VISCOSITY END ELECTRICAL CONDUCTIVITY OF LIQUID HYPEREUTECTIC ALLOYS Al-Si

Olga A. Chikova1), Konstantin V. Nikitin2), Olga P. Moskovskikh1), Vladimir S. Tsepelev1)
1) Ural Federal University, Ekaterinburg, Russian Federation
2) Samara State Technical University, Samara, Russian Federation

Received: 25.08.2016
Accepted: 15.09.2016

*Corresponding author: e-mail: chik63@mail.ru Tel.: +7(912)238-38-16, Department of physics, Ural Federal University, Mira st., 19, 620002, Ekaterinburg, Russian Federation

Abstract
The kinematic viscosity of AlSi20 liquid alloy was measured by using the crucible rotating oscillation damping method, and the viscosity-temperature relation curve v(T) in the temperature range of 850~1200K was obtained. The viscosity changed abnormally with temperature in the heating process, i.e., the viscosity turned from rapid increase to gradual decrease when the temperature increased to 1000~1100 K, while the viscosity diminishes exponentially with temperature in the subsequent cooling process. The microscopic mechanism of the evolution of viscosity was analyzed from the viewpoint of the micro-inhomogeneity theory of metallic melts, and it was found that the destruction of the β-Si phase was the basic reason of the head-turning change of viscosity. The paper discussed the correlation of the viscosity and atomic density, which is thought that the viscosity corresponds to the atomic density to some extent. The abstract should be written in the past tense, because it refers to work which was already done. Any equations and references are not allowed. It must state the main object, scope, findings, describe the methodology, summarize the results and state the principal conclusions.

Keywords: aluminium alloys, liquids, crystallization, microstructure, segregation

1 Introduction
Al–Si alloys are amongst the most widely used industrial metallic alloys due to a combination of good cast ability and mechanical performance [1]. Modification of the complex solidification microstructure, aimed at improving the process ability and the mechanical performance, has received continued research attention in these alloys [2-4]. Were investigated of influence of melt overheating (up to defined temperature for each alloy) on structure and phase composition of ingots hypereutectic silumin [5]. It is shown that hypereutectic silumin melt keeps the inhomogeneous state in a wide range of overheating above the liquidus temperature TL, and the most significant structure rearrangement is observed only when heated above the temperature Tk. The large amount of eutectic and primary coarse Si-flakes that form during solidification of the Al–Si hyper-eutectic alloys leading to reduced ductility and wear performance [6-7]. The sessile-drop method and high-temperature small-angle x-ray diffraction technique were used in work [8] to characterize the density of liquid Al-Si alloys with Si content to 22 wt.%. A distinct abnormal volume expansion of the hyper-eutectic melts was identified just above the liquidus (within TL~Tk) during the heating sequence, which is irreversible during the cooling sequence. This phenomenon is explained by the segregation of Si atoms from the supersaturated “quasi-
eutectic” structure and formation of silicon clusters in the superheated melt. The microstructure of liquid alloys Al80Si20 have been investigated by Small Angle Neutron Scattering (SANS) during thermal cycles above liquidus temperature [9]. The SANS results unambiguously show that for the hypereutectic (x = 0.20) alloy the change is almost completely irreversible. This change in microstructure also manifests itself in the shape of the static structure factor S(Q) [10]. According to the present results [11], the morphologies of primary silicon are a strong function of the solidification conditions such as cooling rate and melt overheating temperature. With the elevation of melt overheating temperature, the morphologies of primary silicon will change the size of primary silicon will gradually decrease. The results show that "particles" of different sizes exist in Al-Si melts and that their distribution change during thermal cycles above the melting point. The microstructures can be well explained by the dissolution and branching temperatures extrapolated from density measurements. During heating up to maximum temperature large "particles" dissolve and recombine into smaller ones. The melt at the maximum temperature after heating is more homogeneous. There exist a temperature Td at which "particles" dissolve above melting and another temperature Tb at which a molten alloy can be considered as fully homogeneous, i.e. in a true equilibrium solution state. To address microstructure modifications using physical fields such as, mechanical or electromagnetic stirring, the effect of ultrasound have been explored [8, 12]. However, the effect of method of alloying on the β-Si-phase remains unclear and the origin of primary-phase modification is highly debated. Following our previous work [13], the present work further investigates the effect of method of alloying on the solidification microstructures in AlSi20 alloys. The main objective is to investigate the exact nature of the modification covering the whole spectrum of phases in AlSi20 alloys. Subsequently, an attempt is made to identify the possible origin of the microstructural changes the during heating liquid alloy AlSi20. Melt mixing treatment process has the characteristic of simple technology and low-cost as well as small negative effect on the environment, provided a new idea to optimize the solidification structure of Al-Si alloys [14]. The reason of melt mixing treatment difficult to industrial production was analyzed.

