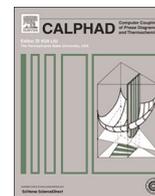




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Modeling of the viscosity in the Al–Cu–Mg–Si system: Database construction

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ABSTRACT

The viscosity database for the Al–Cu–Mg–Si system was constructed using the CALPHAD (CALculation of PHase Diagram)-type formalism. Viscosities of pure elements were described with the Arrhenius formula based on the experimental data. Subsequently, viscosities of the Al–Cu, Al–Si, Al–Mg and Cu–Si binary systems were assessed via CALPHAD technique and compared with the corresponding experimental data. Due to the lack of experimental data, viscosities in the Mg–Si and Cu–Mg systems were estimated by means of the Hirai's equation. The viscosities of the ternary Al–Cu–Si system were then predicted based on the binary parameters and compared with the experimental results. Using the established viscosity database for the quaternary Al–Cu–Mg–Si system, the viscosities of some commercial aluminum alloys were predicted. The reasonable agreement between calculations and experiments in Al-rich corner indicates that the CALPHAD-type database for the viscosity is valid and the database is suitable for predicting the viscosity of the commercial Al–Cu–Mg–Si based alloys.

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1. Introduction

Viscosity is used to describe the fluid resistance to flow, and it is the ratio of the shearing stress to the velocity gradient. Therefore, viscosity is a very important physical property of melts for the solidification simulation of the industrial cast metals and the modeling associated with fluid flow. In general, viscosity varies with the temperature and composition of the liquid and it can be measured using experimental techniques, such as the capillary and oscillating vessel methods. However, it is time-consuming and expensive to realize the viscosities of ternary or multicomponent melts. Therefore, many attempts [1–7] were performed to predict the viscosity of multicomponent system only using thermodynamic parameters. However, the liquid phase is not an ideal mixture and some discrepancies between prediction and experiment exist because of the unreliable description for the complicated physical characteristics of the liquid phase [8,9], such as short range order and associates.

The Al–Cu–Mg–Si alloys are widely used in automotive engine compartments due to their good fluidity and castability [10]. Knowledge on the solidification process of this system is needed to

optimize the casting process and improve the performance of materials. For that purpose, thermophysical properties of the liquid metals, such as thermal conductivity, viscosity, surface tension and density, are required. The aim of this work is to establish the viscosity database for the Al–Cu–Mg–Si system using the CALPHAD approach. CALPHAD method permits prediction of thermodynamic, and thermo physical properties of multi-component systems from those of binary and ternary subsystems.

2. Critical review of the experimental viscosity in the Al–Cu–Mg–Si system

There are a number of methods to measure the viscosity of liquids. However, those suitable for liquid metals are limited due to the low viscosities of metals, their chemical reactivity, dramatic volatilization and generally high melting points. Assael et al. [11] proposed several methods to determine the viscosities of liquid metals, such as capillary, oscillating vessel, rotational crucible, oscillating plate, draining vessel, and levitation using the damping of surface oscillations. However, it was realized that the capillary method is not suitable for measuring the viscosities of aluminum alloys because of the blockage of the capillary via oxide inclusions. In the following, the viscosity data of the Al–Cu–Mg–Si system and its constitute unary, binary and ternary systems reported in the literature were carefully analyzed.

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2.1. Pure liquid

There are plenty of viscosity data about the pure Al, Cu, Mg and Si liquid melts. In this work the data which are consistent with each other were chosen. Sato [12], Mills [13], Wang and Overfelt [14], Yamasaki et al. [15], Arsent and Polyakova [16], Pakiewicz [17] and Gebhardt et al. [18] measured the viscosity of the pure Al melts from 933 K to 1300 K using the oscillating vessel method employing the Roscoe equation or the modified Roscoe equation, respectively. Using the same method, Rothwell [19] determined the viscosity of the liquid aluminum from 933 K to 1200 K. These data [12–19] agree with each other very well and were accepted in the present assessment.

Kehr et al. [20], Brillo et al. [21], Schenck et al. [22], Cavalier [23], Barfield and Kitchener [24], Gebhard and Kostlin [25], and Gebhardt and Worwag [26] measured the viscosities of the liquid Cu between 1300 K and 2000 K using the oscillating cup methods. Their experimental data are self-consistent and accepted in this work. It is worth mentioning that some data below the melting temperature of the copper were not used in the present work because these data correspond to the supercooled liquid. Using the capillary method, Iida et al. [27] determined the viscosities of the copper, which are consistent with the data [20–26]. Consequently, their data [27] are also accepted in the present work.

Very few experimental viscosity data on the liquid Mg and Si could be found because of the high volatility of Mg or the high melting temperature of Si. Lihl et al. [28], Culpin [29] and Gebhardt et al. [30] determined the viscosities of the liquid magnesium from 923 K to 1173 K using the oscillating vessel method. Their data are consistent with each other and could be accepted. Sato et al. [31] measured the viscosity of the liquid silicon using the modified high oscillating vessel viscometer with various of crucibles. Using the similar method, Nishimura et al. [32] determined the viscosity of the liquid silicon from 1700 K to 1800 K. Recently Zhou et al. [33] measured the viscosity of the melted silicon by means of the electromagnetic levitation methods. The experimental data from the above authors [31–33] are self-consistent and accepted in this work. Besides, Sasaki et al. [34] also determined the viscosities of Si from 1700 K to 1900 K using the modified high oscillating vessel viscometer. However, these data from Sasaki et al. [34] were not consistent with the others. They were questionable and not accepted in this work. The experimental viscosities of Si were assessed by Assael et al. [35]. However, the experimental data from Sasaki et al. [34] are also accepted by Assael et al. [35] regardless of the large deviation with the others. In this work, the experimental viscosities of Si from the authors [31–33] are used.

