNiAlCo alloy is heated to 2070 K (**Fig. 2**). This means that destruction of microheterogeneity and the transition of the melt state into the true solution after heating to 2070 K for CuNiAlCo, CuNiAlCoFe alloys did not occur. It is interesting to note that viscosity values for all studied melts during cooling were equal to or higher than the corresponding values recorded during heating (**Fig. 1-3**). The most significant

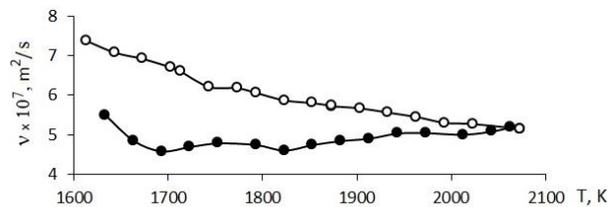
increase in the viscosity at low temperatures (near liquidus) is characteristic for CuNiAlCoFe melt. An increase in melt viscosity during cooling in a microinhomogeneous state can be explained by process of dispersion of microheterogeneities. The changes in viscosity occurred non monotonically when heating of the liquid alloys CuAlNi, CuNiAlCoFe. The temperature dependency of viscosity for cooling is monotonic and obeys an Arrhenius law  $\nu = A \exp(E/RT)$  for all alloys (Fig. 4). Our attention was focused on changing the characteristics of the viscous flow of melts. The activation energy of viscous flow E and the entropy factor A in the Arrhenius equation change when a liquid alloy is heated to the temperature T\* (T\* - is temperature of structural transformations).



**Fig. 1** The temperature dependences of the kinematic viscosity of the CuNiAl melts (● - heating, ○ - cooling)



**Fig. 2** The temperature dependences of the kinematic viscosity of the CuNiAlCo melts (● - heating, ○ - cooling)



**Fig. 3** The temperature dependences of the kinematic viscosity of the CuNiAlCoFe melts (● - heating, ○ - cooling)

According to absolute reaction rate theory [19], the melt viscosity is described by the equation:

$$\nu = \frac{hN_A}{\mu} \exp(\Delta G^\ddagger/RT) = \frac{hN_A}{\mu} \exp\left(-\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{\Delta H^\ddagger}{RT}\right),$$

where h-Planck's constant,  $N_A$ -Avogadro,  $\Delta G^\ddagger$ -the

free activation energy of viscous flow,  $\mu$ -Molar mass,  $\Delta H^\ddagger$ -the enthalpy of activation of viscous flow,  $\Delta S^\ddagger$ -the entropy of activation of viscous flow,  $R$ -the universal gas constant and  $T$ -temperature. The Entropy factor in the Arrhenius equation  $A = \frac{hN_A}{\mu} \exp\left(-\frac{\Delta S^\ddagger}{R}\right)$  depends on the

entropy of viscous flow  $\Delta S^\ddagger$ . We calculated the free activation energy of viscous flow  $\Delta G^\ddagger$  and the entropy of activation  $\Delta S^\ddagger$  of viscous flow for all liquid alloys upon cooling (**Table 1**). Increasing of components quantity in melt leads to increasing of the free activation energy of viscous flow  $\Delta G^\ddagger$  and the entropy of activation of the viscous flow  $\Delta S^\ddagger$ . In accordance [16, 20] entropy factor  $A$  in the Arrhenius equation is presented in this work as a function of volume per melt

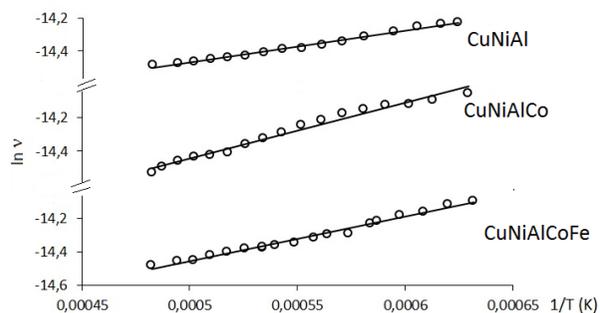
structural unit (ion, atom, or cluster)  $\nu$ :  $A = \frac{h}{\nu \cdot d}$ . The volume per structural unit of the melt

(ion, atom, or cluster) is in this case  $\nu = \frac{h}{A \cdot d} = \frac{\mu}{N_A \cdot d} \cdot \exp\left(\frac{\Delta S^\ddagger}{R}\right)$ , where  $d$  is the density of the

melt. Thus, an increase in the number of components in the alloy leads to an increase in the free activation energy of viscous flow  $\Delta G^\ddagger$  and volume per structural unit of the melt (ion, atom, or cluster)  $\nu$ .