2 Experimental Materials and Methods

The kinematic viscosity of AlSi20 liquid alloy was measured by using the crucible rotating oscillation damping method, and the viscosity-temperature relation curve v(T) in the temperature range of 850-1400 °C was obtained. In the previous study [15], samples were prepared from aluminum of grade А999 and purity semiconductor silicon by fusing them at 950 °C in a dynamic vacuum of ~ 1 Pa. Holding at this temperature was 1-3 hours after which the viscosity values stabilize. A sample crystallized. Is filled with helium installation, re-melted and beginning to sample measurement. Random error of measurement of kinematic viscosity v does not exceed 2% at a confidence level p = 0.95.

The present paper deals with results of comparative analysis of structural state of solid and liquid AlSi20 samples produced with different melt holding time in solid-liquid state after addition of silicon powder at 560-570°C. The industrial charge materials of standard grade were used in all experiments, i.e. silicon powder (Si ≥ 98.8%, fraction 25-30 μ), alloys AlSi9 and Al99.7. AlSi9 was chosen as a base for melt due to wide crystallization range which allows of keeping the melt in solid-liquid state to prevent the silicon particles sedimentation. The crystallization range of AlSi9 was not less than 30 °C. We added silicon powder by portions after AlSi9 partial melting at 560±5 °C. The melt was keeping during 15 min in solid-liquid state
after silicon addition was completed. Then the melt temperature was raised up to 700°C. The samples for microstructure analysis and silicon assimilation grading were taken periodically after 5, 10, 15 min. The samples were crystallized in the chill mould at cooling rate 10°C/sec. Then melt temperature was raised up to 750-770°C, the melt was kept during 15 min. Further we removed slag and poured the test sample into water-cooling crystallizer. The microstructure of solid samples was examined using optical microscopy by traditional metallographic methods. The kinematic viscosity was measured by method of damping of torsion vibrations of the crucible when the melt heating subsequent cooling. The isothermal holding for at least 30 min at relatively small step like (10–15K) is temperature changes. The temperature was maintained at a given level accurate to 1K using a high accuracy controller. During the measurements, the oscillation parameters were detected by an optical method using a system of oscillation photo detection. The techniques of measure and processing experimental data were described in detail in [16]. The copper and tin Reagent grade served as charge materials. In all experiments, we used BeO crucibles. The viscosity was measured in a high purity helium atmosphere at a pressure of 105 Pa. The systematic error of measuring was 3%, and the random error, which determines the scatter of points during one experiment, did not exceed 1.5% at a confidence probability 95%.

The electrical resistivity of liquid Al-Si alloys were measured by the rotating magnetic field during heating to 1400 °C and subsequent cooling of the sample. Working chamber previously evacuated to 0.001 Pa. He then ran to a pressure of about 105 Pa. Isothermal holding in the reference point is at least 15 minutes. Signs of melt evaporation, reducing the weight of the sample was observed. Measurements of resistivity carried setup described in [17]. Evaluation of the measurement error of the electrical resistivity by the method showed that when using crucibles of BeO total relative error of close to 3%. Its random component, which determines the accuracy of the fixing points on the anomalous temperature dependence of ρ is less than 2% at a confidence level p = 0.95.

3 Results and Discussion
The variation rule of the sensitive physical properties of Al-Si alloy melt was studied. The results show that within a certain temperature range, the electrical resistivity of Al-16%Si alloy melt changes abruptly in the forms of inflection points or platforms, which is ascribed to the changes in the internal microstructure of the melt. Based on this rule, the variation characteristics of microstructure can be revealed. When remelting and overheating Al-16%Si alloy to 1050°C, the hereditary effects of different original structure on solidification structure after remelting can be eliminated, which can provide scientific foundation for properly controlling the hereditary factors transmitting the structural information of melt [17].

The relationship between the viscosity and temperature of Al-Si alloy melts was investigated. The viscosity of three different types of Al-Si alloy melts was measured. It was showed that the relationship between the viscosity and temperature of hypoeutectic Al-5%Si and eutectic Al-12.5% Si alloy melts is approximately exponential except for some special zones, but that of the hypereutectic melt is different. The paper discussed the correlation of the viscosity and atomic density, which is thought that the viscosity corresponds to the atomic density to some extent [18].