2.2. Binary liquid

Lihl et al. [28] determined the viscosities of a series of the binary aluminum alloys using the oscillating vessel method. Their investigated alloys include the Al–Cu, Al–Mg and Al–Si systems with different compositions and temperatures. Besides, Gebhardt and Detering [36], Sklyarchuk et al. [37] and Geng et al. [38] measured the viscosities of the Al–Si system. Gebhardt et al. [36] measured the viscosity of the Al–Si system from 973 K to 1173 K with the concentration of Si between 0% and 25% using the oscillating vessel method. Their data show a small deviation from the data of Lihl et al. [28] and can be accepted in this work. Using the oscillating vessel method, Sklyarchuk et al. [37] determined the viscosities of Al–7 wt% Si. Their results [37] show a good agreement with the data of Lihl et al. [28]. These data [28,36,37] are generally consistent with each other and accepted in this work. It is worth mentioning that the viscosities from Sklyarchuk et al. [37] were not presented because only one point can be found. Besides, Geng et al. [38] measured the viscosities of the Al–Si

system using the oscillating vessel method at the different temperatures and compositions. If extrapolating to the pure aluminum is made by means of the data from Geng et al. [38], the value is about 0.55 mPa s at 1073 K, which is not consistent with the accepted viscosity of the pure liquid aluminum (near 1.0 mPa s at 1073 K). Their data [38] are abnormally low and not accepted in the present work.

Using the oscillating cup viscometer, Schick et al. [39] determined the viscosities of liquid Al–Cu alloys with the whole composition range at 1500 K. Plevachuk et al. [40] measured the viscosities of the Al–Cu system using the oscillating cup method at the concentration of 4, 20 and 30 wt% Cu from 900 K to 1300 K. The above data [39,40] are consistent with the data of Lihl et al. [28] and are accepted in the present work.

Gruner and Hoyer [41] determined the viscosities of the liquid Cu–Si alloys in the Cu-rich composition range (up to 40 at% Si) at 1273–1473 K. These data are accepted in this work except for the datum at 40 at% Si. Since the viscosities at 40 at% Si dramatically decreased, they are questionable and not used in this work. As comparison, the extrapolated data at 40 at% Si from Kobatake et al. [42] were presented. No experimental data of the Mg–Cu and Mg–Si systems are reported probably due to the volatilization of magnesium.

2.3. Multicomponent liquid

Very few experimental data about the multicomponent aluminum liquid can be found. Using the high temperature oscillating cup viscometer, Kobatake et al. [42] measured the viscosities of the ternary liquid Al–Cu–Si alloys over a wide temperature and composition range. Employing the similar method, Wang and Overfelt [43] investigated the viscosities of aluminum alloys (A201, A319 and A356) from 900 K and 1200 K. A201 has the composition of Al–4.7Cu–0.28Mg–0.31Mn–0.21Ti–0.59Ag (wt%). A319 has the composition of Al–3.01Cu–6.1Si–0.3Mg–0.68Fe–0.71Mn (wt%). A356 has the composition of Al–6.9Si–0.34Mg–0.08Fe (wt%). These data are used for the validation of the prediction of the viscosity of the Al–Cu–Mg–Si based alloys.

3. Models to describe the viscosity

3.1. Unary liquid

Viscosity of the pure liquid phase could be measured easily even though there are some equations [5,44,45] to perform the predictions. The Arrhenius equation describing the temperature dependence of the viscosity holds for the pure liquids. In this work, we use the Arrhenius equation (Eq. (1)) to express the viscosity of the pure Al, Cu, Mg and Si with the pre-exponential (η_0) and the activation energy (E). Through fitting the accepted experimental values, these two parameters could be obtained.

$$\eta = \eta_0 \exp\left(\frac{E}{RT}\right) \quad (1)$$

where R is the universal gas constant.

3.2. Binary liquid

3.2.1. Comparison of different theoretical models

Many models were developed to predict the viscosity of the binary systems theoretically. The models include Molwyn–Hughes (MH) equation [1], Kozlove–Romanov–Petrov (KRP) equation [3], Kucharski model [4], Seetharaman–Du Sichen (SDS) equation [6], Hirai (H) equation [5], Kaptay (K) equation [7] and so on. The

calculations of these equations all rely on the thermodynamic parameters of the liquid phase in the binary systems. The calculations based on these equations are reasonable for some systems but inaccurate in some cases. That is due to the fact that the physical characteristics of the liquid metals are not always regular and sometimes show the short range ordering or associates phenomenon [8,9]. However, the proposed models neglect this phenomenon. Recently, Schick et al. [39] suggested one new equation to describe the viscosities of the Al–Cu system which exhibit the associates in the liquid phases. In their calculations, they ignore the effects of the associates as well. In this work, we use the SDS, K and Schick equations to calculate the viscosities of the Al–Cu and Al–Mg systems and compared the calculations with the experimental data [28,39,40]. The expressions of the SDS, K and Schick equations are shown in Eqs. (2)–(4), respectively.

$$\eta = \frac{hN_A}{V} \exp\left(\frac{x_A \Delta G_A^* + x_B \Delta G_B^* + \Delta G_{mix} + 3RTx_A x_B}{RT}\right) \quad (2)$$

where N_A is the Avogadro number, h is the Planck constant, T is the temperature, ΔG_A^* and ΔG_B^* are the activation energies of pure A and B components, ΔG_{mix} is the Gibbs energy of mixing of liquid system, x_A and x_B are the mole fractions of the components and V is the molar volume of the liquid phase.

$$\eta = \frac{hN_A}{V} \exp\left(\frac{x_A \Delta G_A^* + x_B \Delta G_B^* - (0.155 \pm 0.015)\Delta H_{mix}}{RT}\right) \quad (3)$$

where ΔH_{mix} is the heat of mixing of the liquid.

$$\eta = \eta_\infty \exp\left(\frac{E_A}{RT}\right) \quad (4)$$

where $E_A = x_A E_A^A + x_B E_A^B - \Delta H_{mix}$ and $\ln \eta_\infty = x_A \ln(x_A \eta_\infty^A) + x_B \ln(x_B \eta_\infty^B)$. E_A^A and E_A^B are also called the activation energies for the pure components, but they are different from the ΔG_A^* and ΔG_B^* . They are independent of the temperature.

