Accurate Viscosity Calculation for Melts in $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ Systems

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(Received on October 1, 2016; accepted on April 13, 2017; J-STAGE Advance published date: July 4, 2017)

The viscosity of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ system and its subsystems are of fundamental importance for control and optimization of metallurgical, material, energy and geological phenomena. In this work, an accurate and simple viscosity model suitable for use in numerical simulations was established for $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ system and its subsystems, based on the physically meaningful MYEGA equation. The model was calibrated by 4403 viscosity data measured in non-graphite crucibles. It was found current model calculates the viscosity with a remarkable overall accuracy of 15.8%. For each of the subsystems, current model also results in very good accuracy lower than 20%. The model could calculate the viscosity very reliably over the entire composition, temperature and viscosity value ranges studied in the work, even for viscosity value as low as 10^{-2} Pa·s. The composition dependences of viscosity for binary, ternary and quaternary systems were derived using established model. The effects of each component on viscosity were interpreted according to the concept of network “former” and “modifier” and the charge compensation effect of Ca^{2+} on the tetrahedral-coordinated structure of Al^{3+} .

KEY WORDS: viscosity; $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ systems; graphite crucible; network former; network modifier; numerical simulation.

1. Introduction

The SiO_2 , Al_2O_3 , CaO and MgO are some of the basic components for metallurgical slags, ceramics, glasses, fuel slags/ashes, magmas, etc. Understanding the thermophysical properties of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ system and its subsystems is crucial for process controlling and optimization. Viscosity is of considerable importance for momentum, heat and mass transfer in melts. However, it is well known that high temperature viscosity measurement is time consuming and costly, thus it is worthwhile to construct viscosity models which enable calculation of viscosity according to melt compositions and temperature.

Viscosity modelings began as early as 1970's. Shaw¹⁾ and Bottinga and Weill²⁾ developed some of the earliest viscosity predicting models, which based on a number of high temperature viscosity measurement. Modeling of viscosity is still an important issue in current metallurgical, material, energy and geological research, especially for fundamental systems like $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$, which have been recently summarized by Gan and Lai³⁾ and Han *et al.*⁴⁾

An ideal viscosity model should be accurate, physically meaningful and simple. Accuracy is always the first priority in viscosity modeling. Variations in reported viscosity values for laboratories using good practice are lower than

10%.⁵⁾ However, when measurement from various laboratories are compiled, experimental viscosity data of molten slags should probably subject to uncertainties of 20%,⁶⁾ which is consistent with accuracies of viscosity models based on carefully selected data.⁷⁾ A physically meaningful viscosity model indicates the model is based on some physical characteristics of the system, for example, the melt structure. The structurally based viscosity model is widely used to elucidate the structure of high temperature melts, which is still not fully understood. Technically, the physically meaningful model enables the viscosity extrapolation outside the composition and temperature ranges of measured data in higher accuracy than empirical models. A simple model does not necessarily mean the number of adjustable parameter is small, but more importantly, means the establishment of the model is straightforward and easily understood. Simple viscosity models are more likely to be applied in industry and used by researchers not familiar with the physics and chemistry of melts. However, it should be noted that the physically meaningful models are not simple for most of the time. Thus it is highly difficult to obtain an accurate, physically meaningful and meanwhile simple viscosity model, especially for systems with multi-components and cover wide ranges.

Numerical simulation has become a routine tool to investigate the complex phenomena in metallurgical and related process in current days. Existing viscosity models can generally meet the demands of process controlling and opti-

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DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2016-581>

mization; however, models with even higher accuracy are still needed for the growing requirement of precise numerical simulations. In addition, simple models are preferred in the numerical simulations, because they can be easily understood, and convenient to be embedded in the program.

The goal of this work is to develop an accurate and simple viscosity model for $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ system and its subsystems. Meanwhile, the model is kept physically meaningful by adopting suitable equation to describe the temperature dependence of viscosity.

2. Method

2.1. Viscosity Data

The viscosity data were collected through open published works. In this work, the viscosity data obtained by different

methods were thought in good agreement, as suggested by previous studies.^{7,8)} Special attention was put on the effect of crucible materials on viscosity measurement. The measurements obtained in graphite crucible are often found scattered by several researchers.^{5,9–11)} Therefore, in this work, the viscosity data measured in graphite crucibles were not used.

Totally more than 4 860 viscosity data obtained in non-graphite crucibles were collected. However, it was found some data are clearly inconsistent with other measurements. These data were removed because it always indicates experimental errors. In this way, roughly 9.4% of collected data were removed, and the remaining 4 403 data representing 873 compositions were used to calibrate of viscosity model. The composition ranges of the data were shown in Table 1

Table 1. Composition ranges of melt in the viscosity database (mass%).