With increasing concentration of silicon is observed an increase in the number and size of the primary crystals; the transition from the compact (in the form of cubes) to the faceted crystal
Melt overheating leads to suppression of the silicon primary crystallization phase. In alloys containing 20 at. % Si is manifested in a decrease in the number of primary phase. The silicon crystals size of about 1 mm. The morphology of the primary crystals also depends on the structural condition of the melt. The overheated samples had dendrites’ growth of silicon phase; and in alloys with concentrations close to the eutectic silicon crystals grow in the form of rounded branched dendrites, increasing the concentration of silicon dendrites growth is observed only in the early stages, and then proceeds to the plate faceted.

The viscosity is displayed in Fig. 1a as a function of the temperature, \( \nu(T) \). Measured values are presented for Al-5\%Si, Al-8\%Si, Al-12\%Si, Al-14\%Si, Al-20\%Si and Al-30\%Si melts together with data for pure Al for comparison.

The temperature dependence of the kinematic viscosity of the molten Al-Si are shown in Fig. 1. Draws attention mismatch curves \( \nu(t) \), obtained by heating and subsequent cooling of samples (hysteresis). For hypoeutectic alloy has a viscosity at higher heating value than with cooling and for hypereutectic contrary, heating is accompanied by increased melt viscosity. This feature of the temperature dependence of the viscosity is called an inversion of the hysteresis. Inverting hysteresis viscosity of liquid alloys of Al-Si eutectic when passing through the concentration recorded for the first time. When the silicon concentration of more than 5% upon heating, and cooling in the curves \( \nu(t) \) appears at least indicative of reversible changes in the regime of viscous flow. Similar features are also the authors have been found [18] and interpreted as evidence of the transition of the melt in the “gaseous” state.

**Fig.1a** The temperature dependence of kinematic viscosity of the liquid alloys Al-Si
As seen from Fig. 1a, the viscosity and the activation energy of liquid aluminum decrease with admixtures of silicon. The viscosity curves of liquid Al-Si alloys are in close agreement with earlier reported data for Al-Si alloys measured by the same oscillating-cup method [16]. The Al-Si system phase diagram is of a simple eutectic type [19]. Structure investigations revealed predominance of clusters, composed mainly of the atoms of different types [20]. These clusters, whose lifetime prevails over the lifetime of clusters containing only one-type atoms, could be considered as self-dependent units of the viscous flow. The valence electrons participate in the formation of inner bonds. As a result, an interaction between the Al-Si clusters and surrounding atoms becomes weaker. As mutual particle displacements are directed towards the weakest bonds, both the viscosity and the activation energy decrease.

The viscosity variation of a metallic melt with temperature can be described by the Arrhenius equation

$$\nu = A \exp \left( \frac{-\varepsilon}{kT} \right)$$

(1.)

where:

- $A = \frac{h}{\nu_m}$,
- $h$ [Dj-s] - Planck’s constant,
- $\nu_m$ [m$^3$] - flow unit (atoms or clusters) volume,
- $d_m = \mu / N_a \cdot \nu_m$ density,
- $\mu$ [kg/mol] - Molar mass,
- $N_a$[mol$^{-1}$] - Avogadro constant,
- $k$ [J/K] - Boltzmann constant,
- $T$ [K] - absolute temperature,
- $\varepsilon$ [J] - activation energy of viscosity.

According to the absolute rate theory melt viscosity described by the equation:

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

(2.)

where:

- $\Delta G^\neq$ [J] - free activation energy of viscous flow,
- $\Delta H^\neq$ [J] - enthalpy of activation of viscous flow,
- $\Delta S^\neq$ [J] - entropy of activation of viscous flow,
- $R$ [kJ/(K-mol)] - universal gas constant.

Entropy factor $A = \frac{hN_A}{\mu} \exp \left( -\frac{\Delta S^\neq}{R} \right)$ is determined by the entropy of viscous flow.

The electrical conductivity is displayed in Fig. 1b as a function of the temperature, $\sigma(T)$. Measured values are presented for Al-5%Si, Al-8%Si, Al-12%Si, Al-14%Si, Al-20%Si and Al-30%Si melts together with data for pure Al for comparison. The $\sigma(T)$ dependence for all the melts is well described by the linear equation:

$$\sigma = \sigma_0 + \frac{d\sigma}{dT} (T - T_L)$$

(3.)
where: $\sigma_0$ [$S \cdot m^{-1}$] - electrical conductivity at the melting point, 
$\frac{d\sigma}{dT}$ [$S \cdot m^{-1} \cdot K^{-1}$] - temperature coefficient of conductivity. The electrical conductivity of all melts considered here decreases gradually with heating according to Eq. 3. It was revealed that silicon decrease the absolute conductivity value as compared with pure Al. The present data are slightly higher than the values reported in [18] (see Fig. 2). The difference could be explained by the deviation in the sample compositions as well as by experimental uncertainties. It is generally assumed that an addition of admixtures decreases the electrical conductivity.

