CHEMICAL THERMODYNAMICS
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Estimating the Parameters of the Microheterogeneous Structure of Metal Melts According to Viscometric Experimental Data in Terms of the Absolute Reaction Rate Theory

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Abstract—The temperature dependences of the viscosity of microheterogeneous metal melts are analyzed in terms of the Frenkel−Eyring theory. Using viscometric experimental data, the sizes of dispersed particles in metal melts whose components undergo eutectic and monotectic interactions are numerically estimated.

INTRODUCTION

Numerous experiments have shown that at temperatures above the liquidus, metal melts whose components undergo eutectic and monotectic interactions can be in a microheterogeneous state for long periods of time [1−5]. Microheterogeneity is hereditary; disperse particles have an elemental composition that differs from the composition of the rest of the melt and exist due to the presence of interfacial excess free energy. To ensure the irreversible destruction of a microheterogeneous state, we must overheat the melt above the liquidus line to temperature T^*, which is specific for each composition, or subject it to other energy impacts. After the irreversible destruction of microheterogeneity, the melt transits to a true solution state; this transition leads to substantial changes in the crystallization conditions of the metal, i.e., enhancement of interfacial supercooling. An increase in the degree of supercooling alters the morphology of the eutectic and proeutectoid phases and results in supersaturation of a solid solution based on a component with a lower melting point.

It has been experimentally determined that the degradation of the microheterogeneous structure of metal melts of eutectic and monotectic systems is generally accompanied by anomalies in the temperature dependence of their properties, e.g., viscosity [6−12]. Discrepancies between the temperature dependences of the viscosities of melts that were recorded during the heating and subsequent cooling of samples have in particular been repeatedly observed. The temperature corresponding to the destruction of the microseparation state of the melt and the transition to the homogeneous state was then determined from the point at which the high-temperature portions of the temperature dependences of kinematic viscosity recorded in the heating and cooling modes began to coincide.

Let us consider some experimental data on the microheterogeneity of Al−Si melts as an example [8, 13, 14]. It was found that the temperature dependences of density, viscosity, and resistivity of Al−Si melts undergo branching when the melts are heated to certain temperatures. The branching temperature values depend on the elemental composition of the samples and are consistent with one another for individual properties. The branching of the temperature dependences of the structure-sensitive properties of a melt is indirect evidence of the irreversible destruction of the microheterogeneity inherited from the two-phase crystalline sample. Direct evidence of the irreversible destruction of the microheterogeneity of Al−Si melts of eutectic and hypereutectic compositions that occurs upon heating samples to a temperature specific to each composition is provided by the results from small-angle neutron scattering experiments [15, 16]. Two families of particles—small particles with sizes of 10−40 Å and large particles with sizes of up to 90 Å—have been identified in diffraction experiments. The scattering curve of a eutectic Al−Si melt changed substantially when the sample was heated from 700 to 1200°C: the number of large particles fell, while the number of small particles rose. Upon subsequent cooling, the size and number of large particles grew, while the size and number of small particles remained virtually the same. Eventually, cooling to 700°C led to the almost complete restoration of the initial size distribution with a certain shift to the region of small sizes. Different results were obtained in experiments

on the small-angle neutron scattering of a hypereutectic Al−Si melt. Upon heating the melt to 1200°C, the number of large particles fell almost to zero; during subsequent cooling, the particles grew again, but only to smaller sizes. Upon heating to 1200°C, the number of small particles increased; however, the particles became even smaller. Small-angle neutron scattering experiments thus revealed a partially reversible change in the microheterogeneity of a eutectic Al−Si melt and a completely irreversible change in the microheterogeneity of a hypereutectic Al−Si melt. According to the authors of [15], heating the melt to 1200°C is not sufficient for the irreversible destruction of the microheterogeneous state and the transition of the microheterogeneous melt into a true solution state.