As shown in Eqs. (2)–(4), these three equations contain no effects of associates or other phenomenon on the viscosity. The molar volumes of the pure Al and Cu liquids at 1500 K are 12.06 and 8.13 cm³/mol [46], and the pure Al and Mg liquids at 1073 K are 11.62 and 15.99 cm³/mol [46,47]. In this work the molar volume of binary liquid is simply treated as the ideal mixture of the pure components. Moreover, the thermodynamic parameters (ΔG_{mix} and ΔH_{mix}) of the liquid Al–Cu and Al–Mg phases are obtained from Refs. [48,49]. Fig. 1 shows the calculated viscosities of

the Al–Cu and Al–Mg systems at 1500 K and 1073 K using these three equations, respectively. Among the three models, the predicted curve from the Schick equation fits best to the experimental data [39,40] in the Al–Cu system at 1500 K. Both the SDS and K equations cannot reproduce the experimental data.

For the Al–Mg system, as shown in Fig. 1b, the Schick equation cannot predict the experimental data [28]. The experimental data exhibited one peak at the middle of the composition. Conversely, the Schick equation suggests a concave. The peak could be predicted by means of both SDS and K equations, even though their predictions are not good as well. However, it does not mean that no equations containing the recent proposed entropy models [50] could reproduce this system. The comparison of the viscosity models indicates that none of these three equations are appropriate to predict the experimental viscosity for both two systems. As a consequence, it is urgent to develop one new and appropriate formula to describe the viscosity of the liquid phase.

3.2.2. CALPHAD-type equation

One CALPHAD-type equation for describing the viscosity of one binary system has been obtained through modifying the equation from Singh and Sommer [51]. Eq. (5) is the relation between η and D_m proposed by Singh and Sommer [51]

$$\eta = \frac{k_B T}{D_m} \left(\frac{x_A}{\sigma_B} + \frac{x_B}{\sigma_A} \right) \frac{d \ln a_A}{d \ln x_A} = \eta_0 \Phi$$

$$\eta_0 = \frac{k_B T}{D_m} \left(\frac{x_A}{\sigma_B} + \frac{x_B}{\sigma_A} \right), \quad \Phi = \frac{d \ln a_A}{d \ln x_A} = \frac{x_A x_B}{S_{cc}(0)} \quad (5)$$

in which k_B is Boltzmann's constant, σ_i ($i=A, B$) depends on the size and shape of the particle i , a_i ($i=A, B$) is the thermodynamic activity of component i , x_i ($i=A, B$) means the concentration of component i , $D_m = x_A D_B + x_B D_A$ is the chemical diffusion coefficient (D_A and D_B are the intrinsic diffusion coefficients of A and B, respectively), η_0 is the prefactor, Φ is the thermodynamic factor and $S_{cc}(0)$ is the concentration fluctuations.

In this work, we propose that the viscosity for the binary system could simply be expressed in two parts through modifying Eq. (5). One is contribution from the ideal mixture, and the other is the excess viscosity. The new equation describing the viscosity is derived as follows.

For an ideal thermodynamic solution ($\Phi=1$) when assuming $D_m = \frac{x_A}{x_B} D_B$ (it is equivalent to $D_m = \frac{x_B}{x_A} D_A$ and $x_B^2 D_A = x_A^2 D_B$), the viscosity of the liquid phase exhibits an ideal mixture. That is to say for an ideal solution, the following formula can be obtained:

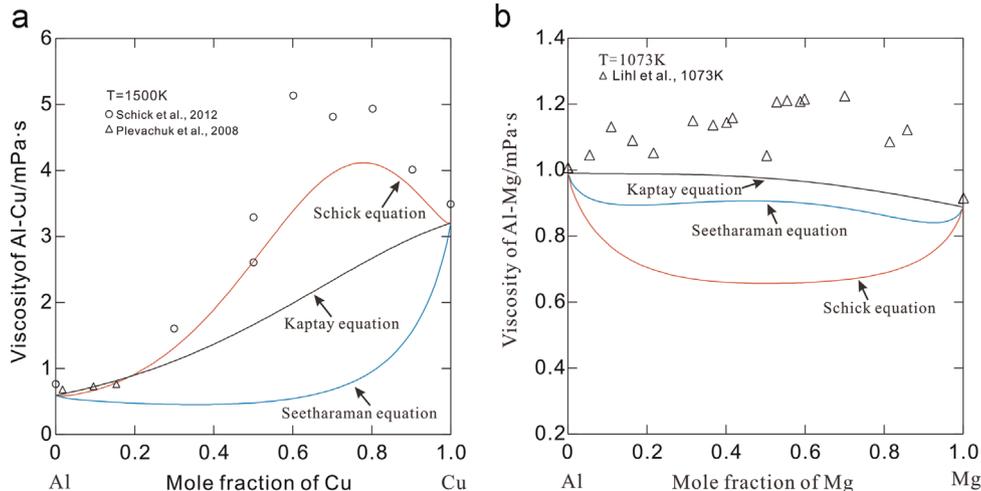


Fig. 1. Calculated viscosities of the Al–Cu and Al–Mg systems at 1500 K and 1073 K using three equations, compared with the experimental data [28,39,40]. (a) Viscosity of the Al–Cu system. (b) Viscosity of the Al–Mg system.