The conductivity increment $\sigma_i$ can be determined from the following equation:

$$\Delta \sigma_i^{-1} = N_i \frac{m \nu F}{e^2} \Sigma_i$$

(4.)

where: $\Sigma_i$ - scattering cross section of the conducting electrons at the admixture particles,
$N_i$ - atomic fraction of these impurities,
$m$ [kg] - electron mass,
e [Kl]- electron charge,

\( \nu_F \) [m/s] - is the electron velocity at the Fermi level [19]. In a simplest case, when the
impurity scattering does not depend on other scattering mechanisms, \( \Delta \sigma_i \) is independent of the
temperature. However, Eq. 4 describes the decrease of the electrical conductivity only roughly.
A better approximation can be attained by using the partial wave method and the Friedel sum
rule [19]. Considering approximated potentials in the scattering cross section, the following
expression is valid:

\[
\Delta \sigma_i^{-1} = N_i \left[ a + b(\Delta Z)^2 \right]
\]  

(5.)

where: \( a \) and \( b \) depend on the host metal and the row of the Periodic Table to which the
solute belongs. The variable \( \Delta Z \) is the difference between valences of an impurity and a
solvent. Such a relationship, the so-called Linde rule, is valid for a number of binary liquid
alloys. The behavior of the electrical conductivity in multicomponent systems is usually more
complicated. The electrical conductivity of the liquid alloy in the free electron approximation is
expressed as [19]:

\[
\sigma = \frac{n_e e^2}{\hbar k_f}
\]

(6.)

where:

- \( \hbar \) [Dj-s] - Planck’s constant,
- \( n_e \) [m\(^{-3}\)] - electron density,
- \( L \) is the mean free path of conduction electrons.

The admixtures inevitably decrease the electron mean free path, which leads, in turn, to a
decrease in the conductivity.

Joffe and A. Regel, shown that the conditions of formation and movement of free electrons are
determined by short-range order in the arrangement of atoms, i.e., the number and the chemical
nature of the nearest neighbors, which are located in the first coordination sphere, the geometry
of their location and the absolute value of the interatomic distances. Entropy factor is determined
by the flow unit (atoms or clusters) volume. The electrical conductivity also is determined by the
flow unit (atoms or clusters) volume. Thus, the amount of free volume of liquid is an indication
of structural changes in the liquid metal alloys. The amount of free volume of liquid alloys can
explain the anomalous behavior of the temperature dependence of the viscosity and conductivity
of liquid metal alloys, to establish a correlation between the two.

Consider changing the free volume of liquid metal alloys within the Faber-Ziman theory [19].
Upon cooling, the liquid steel the \( z \) number of conduction electrons, hence the wave number \( k_F \)
Fermi increases (\( k_F = (3\pi^2 z / \Omega)^{1/3} \)). In accordance with the theory of the Faber-Ziman
determining factor is the increase in the value of the structure factor \( a(2k_F) \). When twice the
Fermi wave vector \( 2k_F \) becomes equal to the wave number corresponding to the position of the
1st peak of the structure factor (\( 2k_F = 2k_p \)), a change in structure-sensitive properties of the melt.
Conditions \( 2k_F = k_p \) is also the basis of representations Nagel S.R. and Tauc J. [20] on the process
of amorphization of metal alloys. According to these ideas when the condition \( 2k_F = k_p \) a
potential barrier for nucleation of the crystallites decreases the melting point of the alloy
(eutectic temperature) and increases the glass transition temperature, which contributes to the
process of amorphization.
Images of microstructures of AlSi20 cast samples (that were selected by different duration of melt holding after addition of silicon powder) are given in Fig. 2.

**Fig. 2** Microstructure of Al80Si20 samples. The samples marked as №1, №2, №3 have different duration of melt holding at temperature 700°C after addition the last portion of silicon - 5, 10, 15 min respectively.