**Table 1** The free activation energy of viscous flow  $\Delta G^\ddagger$ , and the entropy of activation of viscous flow  $\Delta S^\ddagger$  for melts upon cooling

The alloy	The entropy of activation of viscous flow $\Delta S^\ddagger$ (J·K <sup>-1</sup> )	The free activation energy of viscous flow $\Delta G^\ddagger$ , (kJ·mol <sup>-1</sup> ·K <sup>-1</sup> )
CuNiAl	-26.65	15.96
CuNiAlCo	-24.30	22.05
CuNiAlCoFe	-21.48	27.29

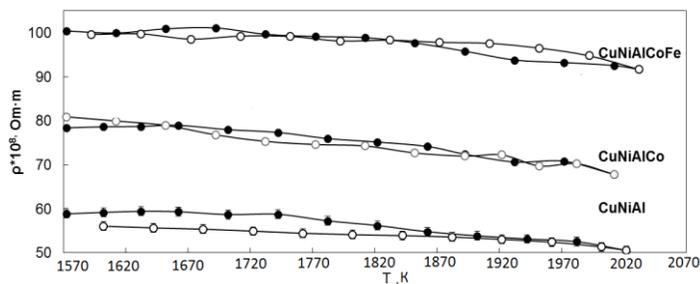


**Fig. 4** The dependences of  $\ln \nu$  ( $1/T$ ) for melts upon cooling

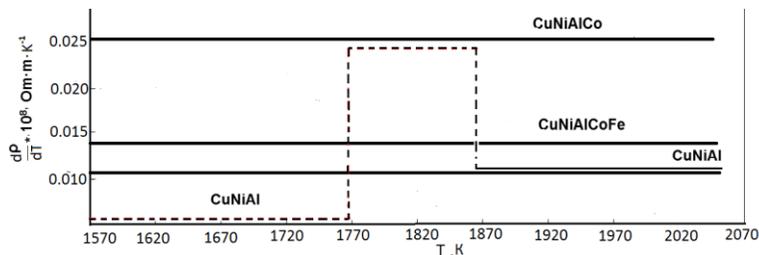
**Fig. 5** shows results of the resistivity study of liquid alloys CuNiAl, CuNiAlCo, CuNiAlCoFe equiatomic composition. The liquid alloy CuNiAl demonstrates a different temperature dependence of the resistivity for heating and cooling, i.e., a hysteresis (**Fig. 5**). The temperature value  $T^*$  for the CuNiAl alloy of equiatomic composition is 1850 K (**Fig. 5**). For CuNiAlCo, CuNiAlCoFe alloys the temperature dependences of the resistivity obtained by heating and cooling coincide. This means that the transition of the state of the melt into the true solution does

not occur after heating to 2070K. When the liquid alloy CuNiAl is heated, the resistivity  $\rho$  does not always linearly increase with temperature. The CuNiAl melt shows a change in the temperature coefficient of resistivity for heating (**Fig 6, dotted line**). The reliability of approximation  $R^2$  of the dependence  $\rho(T)$  in the heating mode from 1570 to 1770 K for CuNiAl alloy is anomalous - 0.17, and for the other dependences  $\rho(T)$ , the values of  $R^2$  are 0.98-0.83. The value of  $R^2$  characterizes the reliability of the approximation: the closer the value of  $R^2$  to unity, the more reliable the trend line shows the process under study. The temperature range in which the destruction of microheterogeneity occurs was defined as 1770 -1870 K.