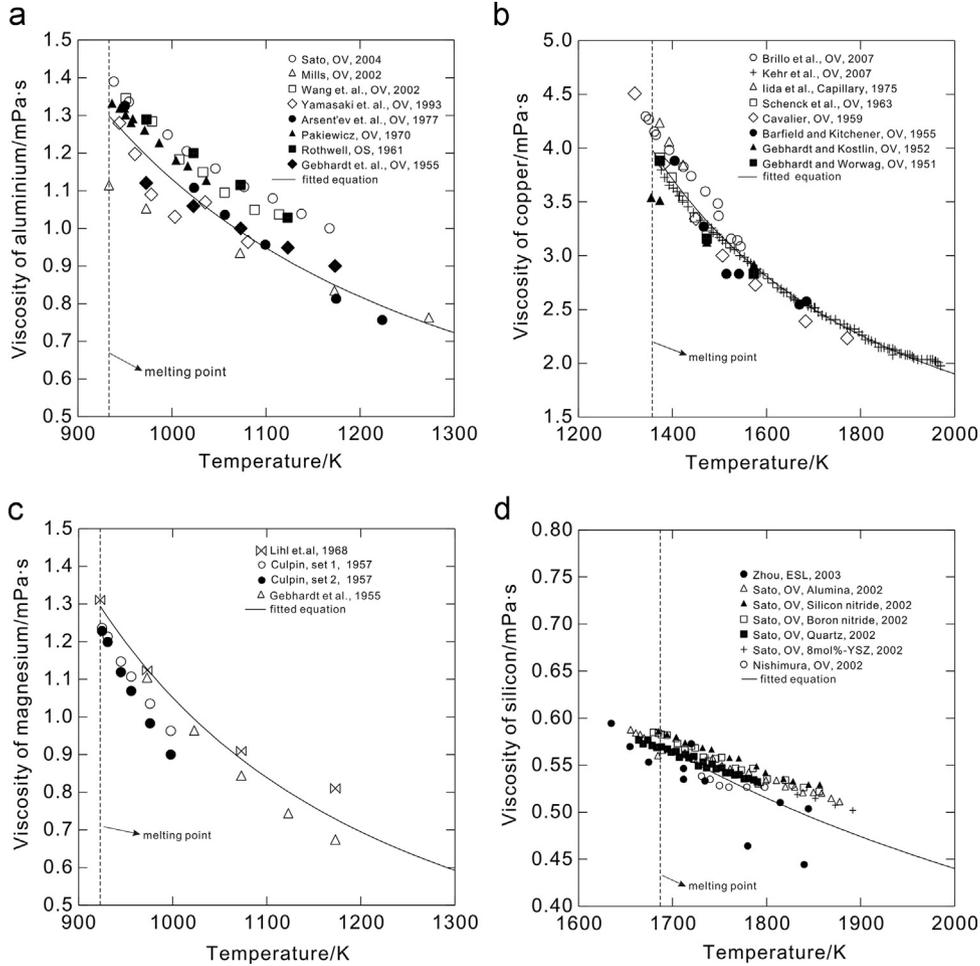


Fig. 2. Calculated viscosities of the pure Al, Cu, Mg and Si compared with the experimental data [12–33]. (a) Viscosity of Al. (b) Viscosity of Cu. (c) Viscosity of Mg. (d) Viscosity of Si.

Table 1
Parameters of the pre-exponential and the activation energy for pure melts.

Parameters	Al	Cu	Mg	Si
η_0 (mPa s)	0.163	0.398	0.0877	0.107
E (J/mol) $\times 10^3$	16.114	25.996	20.655	23.488

$$\eta = \eta_0 = \frac{k_B T}{D_m} \left(\frac{x_A}{\sigma_B} + \frac{x_B}{\sigma_A} \right) = \frac{k_B T}{\frac{x_A}{x_B} D_B} \text{ or } \frac{k_B T}{\frac{x_B}{x_A} D_A} \left(\frac{x_A}{\sigma_B} + \frac{x_B}{\sigma_A} \right)$$

$$= \frac{k_B T}{D_B} \frac{x_B}{\sigma_B} + \frac{k_B T}{D_A} \frac{x_A}{\sigma_A} = x_B \eta_B + x_A \eta_A \quad (6)$$

For the regular liquid solution, the excess viscosity of the pre-factor could be introduced and described by $x_A x_B \eta_0^E$. That is to say when $D_m \neq \frac{x_A}{x_B} D_B$, we can assume that $\eta_0 = x_A \eta_A + x_B \eta_B + \Delta \eta_0^E$, and $\Delta \eta_0^E = x_A x_B \eta_0^E$ is the excess viscosity.

Now thermodynamic factor Φ is investigated. For the regular solution, Singh and Sommer expressed thermodynamic factor as $\Phi = 1 - x_A x_B g(\gamma, W)$. $g(\gamma, W)$ incorporates both energetic and size effects. Finally the following equation can be deduced.

$$\eta = \eta_0 \Phi$$

$$= (x_A \eta_A + x_B \eta_B + x_A x_B \eta_0^E) (1 - x_A x_B g(\gamma, W))$$

$$= x_A \eta_A + x_B \eta_B + x_A x_B \eta_0^E - x_A x_B g(\gamma, W) (x_A \eta_A + x_B \eta_B + x_A x_B \eta_0^E)$$

$$= x_A \eta_A + x_B \eta_B + x_A x_B \left[\eta_0^E - g(\gamma, W) (x_A \eta_A + x_B \eta_B + x_A x_B \eta_0^E) \right]$$

$$= x_A \eta_A + x_B \eta_B + x_A x_B \eta^E \quad (7)$$

According to the above equation, the viscosity for the binary system can simply be defined as be two parts: one is the ideal mixture ($x_A \eta_A + x_B \eta_B$) and the other is the excess viscosity ($x_A x_B \eta_0^E$). η^E is related with the concentration and thermodynamic property of liquid phase. In the present work the excess viscosity is expressed by the Redlich–Kister polynomial [52] and it is equal to $x_A x_B \eta^E = x_A x_B \sum_{k=0}^n A_k (x_A - x_B)^k$. A_k is assessed from the experimental data. In this work A_k is assumed to be a constant. In other words, the change along with the temperature in the binary liquid is only affected by the end-member (η_A and η_B). This assumption means that the viscosities of one binary system show a similar shape at different temperatures. Actually, the previous experiments could confirm this viewpoint (in Refs. [28,36,41]). However, it does not mean that the $A(k)$ parameters are independent of T at all temperatures for any systems. Besides, the temperature is very important to the $A(k)$ parameter when it is very close to melting point. The CALPHAD-type equation is thus used to describe the viscosities of the binary systems in the present work.