Systems	SiO ₂	Al ₂ O ₃	CaO	MgO
SiO ₂ –Al ₂ O ₃	20.0–89.9	10.1–80.0	/	/
SiO ₂ –CaO	41.7–71.4	/	28.6–58.3	/
SiO ₂ –MgO	44.4–67.8	/	/	32.2–55.6
Al ₂ O ₃ –CaO	/	29.5–80.0	20.0–70.5	/
SiO ₂ –Al ₂ O ₃ –CaO	10.0–71.0	3.4–65.0	8.7–60.0	/
SiO ₂ –Al ₂ O ₃ –MgO	22.0–73.5	9.2–55.9	/	7.6–50.0
SiO ₂ –CaO–MgO	44.1–60.0	/	10.0–50.0	5.0–31.1
SiO ₂ –Al ₂ O ₃ –CaO–MgO	2.7–65.0	3.7 to 40.0	1.8–58.0	2.6–34.5

Fig. 2. Viscosity and temperature ranges of viscosity data. (Online version in color.)

Fig. 1. Composition of melts in the viscosity database expressed in form of: (a) normalized $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$ system; (b) normalized $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ system; and (c) normalized $\text{SiO}_2\text{--CaO--MgO}$ system. (Online version in color.)

Table 2. Sources of viscosity data.