In this work, data on the size of the structural units of a viscous flow (molecules for a homogeneous melt and particles for a disperse system) were derived by analyzing the experimental temperature dependences of the viscosities of Al−Sn, Al−Si, Al−Ge, Cu−Pb, and Cu−Bi−Sn−In−Pb melts. In line with the concepts of rheology of disperse systems [17], the structural units of the viscous flow of a microheterogeneous melt were assumed to be dispersed particles of hereditary nature. The temperature dependences of the viscosity of microheterogeneous metal melts were analyzed in terms of the Frenkel−Eyring theory [18].

At the first stage of our discussion, the flow of a molecular liquid will be analyzed, and an equation describing the variation in viscosity with temperature with allowance for the size of the structural units of a viscous flow will be derived. We shall assume that two layers of molecules of a liquid are spaced at distance λ_1 from one another and one of the layers slides along the other under the action of a force. If f is the force per square meter that tends to shift one layer relative to another and Δn is the difference between the velocities of the two layers, then $\eta = f\lambda_1/\Delta n$, where η is the viscosity coefficient. The motion of one layer relative to another occurs owing to the molecules transitioning from one equilibrium state to another in the same layer; this is regarded as the system passing through a potential energy barrier. Let λ be the distance between two equilibrium positions in the direction of motion, λ_3 be the distance between the adjacent molecules in the direction of motion; and λ_2 be the average distance between two adjacent molecules of the moving layer in the direction perpendicular to the motion; λ and λ_3 are not necessarily equal to each other, but they can have similar values. The action of the force that causes the liquid to flow is a drop of $f\lambda/2 = \lambda_1\lambda_3$ in the height of the energy barrier. If ε_0 is the potential height of the energy barrier when the force does not act on the liquid, the number of passes the molecule makes through the potential energy barrier per second during motion in any direction is

$$k = \frac{kT}{h}\frac{F_+^+}{F}e^{\varepsilon_0/k_BT},$$

where F_+^+ and F are the partition functions per unit volume for a particle in the activated and initial state, respectively; k_B is the Boltzmann constant; h is Planck's constant; and T is the absolute temperature. The partition function of the structural unit of a viscous flow is $F_l = [(2\pi mk_BT)^{3/2}/h^3]v_f b_e e^{-E_0/k_BT}$ [18], where b_e allows for the vibrational and rotational degrees of freedom, E_0 is the difference between the energies per mole for the particles in the liquid and in the gas at 0 K, and v_f is the fluctuation free volume. The following expression is derived for the viscosity coefficient [18]:

$$\eta = \lambda_1 f/2k\lambda\, sh(f\lambda_2\lambda_3\lambda/kT), \qquad (1)$$

where f is small for a conventional viscous flow (it is on the order of 1 dyn/cm^2).

If we assume that λ_2, λ_3, and λ have molecular sizes on the order of 10^{-8} cm^3, then $2kT \gg f\lambda_2\lambda_3\lambda$. Expanding the exponential terms in a series and ignoring all but the first, we obtain

$$\eta = \lambda_1 kT/\lambda_2\lambda_3\lambda^2 k = (\lambda_1 hF/\lambda_2\lambda_3\lambda^2 F_+^+)e^{\varepsilon_0/k_BT}. \quad (2)$$

Assuming that $\lambda \approx \lambda_1$ and $\lambda_2\lambda_3\lambda_1$ is approximately equal to the volume occupied by one molecule in the liquid V_μ/N_A (where V_μ is the molar volume and N_A is Avogadro's number), we find

$$\eta = (hN_A/V_\mu)(F/F_+^+)e^{\varepsilon_0/k_BT}, \qquad (3)$$

where $F/F_+^+ = (2\pi mk_BT)^{1/2}v_f^{1/3}$ [18]. Let us use a simple relationship for cubic packing between free volume v_f and volume v occupied by one molecule in the liquid [18]. If d is the effective diameter of each molecule, then $(2v^{1/3} - 2d)$ is the interval in which the central atom is free to move along each of the axes and $(2v^{1/3} - 2d)^3$ is equal to the free volume of the liquid $v_f = 8(v^{1/3} - d)^3$. In this case,