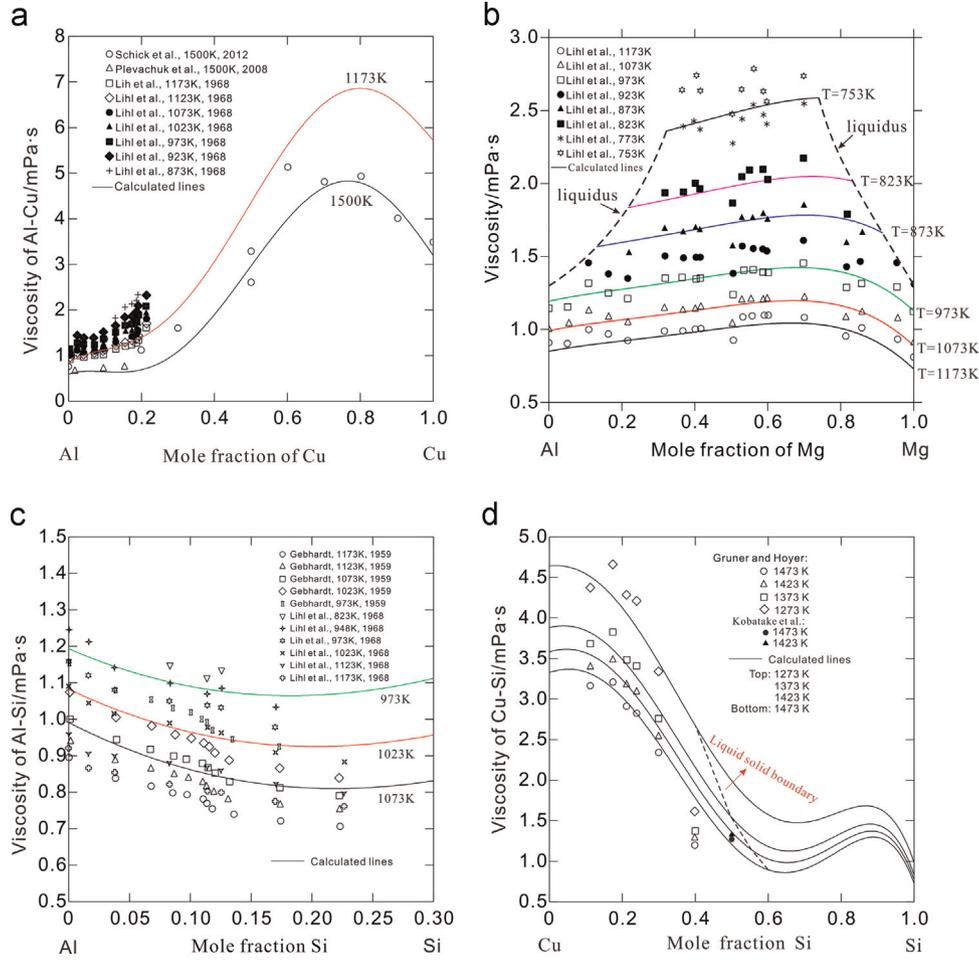


Fig. 3. Calculated viscosities of the Al–Cu, Al–Mg, Al–Si and Cu–Si systems at different temperatures, compared with the experimental data [28,36,39–42]. (a) Viscosity of the Al–Cu system. (b) Viscosity of the Al–Mg system. (c) Viscosity of the Al–Si system. (d) Viscosity of the Cu–Si system.

Table 2

Parameters for the viscosity of the binary systems.

Parameters	Al–Cu	Al–Mg	Al–Si	Cu–Si	Mg–Cu ^a	Mg–Si ^a
A_0 (mP s)	4.248	0.898	–0.826	–3.274	–4.593	3.352
A_1 (mP s)	–16.750	–0.830	–1.790	4.120	–2.760	4.336
A_2 (mP s)	2.866	0.545	0.418	10.078	–2.134	–
A_3 (mP s)	9.807	–	–	–6.827	–	–

^a No experimental data.

3.3. Multicomponent liquid

The viscosities of multicomponent liquid system are extrapolated from the parameters of the binary systems, and the excess viscosities are defined as the Redlich–Kister–Muggianu equation

$$\eta = \sum_{i=1}^m x_i \eta_i + \sum_i \sum_{j>i} x_i x_j \sum_{k=0}^n A_{ij}^k (x_i - x_j)^k \quad (8)$$

where A_{ij}^k are polynomial parameters related to the binary i – j systems. It implies if the excess viscosities of the binary systems were known, the viscosity of the multicomponent system could be predicted.

4. Results and discussion

4.1. Viscosity for pure liquid

Fig. 2a–d shows the calculated viscosities of the pure liquid Al, Cu, Mg and Si in comparison with the experimental data [12–33] at different temperatures. The dot line means the melting temperature of pure element. The largest errors of the experimental data between different researchers are nearly 20%, so not all the experimental data were set to be the same weight during the assessment. The criteria for the selection of the weight associated with experimental values are the consistency. That means the data largely deviating from the center of the average value were set a low weight. Table 1 lists the parameters of the pre-exponential (η_0) and the activation energy (E) for unary system. Most of the previously measured data agree with each other and the calculated viscosity can reproduce these experimental data well.