Systems	References	Method*	Crucible	Data
SiO ₂ –Al ₂ O ₃ Data: 22	Kozakevitch,1960 ²⁴⁾	Rotating	Mo-W	3
	Urbain,1982 ²⁵⁾	Rotating	Mo	19
	Machin,1948 ²⁶⁾	Oscillating	Pt	1
	Machin,1954 ²⁷⁾	Oscillating	Pt	4
	Bockris,1954 ²⁸⁾	Rotating	Mo	99
	Kozakevitch,1960 ²⁴⁾	Rotating	Mo-W	24
	Hofmaier,1968 ²⁹⁾	Rotating	Mo	37
	Yakushev,1977 ³⁰⁾	Vibrating	Mo	3
	Kou,1978 ³¹⁾	Rotating	Pt	5
	Urbain,1982 ²⁵⁾	Rotating	Mo	31
SiO ₂ –CaO Data: 235	Licko,1986 ³²⁾	Oscillating	Pt-Rh	8
	Solvang,2005 ³³⁾	Rotating	Pt-Rh	16
	Zhang,2012 ³⁴⁾	Rotating	Mo	5
	Han,2015 ³⁵⁾	Rotating	Pt	2
	Bockris,1955 ³⁶⁾	Rotating	Mo	25
	Hofmaier,1968 ²⁹⁾	Rotating	Mo	12
	Urbain,1982 ²⁵⁾	Rotating	Mo	27
	Licko,1986 ³²⁾	Oscillating	Pt-Rh	4
	Shimizu,2006 ³⁷⁾	Rotating	Pt-Rh	3
	Han,2015 ³⁵⁾	Rotating	Pt	1
SiO ₂ –MgO Data: 72	Kozakevitch,1960 ²⁴⁾	Rotating	Mo-W	32
	Hofmaier,1968 ²⁹⁾	Rotating	Mo	24
	Tsubulnikov,1973 ³⁸⁾	Vibrating	Mo	3
	Urbain,1983 ³⁹⁾	Rotating	Mo	37
	Oliveira,1999 ⁴⁰⁾	Rotating	Mo	4
Al ₂ O ₃ –CaO Data: 100	Machin,1945 ⁴¹⁾	Oscillating	Pt	25
	Machin,1948 ²⁶⁾	Oscillating	Pt	163
	Machin,1952 ⁴²⁾	Oscillating	Pt	48
	Machin,1954 ²⁷⁾	Oscillating	Pt	43
	Johannsen,1959 ⁴³⁾	Rotating	Pt-Rh	64
	Kozakevitch,1960 ²⁴⁾	Rotating	Mo-W	197
	Bills,1963 ⁴⁴⁾	Rotating	Pt/Ir	15
	Benesch,1964 ⁴⁵⁾	Rotating	Ir	14
	Kato,1965 ⁴⁶⁾	CBS	Pt	46
	Muratov,1965 ⁴⁷⁾	Rotating	Mo	8
SiO ₂ –Al ₂ O ₃ –CaO Data: 1379	Hofmaier,1968 ²⁹⁾	Rotating	Mo	34
	Cukierman,1973 ⁴⁷⁾	Rotating	Mo	7
	Kou,1978 ³¹⁾	Rotating	Pt	30
	Urbain,1982 ²⁵⁾	Rotating	Mo	58
	Searfe,1983 ⁴⁸⁾	Rotating	Pt	11
	Taniguchi,1992 ⁴⁹⁾	CBS	Pt	7
	Okazawa,2003 ⁵⁰⁾	Rotating	Pt-Rh	19
	Saito,2003 ⁵¹⁾	Rotating	Pt-Rh	4
	Park,2004 ²¹⁾	Rotating	Pt-Rh	19
	Solvang,2004 ⁵²⁾	Rotating	Pt-Rh	98
SiO ₂ –Al ₂ O ₃ –MgO Data: 573	Toplis,2004 ⁵³⁾	Rotating	Pt-Rh	252
	Solvang,2005 ³³⁾	Rotating	Pt-Rh	11
	Sukenaga,2006 ⁵⁴⁾	Rotating	Pt-Rh	5
	Moesgaard,2009 ⁵⁵⁾	Rotating	Pt-Rh	95
	Zhang,2012 ³⁴⁾	Rotating	Mo	17
	Zhang,2013 ⁵⁶⁾	Rotating	Mo	59
	Higo,2014 ⁵⁷⁾	Rotating	Pt-Rh	5
	Li,2016 ⁵⁸⁾	Rotating	Mo	6
	Veit,2016 ⁵⁹⁾	Rotating	Pt	19
	Machin,1954 ²⁷⁾	Oscillating	Pt	27
SiO ₂ –CaO–MgO Data: 139	Lyutikov,1963 ⁶⁰⁾	Rotating	Mo	267
	Rlebling,1964 ⁶¹⁾	CBS	Pt-Rh	55
	Hofmaier,1968 ²⁹⁾	Rotating	Mo	22
	Mizoguchi,1982 ⁶²⁾	Rotating	Pt	33
	Urbain,1982 ²⁵⁾	Rotating	Mo	29
	Zhilo,1982 ⁶³⁾	Vibrating	Mo	27
	Toplis,2004 ⁵³⁾	Rotating	Pt-Rh	113