$$\eta = \frac{N_A}{V_\mu}(2\pi mk_BT)^{1/2}e^{\varepsilon_0/k_BT}v_f^{1/3}, \qquad (4)$$

with respect to the behavior of the temperature dependence of viscosity, Eq. (4) is similar to the well-known formula derived by Panchenkov [19], which is used to approximate the temperature dependences of the viscosity of metal melts:

$$\eta = AT^{1/2}\exp(\varepsilon_0/k_BT), \qquad (5)$$

where $A(v_f) = \text{const}$.

At the second stage of the discussion, the temperature dependence of viscosity similar to the Panchenkov's formula for disperse systems will be obtained. In this case, a microheterogeneous melt is considered to be composed of dispersed particles, each of which moves in a potential field generated by the adjacent particles. In the rheology of disperse systems, this approach is known as the Frenkel−Eyring theory for disperse systems undergoing limited volume-induced structuring [17].

As in the Frenkel−Eyring theory, the distance between the particles and the size of the particle are considered equal; in this case, the fluctuation free volume is $v_f = 8(2d − d)^3 = 8d^3$ and the volume occupied by one particle is $v = 8d^3$. Hence, for the effective viscosity of the disperse system, we obtain

$$\eta = \left[(2\pi m k_B T)^{1/2} / v \right] 2d e^{\varepsilon_0/k_B T}. \tag{6}$$

Assuming that $m = \rho \frac{1}{6} \pi d^3$, the kinematic viscosity of the disperse system can be defined as

$$\nu = B d^{-1/2} T^{1/2} e^{\varepsilon_0/k_B T}, \tag{7}$$

where d is the size of the dispersed particle and $B = \frac{\pi}{4} \left(\frac{k_B}{3\rho} \right)^{1/2}$. Based on data from viscometric studies of metal melts, we can determine the size of a dispersed particle of a microheterogeneous melt according to the preexponential factor.

In this work, the characteristic size of the structural units of a viscous flow was determined on the basis of the experimental temperature dependences of viscosity obtained in [6−8, 20, 21] for melts whose components undergo eutectic (Al−Sn, Al−Si, and Al−Ge) and monotectic interactions (Cu−Pb), and for Cu−Bi−Sn−In−Pb melts of equiatomic compositions. In each case, calculations were performed for two polytherms. The first polytherm was described according to Eq. (7) by approximating the experimental data obtained upon heating the melt to temperature T^*. This polytherm was used to determine the characteristic size of the structural unit of a viscous flow in heating mode d_{heat}. The second polytherm was derived by approximating viscometric experimental data obtained upon heating a melt to temperatures above T^* and in the cooling mode. The second polytherm was also used to determine the respective size of the structural units of a viscous flow d_{cool}. Since the calculations were for estimates, the densities of the aluminum- and copper-based melts were assumed to be equal to those of liquid aluminum at 700°C and liquid copper at 1100°C, respectively.

The experimental data on the temperature dependences of the kinematic viscosity of melts $\nu(T)$ were interpreted in terms of the concepts of the microheterogeneity of liquid alloys [7−9, 15]. According to these concepts, the solution formed immediately after crossing the dome of macroseparation and the liquidus line is not homogeneous at the atomic level, and the state of the microseparation of the melts into two phases with different elemental compositions is preserved in the temperature range specific to each composition. In the region of states where the microheterogeneity of the liquid metal is observed, the viscosity values determined upon heating and cooling the sample are not the same. At higher temperatures, the difference between the viscosity values lies in the range of random measurement errors.

The temperature at which the $\nu(T)$ curves branch corresponds to the transition of the melt to the state of a true solution. After crossing the liquidus line, the melt is in a microheterogeneous state that is preserved up to the temperatures corresponding to the branching points of the $\nu(T)$ curves.