4.2. Viscosity for binary liquid

The CALPHAD-type formula was proposed to describe the viscosity of the binary liquid. In the present work, the viscosities of the Al–Cu, Al–Mg, Al–Si, Cu–Mg, Cu–Si and Mg–Si binary systems were assessed using Eq. (7). Fig. 3a–d shows the calculated viscosities of the Al–Cu, Al–Mg, Al–Si and Cu–Si systems at different temperatures, in comparison with the experimental data

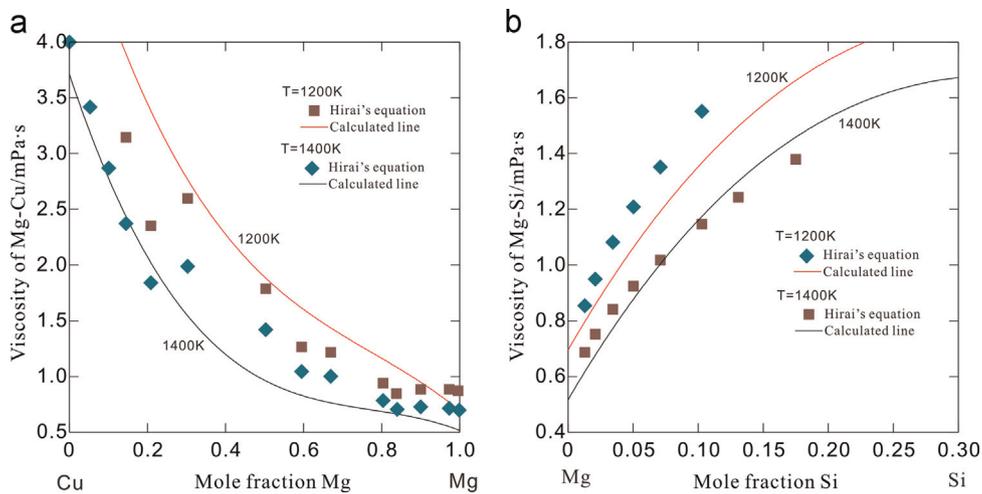


Fig. 4. Calculated viscosities of the Mg–Cu and Mg–Si systems, compared with Hirai's data. (a) Viscosity of the Mg–Cu system. (b) Viscosity of the Mg–Si system.

[28,36,39–42]. The calculations can reproduce the experimental data very well. Moreover, it is obvious that the change tendencies versus the concentration at different temperatures for the experimental viscosity are similar. The pure viscosities (η_A and η_B) in the formula are obtained from the present work and the parameters of excess viscosity A_k are listed in Table 2.

There are no experimental data for the Mg–Cu and Mg–Si systems. Obviously the parameters of the Mg–Cu and Mg–Si systems show some weak influence on the viscosity of aluminum

alloys. The Hirai (H) equation [5], which only employed the melting temperature of the liquid alloys, is a very simple formula to predict the binary viscosity. Using this equation, the binary viscosities of the Mg–Cu and Mg–Si systems at 1200 K and 1400 K were predicted. The assessed parameters are listed in Table 2, and Fig. 4 compared the viscosities derived from Hirai equation and the calculated results via CALPHAD method.

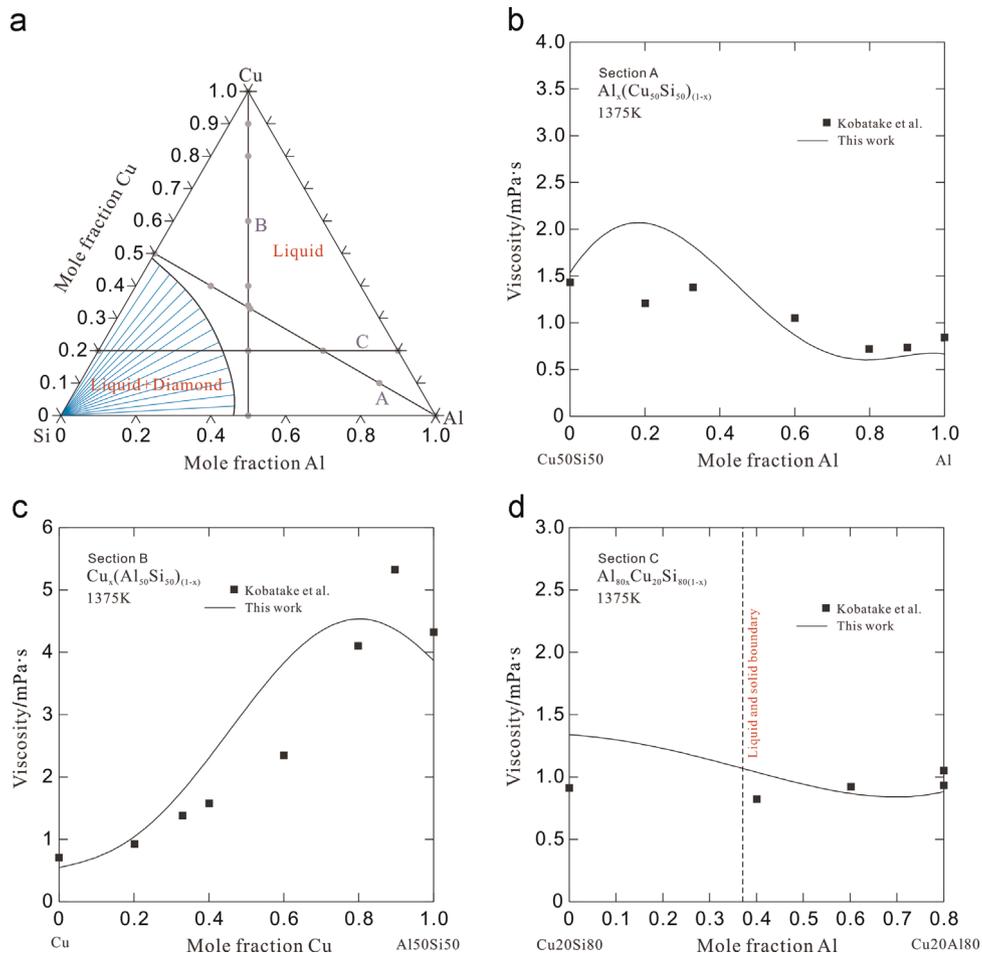


Fig. 5. Calculated viscosities of the Al–Cu–Si system compared with Kobatake's data [42]. (a) Locations of the experimental data. (b) Calculated viscosities at the section A. (c) Calculated viscosities at the section B. (d) Calculated viscosities at the section C.