	Machin,1952 ⁴²⁾	Oscillating	Pt	27
	Machin,1954 ²⁷⁾	Oscillating	Pt	20
	Kirkpatrick,1974 ⁶⁴⁾	Rotating	Pt	6
SiO ₂ –Al ₂ O ₃ –CaO–MgO Data: 1883	Urbain,1982 ²⁵⁾	Rotating	Mo	7
	Searfe,1983 ⁴⁸⁾	Rotating	Pt	6
	Licko,1986 ³²⁾	Oscillating	Pt-Rh	52
	Scarfe,1986 ⁶⁵⁾	Rotating	Pt	6
	Sykes,1993 ⁶⁶⁾	Rotating	Pt-Rh	5
	Kim,2013 ⁶⁷⁾	Rotating	Pt-Rh	6
	Han,2015 ³⁵⁾	Rotating	Pt	4
	Machin,1945 ⁴¹⁾	Oscillating	Pt	81
	Machin,1952 ⁴²⁾	Oscillating	Pt	257
	Machin,1954 ²⁷⁾	Oscillating	Pt	152
SiO ₂ –Al ₂ O ₃ –CaO–MgO Data: 1883	Kozakevitch,1954 ¹⁰⁾	Rotating	Mo-W	27
	Benesch,1964 ⁴⁵⁾	Rotating	Ir	20
	Muratov,1965 ⁴⁷⁾	Rotating	Mo	37
	Kozakevitch,1966 ⁶⁸⁾	Rotating	Mo-W	160
	Hofmaier,1968 ²⁹⁾	Rotating	Mo	6
	Tsubulnikov,1973 ³⁸⁾	Vibrating	Mo	15
	Yakushev,1977 ³⁰⁾	Vibrating	Mo	74
	Searfe,1983 ⁴⁸⁾	Rotating	Pt	58
	Taniguchi,1987 ⁶⁹⁾	CBS	Pt	32
	Taniguchi,1992 ⁴⁹⁾	CBS	Pt	24
SiO ₂ –Al ₂ O ₃ –CaO–MgO Data: 1883	Iida,2000 ²⁰⁾	Oscillating	Pt	166
	Wright,2001 ⁷⁰⁾	Rotating	Pt-Rh	24
	Forsbacka,2003 ⁷¹⁾	Rotating	Mo	72
	Saito,2003 ⁵¹⁾	Rotating	Pt-Rh	15
	Kim,2004 ⁷²⁾	Rotating	Mo	8
	Lee,2004 ⁷³⁾	Rotating	Pt-Rh	14
	Nakamoto,2004 ⁷⁴⁾	Rotating	Fe	10
	Park,2004 ²¹⁾	Rotating	Pt-Rh	5
	Sukenaga,2006 ⁵⁴⁾	Rotating	Pt-Rh	28
	Getson,2007 ⁷⁵⁾	Rotating	Al ₂ O ₃	165
SiO ₂ –Al ₂ O ₃ –CaO–MgO Data: 1883	Shankar,2007 ⁷⁶⁾	Rotating	Mo	15
	Park,2008 ⁷⁷⁾	Rotating	Pt-Rh	5
	Kim,2010 ⁷⁸⁾	Rotating	Pt-Rh	12
	Song,2011 ¹⁸⁾	Rotating	Mo	182
	Tang,2011 ⁷⁹⁾	Rotating	Mo	36
	Wu,2011 ⁸⁰⁾	Rotating	Mo	9
	Liao,2012 ⁸¹⁾	Rotating	Mo	18
	Park,2012 ⁸²⁾	Rotating	Pt-Rh	10
	Chevrel,2013 ⁸³⁾	Rotating	Pt-Rh	17
	Kim,2013 ⁶⁷⁾	Rotating	Pt-Rh	64
SiO ₂ –Al ₂ O ₃ –CaO–MgO Data: 1883	Chen,2014 ⁸⁴⁾	Rotating	Mo	20
	Zhang,2014 ⁸⁵⁾	Rotating	Mo	4
	Li,2016 ⁵⁸⁾	Rotating	Mo	41
	Toplis,2004 ⁵³⁾	Rotating	Pt-Rh	252
	Solvang,2005 ³³⁾	Rotating	Pt-Rh	11
	Sukenaga,2006 ⁵⁴⁾	Rotating	Pt-Rh	5
	Moesgaard,2009 ⁵⁵⁾	Rotating	Pt-Rh	95
	Zhang,2012 ³⁴⁾	Rotating	Mo	17
	Zhang,2013 ⁵⁶⁾	Rotating	Mo	59
	Higo,2014 ⁵⁷⁾	Rotating	Pt-Rh	5
SiO ₂ –Al ₂ O ₃ –CaO–MgO Data: 1883	Li,2016 ⁵⁸⁾	Rotating	Mo	6
	Veit,2016 ⁵⁹⁾	Rotating	Pt	19
	Machin,1954 ²⁷⁾	Oscillating	Pt	27
	Lyutikov,1963 ⁶⁰⁾	Rotating	Mo	267
	Rlebling,1964 ⁶¹⁾	CBS	Pt-Rh	55
	Hofmaier,1968 ²⁹⁾	Rotating	Mo	22
	Mizoguchi,1982 ⁶²⁾	Rotating	Pt	33
	Urbain,1982 ²⁵⁾	Rotating	Mo	29
	Zhilo,1982 ⁶³⁾	Vibrating	Mo	27
	Toplis,2004 ⁵³⁾	Rotating	Pt-Rh	113
Total data				4 403