The results from calculating the characteristic size of the structural units of a viscous flow for aluminum-based simple eutectic melts Al−Sn, Al−Si, and Al−Ge are presented in Table 1. The results from determining the characteristic sizes of the structural units of a viscous flow in the heating mode (d_{heat}) and the cooling mode (d_{cool}) suggests that the structural units of a viscous flow in the heating mode can be nanoparticles. The overheating of a metallic liquid above homogenization temperature T^* leads to a two- to tenfold reduction in the characteristic size of the structural units of a viscous flow; this level corresponds to the formation of an atomically homogeneous solution (the characteristic size of a unit of a viscous flow corresponds to that of a molecule with an accuracy of one order of magnitude). An exception is simple eutectic melts Al−Si and Al−Ge of hypoeutectic compositions. In all cases, homogenization of the melt leads to a reduction in particle size. In the cooling mode, the particle size is always several fractions of a nanometer.

The results from calculating the characteristic sizes of the structural units of a viscous flow for Cu−Pb monotectic melts are shown in Table 2. The result from determining the characteristic size of the structural unit of a viscous flow suggests that the structural units of a viscous flow in the heating mode can be nanoparticles. The overheating of a metallic liquid above homogenization temperature T^* leads to a five- to tenfold reduction in the characteristic size of the structural units of a viscous flow; this level corresponds to the formation of an atomically homogeneous solution (the characteristic size of the unit of a viscous flow corresponds to the size of a molecule with an accuracy of one order of magnitude). An exception is the melts of hypomonotectic compositions. In all cases, homogenization of the melt leads to a reduction in particle size. In the cooling mode, the particle size is always several fractions of a nanometer.

The results from calculating the characteristic size of the structural units of a viscous flow for Cu−Bi−

Table 1. Characteristic size of the structural units of a viscous flow for Al–Si, Al–Sn, and Al–Ge melts at $T = 700°C$

Melt, at %	d_{heat}, nm	d_{cool}, nm	$d_{\text{heat}}/d_{\text{cool}}$
Al–3Sn	0.9	0.4	2.1
Al–5Sn	4.0	1.7	2.3
Al–9Sn	2.0	0.4	5.2
Al–19Sn	2.0	0.2	11.1
Al–48Sn	3.0	0.9	3.3
Al–67Sn	0.7	0.5	1.5
Al–5Si	0.1	0.1	1.0
Al–20Si	0.2	0.2	1.0
Al–10Ge	0.3	0.3	1.0
Al–40Ge	1.4	0.2	6.8

Table 2. Characteristic size of the structural units of a viscous flow for Cu–Pb melts at $T = 1100°C$

Melt, at %	d_{heat}, nm	d_{cool}, nm	$d_{\text{heat}}/d_{\text{cool}}$
Cu–3Pb	5.4	0.1	54
Cu–7Pb	3.5	0.1	35
Cu–12Pb	3.2	0.1	32
Cu–17Pb	2.4	0.3	8
Cu–32Pb	2.5	0.2	12.5
Cu–42Pb	4.0	0.4	10
Cu–50Pb	0.5	0.4	1.25
Cu–55Pb	0.4	0.2	2
Cu–73Pb	0.5	0.1	5

Sn–In–Pb melts of equiatomic compositions are shown in Table 3. Since the calculations were for estimates, the density of the melt was determined from the additive dependence. The result from determining the characteristic size of the structural unit of a viscous flow leads to similar conclusions. It was found in particular that heating a melt above homogenization temperature T^* leads to a 5- to 20-fold reduction in the characteristic size of the structural unit of a viscous flow; the $d_{\text{heat}}/d_{\text{cool}}$ value grows along with the number of components, i.e., with the entropy of mixing. Multicomponent metal alloys of equiatomic compositions are thought of as high-entropy objects [22–25]. The entropy of mixing of a multicomponent melt is generally estimated as the entropy of formation of an ideal solution:

$$S_{\text{ideal}} = -(x_1 \ln x_1 + x_2 \ln x_2 + \ldots)k_{\text{B}},$$

where x_i is the mole fraction of component i. The greatest entropy of mixing for a given number of elements is thus exhibited by alloys of equiatomic compositions. In accordance with these concepts, a high entropy of mixing can stabilize the formation of solid solutions and hinder the formation of intermetallic phases during crystallization. High-entropy alloys can thus exhibit high strength and thermal stability combined with fairly high resistance to oxidation and corrosion. For high-entropy melts, a discrepancy between the temperature dependences of kinematic viscosity measured during the heating and cooling of a melt was observed [25]. Temperatures T^* were determined from the points at which the high-temperature portions of the temperature dependences of the kinematic viscosity of the melts, recorded in the heating and cooling modes, began to coincide. It was found that the T^* value grew along with the number of components. In addition, the supercooling of melts has been observed in viscometric experiments, providing still more evidence of their transition to the state of a true solution. According to Eyring's theory [17], the temperature dependence of the kinematic viscosity of a melt can be described by the equation

$$\nu = \frac{hN_A}{\mu} \exp\left(\frac{\Delta G^{\neq}}{RT}\right)$$
$$= \frac{hN_A}{\mu} \exp\left(-\frac{\Delta S^{\neq}}{R}\right)\exp\left(\frac{\Delta H^{\neq}}{RT}\right), \tag{8}$$

where $\Delta G^{\neq}$ is the free energy of activation of a viscous flow, μ is the molar mass, $\Delta H^{\neq}$ is the enthalpy of activation for a viscous flow, $\Delta S^{\neq}$ is the entropy of activation for a viscous flow, and R is the universal gas constant. A comparison of the Arrhenius equation

$$\nu = A \exp(E/k_{\text{B}}T)$$

and Eq. (8) suggests that the entropy factor

$$A = \frac{hN_A}{\mu} \exp\left(-\frac{\Delta S^{\neq}}{R}\right)$$

is determined by the entropy of a viscous flow, $\Delta S^{\neq}$. The results from calculating the entropy of a viscous flow of Cu–Bi–Sn–In–Pb melts of equiatomic compositions are shown in Table 3. The point at issue is in this case the destruction of microheterogeneities of hereditary nature and the change in the characteristic size of the structural units of a viscous flow. It is known that heating is associated with an increase in entropy, and the substance is generally transformed into a modification with greater structural disorder. Upon the homogenization of a microheterogeneous melt, the kinetic units of a viscous flow are individual atoms, rather than dispersed particles. The viscosity coefficient drops abruptly, corresponding to an increase in the entropy of a viscous flow in Eq. (8). A microheterogeneous melt is an ensemble of disperse particles, and it is these particles that are the structural units of a viscous flow. When the melt transits to an atomically homogeneous state (i.e., upon homogenization), the structural units of a viscous flow are individual atoms [15].

Table 3. Characteristic size of the structural units of a viscous flow for Cu−Bi−Sn−In−Pb melts of equiatomic compositions at $T = 1100°C$

Melt, at %	d_{heat}, nm	$-\Delta S^{\neq}$, J/K	d_{cool}, nm	$-\Delta S^{\neq}$, J/K	d_{heat}/d_{cool}
	heating		cooling		
Cu−50Bi	1.4	17.64	0.3	24.74	4.7
Cu−25 Bi−25Sn	1.4	16.63	0.2	27.20	7.0
Cu−25 Bi−25Sn−25 In	1.5	15.89	0.2	24.13	7.5
Cu−20Bi−20Sn−20In−20Pb	4.1	11.92	0.2	25.16	20.5

CONCLUSIONS

The characteristic size of the structural units of a viscous flow (the disperse particles of a microheterogeneous melt) can be determined from the data of viscometric studies of metal melts according to the pre-exponential factor. Assuming that the size of the disperse particles is constant in both the heating and cooling mode, we can determine changes in the size of the structural units of a viscous flow. It was found that the size of the structural units of a viscous flow is an order of magnitude higher in the heating mode than in the cooling mode. The d_{cool} value corresponds to the size of an atom, suggesting that a melt has undergone homogenization and its microheterogeneity has been destroyed. The d_{heat}/d_{cool} value grows along with the number of components, i.e., along with the entropy of mixing.