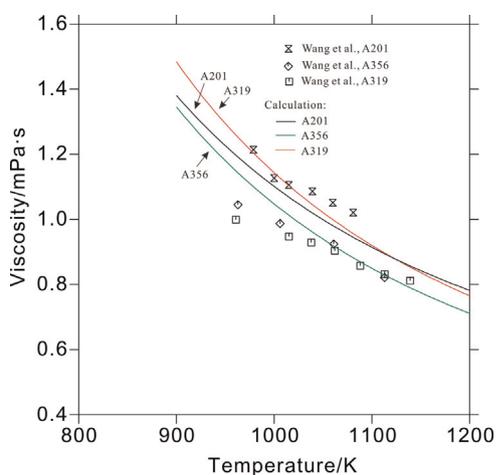


Fig. 6. Calculated viscosities of some aluminum alloys, in comparison with the experimental data [43].

4.3. Viscosity database of the Al–Cu–Mg–Si system and application

As mentioned above, the viscosities of multicomponent liquid were extrapolated from the binary parameters. Therefore, the viscosity database of the Al–Cu–Mg–Si system was constructed based on the obtained binary parameters. Subsequently, we use this database to predict the viscosities of the Al–Cu–Si system and some Al–Cu–Mg–Si based aluminum alloys.

Fig. 5b and c shows the predicted viscosity of the Al–Cu–Si system at 1375 K using the present database, in comparison with Kobatake's data [42]. Fig. 5a is the calculated isothermal section [53] of the Al–Cu–Si system at 1375 K with the composition locations. As shown in Fig. 5b and c, the predicted viscosities are consistent with the tendency of the experimental data [42]. In Fig. 5b, the predicted viscosity curve shows excellent agreement with the experimental data [42] at the Al-rich region. But some deviations (maximum 50% larger) at the Al-poor corner are observed. Fig. 5c shows the predicted viscosity curve along the section B. The experimental values exhibit that the viscosities drastically increase as the maximum attaining to 5 mPa s along the section B. The predicted viscosity curve could present the maximum but the value is about 4.5 mPa s. However, the differences between the maximum and the value at the pure Cu composition through the calculation and in the experiment [42] are about 0.6 mPa s and 0.7 mPa s, which are very alike. Fig. 5d shows the predicted curve along the section C. The calculated values fit well with the measured values when the compositions are in the single liquid phase region. To sum up, the predicted curve can reproduce the measured values reasonably especially at the Al-rich region, confirming that the database is accurate.

Besides, the viscosities of some Al–Cu–Mg–Si based commercial aluminum alloys have been predicted when neglecting the influence of the trace element as shown in Fig. 6. The predicted results indicate some small deviations (maximum about 20%) from the experimental data [43], especially for the A319. Perhaps it is because that the A319 alloys contain about 0.7 wt% Fe and 0.7 wt% Mn. These two elements are not included in this database. The above calculations indicate that this database is useful to predict the viscosities of the Al–Cu–Mg–Si based aluminum alloys especially at the Al-rich corner. Moreover, further work is necessary to include more elements to the Al–Cu–Mg–Si system for the sake of commercial aluminum alloys.

5. Conclusion

Unary viscosities of Al, Cu, Mg and Si were assessed using the

Arrhenius equation. Theoretical models for the binary system were critically analyzed and the CALPHAD-type equation was proposed to assess the viscosities of the Al–Cu, Al–Mg, Al–Si, Cu–Mg, Cu–Si and Mg–Si binary systems. Based on the parameters of the binary systems, the viscosity database of the Al–Cu–Mg–Si system was constructed. This database was utilized to predict the viscosities of Al–Cu–Si system and some commercial aluminum alloys, and the predictions at the Al-rich corner show a good agreement with the experimental data. It is expected that this database resulting from CALPHAD is available to predict the viscosity of the Al–Cu–Mg–Si based commercial aluminum alloys.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.calphad.2015.04.001>.

