

Viscosity and Separation of Fe–Cu Melts

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Abstract—A viscosimetric study of Fe–Cu melts is performed on heating and subsequent cooling of samples. The results of measurements in the above-liquidus part of the phase diagram are used to construct the boundaries of colloid-scale microheterogeneities in a melt.

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INTRODUCTION

In recent years, Fe–Cu alloys characterized by the existence of a miscibility gap in the phase diagram attract attention of researchers [1]. The alloys exhibit good damping characteristics and high corrosion resistance in a damp atmosphere and salt solutions. The main problem of production of Fe–Cu alloys is related to the formation of a structure uniform in cross section with highly dispersed precipitates. On cooling, the alloys heated above the miscibility-gap temperature separate before solidification into two liquids, which are separated in density in the gravitational field. As a result, a heterogeneous ingot whose bottom part is enriched in the heavy component forms during solidification. The separation can be suppressed by either solidifying a liquid metal at a high (10^3 – 10^6 K/s) cooling rate or in the absence of the gravitational field [2, 3].

A miscibility gap forms in liquid Fe–Cu alloys in a supercooled melt (the degree of supercooling to 100°C or higher) [4, 5]. In the phase diagram, the curve of separating the Fe–Cu system into two phases enriched in iron and copper disposes below the liquidus curve.

Binodal T_{bin}^L , spinodal T_{spin}^L , and line $T_0^{L/\text{fcc}}$ that is the geometric place of points corresponding to the equality of the Gibbs energies of phases were calculated in [4]. Figure 1 depicts the line of separating supercooled Fe–Cu melts L_1 and L_2 , i.e., liquids enriched in copper and iron, respectively, calculated in [4]. The coordinates of the upper critical point are $x_{\text{Fe}} = 0.548$ at 1701 K. The spinodal of a liquid solution is the line corresponding to points in which the second derivative of the Gibbs free energy of a phase with respect to its composition is zero. In the region limited by the spinodal, the system is unstable, and it should decompose before any further transformations with the participation of this system. Thus, the intersections of line $T_0^{L/\text{fcc}}$ and the liquid phase spinodal deter-

mine the theoretical saturation limit of the ε and γ phases during quenching from the liquid state. The coordinates of the corresponding intersection points are $x_{\text{Fe}} = 0.194$ at 1430 K for the ε phase and $x_{\text{Fe}} = 0.656$ at 1660 K for the γ phase. The curve of separation of the Fe–Cu system into two phases enriched in iron and copper is known. It was constructed using the measured data on magnetic susceptibility [5]. The position of this curve in the Fe–Cu phase diagram (Fig. 2) agrees with the data from [4].

Thus, as follows from [4, 5], an Fe–Cu melt can undergo separation in supercooling. The binodal near the equiatomic composition is most close to the equilibrium liquidus line. The supercooling of melts with $x_{\text{Fe}} = 0.08$ – 0.75 that is necessary to approach the binodal boundary does not exceed 70 K. In this case, similar supercooling in the concentration range $x_{\text{Fe}} = 0.35$ – 0.65 leads to the separation of the metal, since

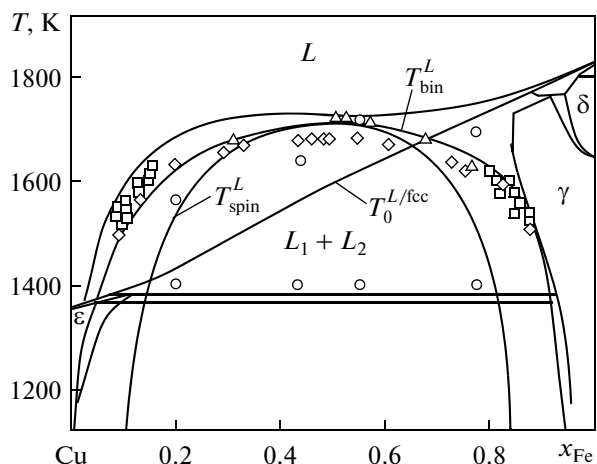


Fig. 1. (points) Experimental and (lines) calculated boundaries of the transformations in Fe–Cu alloys.