REFERENCES

1. P. S. Popel, O. A. Chikova, and V. M. Matveev, High Temp. Mater. Processes **14**, 219 (1995).
2. J. Wang, S. He, B. Sun, Q. Guo, M. Nishio, J. Mater. Process. Technol. **141**, 29 (2003).
3. P. S. Popel', Rasplavy, No. 1, 22 (2005).
4. V. M. Zalkin, Russ. J. Phys. Chem. A **79**, 655 (2005).
5. S. Mudry, A. Korolyshyn, V. Vus, and A. Yakymovych, J. Mol. Liq. **179**, 94 (2013).
6. P. S. Popel' and O. A. Korzhavina (Chikova), Zh. Fiz. Khim. **63**, 838 (1989).
7. O. A. Korzhavina (Chikova), P. S. Popel', and B. P. Domashnikov, Izv. Akad. Nauk SSSR, Neorg. Mater. **27**, 1424 (1991).
8. O. A. Korzhavina (Chikova), Rasplavy, No. 1, 10 (1991).
9. P. S. Popel', O. A. Chikova, I. G. Brodova, and I. V. Polents, Fiz. Met. Metalloved., No. 9, 111 (1992).
10. T. D. Kolobova, O. A. Chikova, and P. S. Popel', Metally, No. 6, 32 (2003).
11. T. D. Sukhanova, O. A. Chikova, P. S. Popel', and I. G. Brodova, Rasplavy, No. 6, 11 (2000).
12. O. A. Chikova, Rasplavy, No. 9, 65 (2008).
13. P. S. Popel', E. L. Demina, E. L. Arkhangel'skii, et al., Teplofiz. Vys. Temp. **25**, 487 (1987).
14. Yu. O. Esin, E. L. Demina, S. E. Demin, and P. S. Popel', Zh. Fiz. Khim. **60**, 1791 (1986).
15. J. R. Morris, U. Dahlborg, and M. Calvo-Dahlborg, J. Non-Cryst. Solids **353**, 3444 (2007).
16. M. Calvo-Dahlborg, P. S. Popel, M. J. Kramer, et al., J. Alloys Compd. **550**, 9 (2013).
17. E. E. Bibik, *Rheology of Disperse Systems* (Leningr. Gos. Univ., Leningrad, 1981) [in Russian].
18. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941; Inostr. Liter., Moscow, 1948).
19. O. I. Ostrovskii, V. A. Grigoryan, and A. F. Vishkarev, *Properties of Metallic Melts* (Metallurgiya, Moscow, 1988) [in Russian].
20. O. A. Chikova, O. P. Moskovskikh, and V. S. Tsepelev, Russ. J. Phys. Chem. A **90**, 783 (2016).
21. O. A. Chikova, V. Yu. Il'in, V. S. Tsepelev, and V. V. V'yukhin, Inorg. Mater. **52**, 517 (2016).
22. Jien-Wei Yeh, US Patent No. US20020159914 (2002).
23. F. Otto, Y. Yang, H. Bei, and E. P. George, Acta Mater., No. 61, 2628 (2013).
24. A. Takeuchi, K. Amiya, T. Wada, et al., Entropy **15**, 3810 (2013).
25. O. A. Chikova, V. S. Tsepelev, and V. V. V'yukhin, Russ. J. Non-Ferrous Met. **56**, 246 (2015).

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