References

- [1] E.A. Moelwyn-Hughes, *Physical Chemistry*, Pergamon Press, Oxford, 1961.
- [2] Z. Morita, T. Iida, M. Ueda, *Liquid metals*, *Inst. Phys. Conf. Ser.* 30 (1977) 600.
- [3] L. Ya Kozlov, L.M. Romanov, N.N. Petrov, *Izv. Vuzov, Chernaya Metall.* 3 (1983) 7.
- [4] M. Kucharski, *Z. Metallkd.* 77 (1986) 393–396.
- [5] M. Hirai, *Iron steel*, *Inst. Jpn. Int.* 33 (2) (1993) 251–258.
- [6] S. Seetharaman, D. Sichen, *Metall. Mater. Trans.* 25B (1994) 589.
- [7] G. Kaptay, *Proceedings of MicroCAD 2003 conference*, International Section Metallurgy, University of Miskolc, Hungary, vol. 23, 2003.
- [8] B. Pilarek, B. Salamon, J. Kapała, *Calphad* 47 (2014) 211–218.
- [9] D. Li, S. Fürtauer, H. Flandorfer, D.M. Cupid, *Calphad* 47 (2014) 181–195.
- [10] S.W. Choi, Y.M. Kim, K.M. Lee, H.S. Cho, S.K. Hong, Y.C. Kim, C.S. Kang, S. Kumai, *J. Alloy. Compd.* 617 (2014) 654–659.
- [11] M.J. Assael, K. Kakosimos, R.M. Banish, J. Brillo, I. Egry, R. Brooks, P.N. Quedsted, K.C. Mills, A. Nagashima, Y. Sato, W.A. Wakeham, *J. Phys. Chem. Ref. Data* 35 (2006) 285–300.
- [12] Y. Sato, Report to the Ministry of Economy, Trade and Industry (METI), Japan, 2004.
- [13] K.C. Mills, *Recommended Thermophysical Properties for Selected Commercial Alloys*, 2002.
- [14] D. Wang, R.A. Overfelt, *Int. J. Thermophys.* 23 (2002) 1063.
- [15] T. Yamasaki, S. Kanatani, Y. Ogino, A. Inoue, *J. Non-Cryst. Solids* 441 (1993) 154–158.
- [16] P.P. Arsen'ev, K.I. Polyakova, *Izv Vyssh. Uchebn. Zaved. Tsvetn. Metall.* 51 (1977) 5.
- [17] M.J. Pakiewicz, Ph.D. Department of Chemistry, Syracuse University, New York, 1970.
- [18] E. Gebhardt, M. Becker, S. Dorner, *Aluminum* 31 (1955) 315.
- [19] E. Rothwell, *J. Inst. Metals* 90 (1961&1962) 389.
- [20] M. Kehr, W. Hoyer, I. Egry, *Int. J. Thermophys.* 28 (2007) 1017.
- [21] J. Brillo, R. Brooks, I. Egry, P.N. Quedsted, *Int. J. Mater. Res.* 98 (2007) 457.
- [22] H. Schenck, M.G. Froberg, K. Hoffmann, *Arch. Eisenhuettenwes.* 34 (1963) 93.
- [23] M. G. Cavalier, The physical chemistry of metallic solutions and intermetallic compounds, in: *Proceedings of a Symposium held at the National Physical Laboratory on the 4th, 5th, and 6th of June 1958* (H. M. Stationery Off., London, 1959), vol. 2, paper 4D.
- [24] R.N. Barfield, J.A. Kitchener, *J. Iron Steel Inst.* 180 (1955) 324.
- [25] E. Gebhardt, K. Kostlin, *Z. Metallkd.* 43 (1952) 292.
- [26] E. Gebhardt, G. Worwag, *Z. Metallkd.* 42 (1951) 358.
- [27] T. Iida, Z.-I. Morita, S. Takeuchi, *J. Jpn. Inst. Met* 39 (1975) 1169.
- [28] F. Lihl, E. Nachtigall, A. Schwaiger, *Z. Metallkd.* 59 (1968) 213–219.
- [29] M.F. Culpin, *Proc. Phys. Soc.* 70 (1957) 1079–1086.
- [30] E. Gebhardt, M. Becket, M. Sebastian, *Z. Metallkd.* 46 (1955) 669–672.
- [31] Y. Sato, Y. Kameda, T. Nagasawa, T. Sakamoto, S. Moriguchi, T. Yamamura, Y. Waseda, *J. Cryst. Growth* 249 (2002) 404.

- [32] S. Nishimura, S. Matsumoto, K. Terashima, *J. Cryst. Growth* 237–239 (2002) 1667.
- [33] Z. Zhou, S. Mukherjee, W.-K. Rhim, *J. Cryst. Growth* 257 (2003) 350.
- [34] H. Sasaki, E. Tokizaki, X. Huang, K. Terashima, S. Kimura, *Jpn. J. Appl. Phys.* 34 (1995) 3432.
- [35] M.J. Assael, I.J. Armyra, J. Brillo, S.V. Stankus, J. Wu, W.A. Wakeham, *J. Phys. Chem. Ref. Data* 41 (2012) 033101-1–033101-16.
- [36] E. Gebhardt, K. Detering, *Z. Metallkd.* 50 (1959) 379–385.
- [37] V. Sklyarchuk, Y. Plevachuk, A. Yakymovych, S. Eckert, G. Gerbeth, K. Eigenfeld, *Int. J. Thermophys.* 30 (2009) 1400–1410.
- [38] H.R. Geng, R. Wang, Z.X. Yang, J.H. Chen, C.J. Sun, Y. Wang, *Acta Metall. Sin.* 18 (2005) 159–163.
- [39] M. Schick, J. Brillo, I. Egry, B. Hallstedt, *J. Mater. Sci.* 47 (2012) 8145–8152.
- [40] Y. Plevachuk, V. Sklyarchuk, A. Yakymovych, S. Eckert, B. Willers, K. Eigenfeld, *Metall. Mater. Trans. A* 39A (2008) 3040–3045.
- [41] S. Gruner, W. Hoyer, *J. Alloy. Compd.* 460 (2008) 496–499.
- [42] H. Kobatake, J. Schmitz, J. Brillo, *J. Mater. Sci.* 49 (2014) 3541–3549.
- [43] D. Wang, R.A. Overfelt, *Int. J. Thermophys.* 23 (2002) 1063–1076.
- [44] G. Kaptay, *Z. Metallkd.* 96 (2005) 24.
- [45] E.N. da, C. Andrade, *Philos. Mag.* 17 (1934) 497.
- [46] J. Brillo, I. Egry, *J. Westphal, Int. J. Mater. Res.* 99 (2) (2008) 162–167.
- [47] R.A. Khairulin, S.V. Stankus, *J. Nucl. Mater.* 377 (3) (2008) 501–505.
- [48] N. Saunders, in: I. Ansara, A.T. Dinsdale, M.H. Rand (Eds.), *COST 507: Thermochemical Database for Lightmetal Alloys*, vol. 2, European Commission, 1998.
- [49] Y. Zuo, Y.A. Chang, *Calphad* 17 (2) (1993) 161–174.
- [50] W. Gąsior, *Calphad* 44 (2014) 119–128.
- [51] R.N. Singh, F. Sommer, *Phys. Chem. Liq.* 36 (1998) 17–28.
- [52] O. Redlich, A.T. Kister, *J. Ind. Eng. Chem.* 40 (1948) 84–88.
- [53] C.Y. He, Y. Du, H.L. Chen, H.H. Xu, *Calphad* 33 (2009) 200–210.