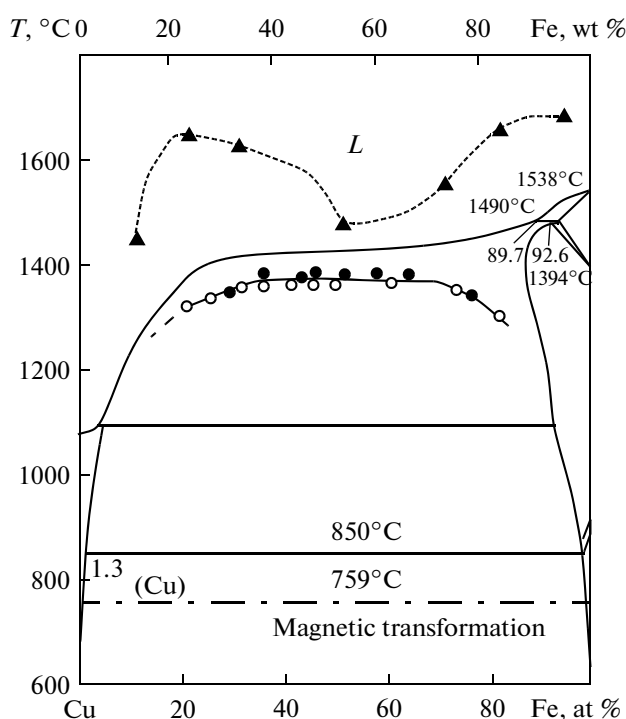


Fig. 2. Fe–Cu phase diagram [4]: (●, ○) miscibility gap into two phases enriched in iron and copper, respectively, that was constructed from the results of studying the magnetic susceptibility [5]; (▲) dome of decomposition of a metastable microheterogeneity that was constructed from the melt viscosities in this work.

the spinodal boundaries of the liquid phase are reached under these conditions. Such a supercooling is easily reached under conditions of real experiments; i.e., the separation of the melt with subsequent fixation of this state in the structure of the solidified metal is possible.

The most promising method of suppressing the separation of an Fe–Cu melt and the production of a material with a homogeneous structure is thought to be homogenizing heat treatment of a metallic liquid [6–8]. This method makes it possible to produce bulk ingots with the required structure under conditions of natural gravitation even at fairly low cooling rates. The method is based on the assumption that fine-dispersed colloid-scale droplets enriched in one of the components can exist beyond the miscibility gap in a metallic liquid for a long time. Energy actions on the melt, e.g., overheating above the miscibility gap to a certain temperature T_{hom} for each composition, are necessary to destroy them. After such an overheating, the melt changes irreversibly to the state of true solution, which substantially changes the conditions of metal solidification. There is a promising homogenization method based on alloying of a melt with materials that decrease the interphase tension at the boundary of colloid particles [9]. This method allows a decrease in

temperature T_{hom} corresponding to an irreversible transition into a homogeneous state.

It was experimentally found in [6–8] that the destruction of the microheterogeneous structure of the melts of monoeutectic systems (Al–In, Al–Pb, Ga–Pb) is usually accompanied by anomalies in the temperature dependences of the metallic liquid properties, in particular, viscosity. A difference was found in the temperature dependences of viscosity measured on heating and subsequent cooling of a sample. In this case, temperature T_{hom} corresponding to the irreversible transition of a melt into a homogeneous state was determined from the onset on high-temperature coinciding segments in heating and cooling polytherms. Experimental studies of melts of monoeutectic systems revealed an anomalously high scatter of kinematic viscosity, which makes it impossible to correctly determine this value. On heating up to temperatures certain for each composition, this scatter decreases irreversibly to values corresponding to the random error of the measurements. In this case, the temperatures corresponding to the destruction of a microscopically layered state of a melt were found from an irreversible decrease in the scatter of kinematic viscosities.

In this work, we studied the temperature dependences of viscosity $\nu(t)$ of Fe–Cu melts to determine the temperatures of their homogenization at various second-component contents.

EXPERIMENTAL

We studied Fe–Cu alloys containing 4.42, 18.01, 27.4, 40.0, 46.78, 60.0, 67.22, 77.86, and 88.77 mol % Cu. Kinematic viscosity ν was measured using damping torsional vibrations of a crucible with a melt during heating and subsequent cooling. The measurements were carried out in the temperature range 1250–1700°C with isothermal holding no less than 30 min at relatively small (10–15°C) stepwise temperature changes. A given temperature was maintained accurate to 1°C using a high-precision controller. The vibration parameters were measured by an optical method using a system of photorecording of vibrations. The experimental technique and the processing of experimental data are described in detail in [10–13]. Charge materials were Mk00 copper and high-purity carbonyl iron ingots. In all experiments, we used BeO crucibles. The viscosity was measured in a high-purity helium atmosphere at a pressure of 10^5 Pa. The systematic error of measuring viscosity was 3%, and the random error determining the scatter of points from experiment to experiment was no higher than 1.5% at a confidence level $p = 0.95$.