The temperature coefficient of the resistivity  $d\rho/dT$  for the CuNiAl alloy of equiatomic composition upon heating to the melt to the temperature of  $T^* = 1850$  K, accompanied by destruction of microheterogeneity and mixing components at the atomic level, irreversibly decreased from  $0.025 \cdot 10^{-8}$  to  $0.012 \cdot 10^{-8} \text{ Om} \cdot \text{m} \cdot \text{K}^{-1}$  (**Fig. 6**).



**Fig. 5** The temperature dependences of the resistivity of CuNiAl, CuNiAl, CuNiAlCoFe equiatomic composition liquid alloys (● - heating, ○ – cooling)



**Fig. 6** The dependences of  $d\rho/dT(T)$  for melts upon cooling. The dependences of  $d\rho/dT(T)$  for CuNiAl melt upon heating (dotted line).

Also the increasing of components quantity in the alloy leads to a decreasing of the temperature coefficient of the resistivity (in cooling mode). A similar result was obtained earlier when the measuring electrical resistivity of liquid steel [18, 20]. As microheterogeneity is destroyed and components are mixed on an atomic scale in a liquid alloy, the number of conduction electrons  $z$  increases and, consequently, Fermi wave number  $k_F = (3\pi^2 z / \Omega)^{1/3}$ , where  $\Omega$  is the crystallite volume. In this case, according to the Faber-Ziman theory, the determining factor is an increase in structure factor  $a(2k_F)$ . When doubled Fermi wave vector  $2k_F$  becomes equal to the wave number corresponding to the position of the first peak of the structure factor ( $2k_F = Kp$ ), the resistivity becomes maximal. According to the Ziman theory, the temperature coefficient of resistivity is close to zero or negative in the region where  $2k_F = Kp$ , since the height of the first

structure factor peak decreases with increasing temperature. It is remarkable that the  $2k_F = K_p$  condition is the basis of the Nagel-Tauc model which explains the high tendency of eutectic alloys to supercooling and the glass transition. According to this model when the condition  $2k_F = K_p$  is fulfilled, a potential barrier appears for nucleation of crystallite, the melting temperature (eutectic temperature) of the alloy decreases, and the glass transition temperature increases [18, 20]. An increase in the supercooling of a liquid alloy is caused by an increase in the volume per structural unit of the melt (ion, atom, or cluster).

#### 4 Conclusion

A promising method for producing multicomponent alloys with a homogeneous structure is heating the melt to destroy microheterogeneity and mixing components at the atomic level, i.e. more than temperature  $T^*$  for each composition. This method makes it possible to produce the bulk ingots with the required structure under conditions of natural gravitation even at fairly low cooling rates. After such overheating, the melt irreversibly goes into the state of the true solution, which substantially changes the solidification conditions. Based on the available microheterogeneity concept the liquid CuNiAl, CuNiAlCo, CuNiAlCoFe alloys were qualitatively studied by measuring the viscosity and resistivity during the heating/cooling.

The results of viscosimetric study of CuNiAl, CuNiAlCo, CuNiAlCoFe liquid alloys of equiatomic composition show that temperature  $T^*$  value for the CuNiAl alloy of equiatomic composition is 1800 K. For CuNiAlCo, CuNiAlCoFe alloys, the coinciding part of the temperature dependences of viscosity which are obtained upon heating to 2070 K and cooling, is absent. The results of the study of resistivity of the liquid alloys CuNiAl, CuNiAlCo, CuNiAlCoFe of equiatomic composition show that the value of temperature  $T^*$  for alloy CuNiAl of equiatomic composition is 1850 K. The temperature dependences of the resistivity of the liquid alloys CuNiAlCo, CuNiAlCoFe by heating and cooling coincide. Heating of liquid alloys CuNiAlCo, CuNiAlCoFe above 2070 K is impossible, since intense evaporation of metal begins. Based on the available microheterogeneity concept of multicomponent liquid alloys and results of the measuring viscosity and resistivity, we assume that the heating the CuNiAl liquid alloy up to 1800 K and subsequent crystallization, even at relatively low speeds, provide with a more homogeneous structure volumetric ingots.

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### Acknowledgement

*Authors are grateful for the support of experimental works by Act 211 Government Russian Federation, contract № 02.A03.21.0006.*