At the beginning of the assimilation process (**Fig. 1**, sample №1, holding time 5 min) almost all section field is occupied by non-released conglomerates of silicon particles. However, the primary silicon crystals ($Si_p$) is observed against a background of the formed dispersive eutectic phase. Probably, these crystals have been formed by release of compact conglomerates. Subsequently, the eutectic silicon is formed and the quantity of $Si_p$ crystals is increased (sample №2, holding time 10 min). Further holding leads to formation of typical hypereutectic silumin structure (sample №3, holding time 15 min). Thus, the formation of eutectic silicon and $Si_p$ crystals is completed. Also particles of non-assimilated silicon powder are observed. Extremely high concentration of aluminium in crystals of primary and eutectic silicon and silicon in aluminium matrix is observed in comparison with equilibrium diagram (**Fig. 2**). Sample №4 (**Fig. 1**) obtained with 15 min holding time at 760±10°C does not contain raw silicon powder. Primary silicon crystals with size 40-50 μ decorated by solid solution dendrites are situated against a background of fine-dispersed eutectic phase. The solid solution dendrites in eutectic phase are also observed. Therefore microstructure of this sample combines the typical hypereutectic and hypoeutectic phases. Similar microstructure is typical for well-modified structure of hypereutectic alloys. Probably the dispersed silicon particles are crystallization centers. Silicon concentration in this sample was 19, 8-20%. Therefore, the silicon assimilation range was 98-99%.

The viscosity of AlSi20 samples №1-3 has been measured. The results are given in **Fig. 3**. The divergence of kinematic viscosity of liquid AlSi20, corresponds to conditions of heating and cooling, points at the changes in molten metal structure [10] when heating above hysteresis temperature $T_{hys}$. $T_{hys}$ is defined as the temperature that corresponds to beginning of high-temperature coincident segment of cooling and heating curves.

Earlier laboratory-scale experiments with Al-Si melt (composed of pure charge Al 99,999% and semi-conductor quality Si), showed that the viscosity of hypoeutectic alloys has higher value during heating than when cooling. On the contrary, the viscosity of hypereutectic alloys increases during heating. This peculiarity of thermal dependence of viscosity is called “hysteresis inversion”, which was registered at first in ref. [10]. The same result was derived in present experiments (**Fig. 3**). The temperature of hysteresis $T_{hys}$ of every examined AlSi20 sample is 1100-1200 °C approximately. The great attention was paid to the closeness of hysteresis temperature $T_{hys}$=1050°C of AlSi20, composed of pure charge in the laboratory to the value determined by **Fig. 1**. The abnormal increase of melts viscosity at heating may be caused...
by formation of colloid melt structure phases based on silicon [1, 11]. The same effect was described by Novohatsky I.A. et al. [14]. High-temperature non-coincident segment of heating and cooling polyterms above \( T_{hsy} \) indicates on “inherited” heterogeneity of the melt.

Temperature dependence of viscosity of melts \( \nu(t) \) has a coinciding segment at high temperatures. We should focus our attention on the excess of the viscosity measured during cooling as compared that during heating. The increase in the viscosity during heating is explained by a microheterogeneity of the melt, which is partially remains during subsequent cooling of the metallic liquid. The increase of the viscosity during heating of the melt, i.e., an increase of the viscosity with the temperature of the metallic liquid was earlier described by Korzhavina O.A. et al. and Novohatsky I.A. et al [10, 14].

In experiment we observed the time dependence of the kinematic viscosities melt during heating of the metal. A change in melt viscosity under isothermal conditions. Performed a correlation
analysis of the dependency "viscosity" -"time" for sample №1. The Pearson correlation coefficient R between the melt viscosity and time of the sample №1 was calculated with an error of 3 %. The results of calculation: $R=0.5 - T=800 \, ^{\circ}C \, (T < T_{hys})$; $R=0.8 - T=1000 \, ^{\circ}C \, (T < T_{hys})$; $R=0.7 - T>T_{hys}=1150 \, ^{\circ}C$. Value Pearson correlation coefficient with 0.7 or more is a strong connection between viscosity and time.

Non-monotonic character of time-kinematic isothermal viscosity curves indicates that formation of homogeneous melt is incomplete. By this means higher overheating temperature is required to complete the melt homogenization.

These results can be qualitatively interpreted using the concepts of microheterogeneity in liquid alloys [10, 11]. According to these concepts, when the miscibility gap or the liquidus line is reached, an atomically homogeneous solution does not form immediately and a microlayered state of melts remains in the definite temperature interval. In the region of temperature where 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 $\nu(t)$ matches to the transition of the melt to the state of true solution.

4 Conclusions

In summary, our experiments show the assimilation of silicon powder in aluminium melt occurs at $570\pm5^{\circ}C$, i.e. close to liquidus temperature within the crystallization range. The adding of silicon powder during time-temperature treatment provides a modifying AlSi20 structure that was confirmed by metallography.

In addition, the low-temperature melt structure has high-grade heterogeneity which is confirmed by hysteresis of viscosity polyterms during heating – cooling cycle and also non-monotonic character of time-kinematic isothermal viscosity curves.

Further investigation of relation between structure and properties of AlSi20 melts in system “solid-liquid-solid” is subject of following research.

References