RESULTS AND DISCUSSION

Figure 3 shows the results of a viscosimetric study of liquid Fe–Cu alloys. The samples containing 4.42, 18.01, 27.4, 46.78, 67.22, 77.86, and 88.77 mol % Cu demonstrate different of heating and cooling polytherms, i.e., a temperature hysteresis. If the temperatures corresponding to branching the kinematic viscosity polytherms of the melts are plotted in the Fe–Cu phase diagram, we obtain a double-peak domelike curve lying 150–200°C higher than the liquidus line (Fig. 2). The viscosity polytherms of the melts with 67.22 and 88.77 mol % Cu have a coinciding segment at low temperatures. We should focus our attention on the excess of the viscosity measured on cooling as compared to the case of heating. The increase in the viscosity on heating above 1620°C is explained by a quasi-gaseous state in the melt, which is retained in part during subsequent cooling of the metallic liquid. The quasi-gaseous behavior of the melt, i.e., an increase in the viscosity with the temperature of the metallic liquid was earlier noted in [14] for one-component metallic liquids and was associated with changes in the vacancy subsystem of the system. As in experiments with monotectic melts Al–In, Al–Pb, and Ga–Pb [6–8], we observed an increased scatter of the kinematic viscosities on heating of the metal.

These results can be qualitatively interpreted using the concepts of metastable microheterogeneity in liquid alloys [6–8]. According to these concepts, when the miscibility gap (Fig. 2) or the liquidus line is reached, an atomically homogeneous solution does not form immediately and a microlayered state of Fe–Cu melts in the form of two phases enriched in iron and copper 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 of a sample are different. At higher temperatures, the difference in the values of viscosity is within the random measurement error. The temperature corresponding to branching curves $v(T)$ corresponds to the transition of the melt to the state of true solution. A double-peak character of the decomposition of the metastable microheterogeneity of the Fe–Cu melts revealed from the results of measuring the viscosity (Fig. 2) is associated with the fact that the compositions of the contacting phases approach each other as the miscibility gap is reached at the concentrations close to critical value $x_{cr} = x_{Fe} = 0.548$ [4] with increasing temperature [8]. Because of this, we do not observe branching of the viscosity curves (as a mark of disruption of the microheterogeneity), and the liquid metal becomes homogeneous even upon crossing the liquidus line. At concentrations far from x_{cr} , the difference in the phase compositions is substantial and is retained over the entire two-phase region. As a result, after pas-

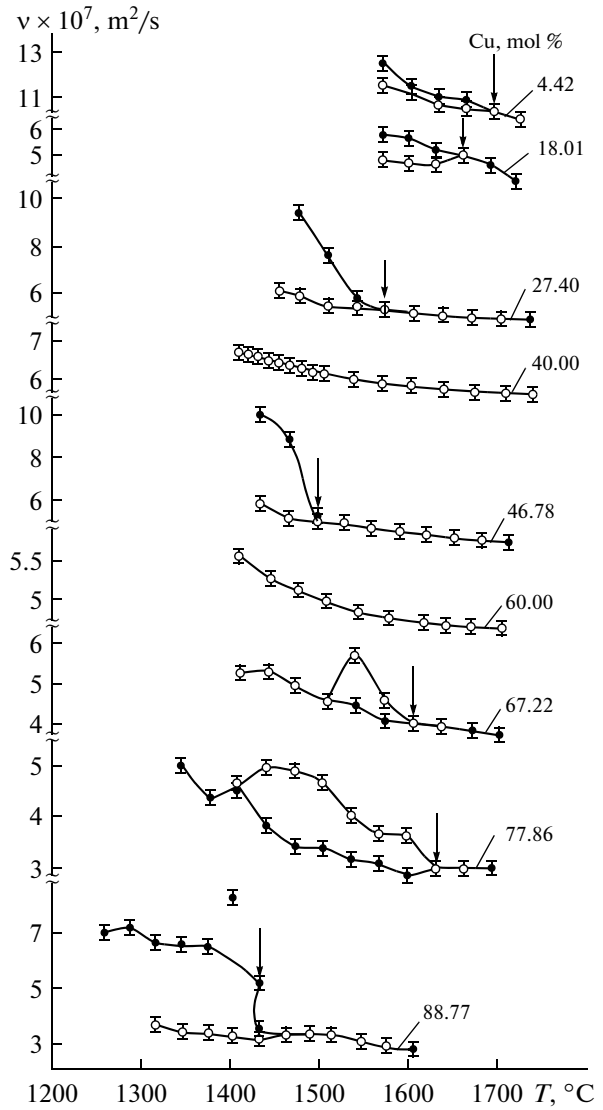


Fig. 3. Temperature dependences of the Fe–Cu melt viscosity measured on (●) heating and (○) cooling. The arrows indicate the homogenization temperature.

sage through the liquidus line, the state of melt becomes microheterogeneous and is retained up to temperatures corresponding to the branching points of the $v(T)$ curves.

CONCLUSIONS

- (1) We performed a viscosimetric study of Fe–Cu melts in heating and subsequent cooling.
- (2) The kinematic viscosity polytherms measured on heating and cooling differ from one other.
- (3) The results of measurements in the above-liquidus part of the Fe–Cu phase diagram were used to plot the boundaries of colloid-scale microheterogeneities in a melt in this diagram.

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