*CBS: counterbalance sphere

and Fig. 1. The ranges of viscosity value and temperature were presented in Fig. 2. The data sources were listed in Table 2.

2.2. Viscosity Model

To calculate viscosity according to the composition and temperature, the physically meaningful MYEGA equation¹²⁾ was used, which based on energy landscape analysis and the temperature-dependent constraint model for configurational entropy. The MYEGA equation has higher fitting accuracies for molten slags than other widely used equations.¹³⁾

The MYEGA equation is expressed as:

$$\log \eta = A + \frac{B}{T} \exp\left(\frac{C}{T}\right) \dots \dots \dots (1)$$

where η is viscosity, T is temperature, and A , B and C are fitting parameters. The parameter A is the value of $\log \eta$ at infinite temperature, B is effective activation energy, and C relates to the energy difference between intact and broken states of network constraints.

In the modeling, parameter A was set as a constant. Parameter B and C were related to the compositions of melt, by simply considering the binary interactions between each component, as organized in the way illustrated in Table 3.

Accordingly, the parameter B and C are expressed as:

$$\begin{aligned} B &= \sum_{i=1}^n \sum_{j \geq i}^n b_{ij} X_i X_j \\ &= b_{11} X_{\text{SiO}_2} X_{\text{SiO}_2} + b_{12} X_{\text{SiO}_2} X_{\text{Al}_2\text{O}_3} + b_{22} X_{\text{Al}_2\text{O}_3} X_{\text{Al}_2\text{O}_3} \dots (2) \\ &\quad + b_{13} X_{\text{SiO}_2} X_{\text{CaO}} + b_{23} X_{\text{Al}_2\text{O}_3} X_{\text{CaO}} + b_{33} X_{\text{CaO}} X_{\text{CaO}} \\ &\quad + b_{14} X_{\text{SiO}_2} X_{\text{MgO}} + b_{24} X_{\text{Al}_2\text{O}_3} X_{\text{MgO}} \\ &\quad + b_{34} X_{\text{CaO}} X_{\text{MgO}} + b_{44} X_{\text{MgO}} X_{\text{MgO}} \end{aligned}$$

$$\begin{aligned} C &= \sum_{i=1}^n \sum_{j \geq i}^n c_{ij} X_i X_j \\ &= c_{11} X_{\text{SiO}_2} X_{\text{SiO}_2} + c_{12} X_{\text{SiO}_2} X_{\text{Al}_2\text{O}_3} + c_{22} X_{\text{Al}_2\text{O}_3} X_{\text{Al}_2\text{O}_3} \dots (3) \\ &\quad + c_{13} X_{\text{SiO}_2} X_{\text{CaO}} + c_{23} X_{\text{Al}_2\text{O}_3} X_{\text{CaO}} + c_{33} X_{\text{CaO}} X_{\text{CaO}} \\ &\quad + c_{14} X_{\text{SiO}_2} X_{\text{MgO}} + c_{24} X_{\text{Al}_2\text{O}_3} X_{\text{MgO}} \\ &\quad + c_{34} X_{\text{CaO}} X_{\text{MgO}} + c_{44} X_{\text{MgO}} X_{\text{MgO}} \end{aligned}$$

where X_i is molar fraction of component i , and b_{ij} and c_{ij} are fitting parameters.

In this work, the b_{ij} and c_{ij} values were obtained by minimization of the function

$$\sum_{i=1}^N \left[\frac{(\eta_{\text{mea.}} - \eta_{\text{cal.}})}{\eta_{\text{mea.}}} \right]^2 \dots \dots \dots (4)$$

where $\eta_{\text{mea.}}$ and $\eta_{\text{cal.}}$ are measured and calculated viscosity, respectively.

All of the 4 403 viscosity measurements were used equally

to derive the optimized b_{ij} and c_{ij} values. The optimization was performed in a commercial solver using non-linear least-squares fitting based on the well-known Levenberg–Marquardt algorithm. In addition, because of the strong non-linear nature of MYEGA equation, a global constraint on the algorithm was also used to avoid local minima.

3. Results and Discussions

3.1. Model Parameters

The optimized model parameter values were listed in Table 4. The obtained parameter A equals to -3.1 , indicating that at infinite temperature all the melts come to a common viscosity of $10^{-3.1}$ Pa·s. It should be care that the parameter A was obtained by extrapolating measured viscosity to infinite temperature according to MYEGA equation. However, the MYEGA equation, as well as other widely equations, were only tested to temperature not much above the liquidus temperature. They may be not adequate to describe the viscosity-temperature relationship extended to infinite temperature.¹⁴⁾ Therefore, further studies may be needed to determine whether $A = -3.1$ is truly meaningful.

The composition dependences of parameter B and C were presented in Fig. 3. However, there are no clear trends of dependence on the content of SiO_2 , Al_2O_3 , CaO and MgO can be found. Although the parameter B roughly increases with increasing SiO_2 and decreasing CaO content (Figs. 3(a) and 3(C)), the scatters are too large to be practically meaningful. There are also no clear trend can be found between parameter B and C (Fig. 3(i)). The parameter B and C are expected to depend on the structure of the melt, thus with strong and complex dependences on compositions.¹⁵⁾ Hence, to model the composition dependences of parameter B and C , at least binary interactions between components as expressed in Eqs. (2) and (3) are necessary. Adding ternary and quaternary interactions would further improve the modeling accuracy, however, it will result in a very complex model.

3.2. Model Quality

The quality of the models on viscosity calculation was evaluated by the difference between measured and calculated viscosity value, which is expressed by:

Table 3. Organization of binary interaction parameters between melt components.

	SiO_2	Al_2O_3	CaO	MgO
SiO_2	<i>Parameter</i> ₁₁	/	/	/
Al_2O_3	<i>Parameter</i> ₁₂	<i>Parameter</i> ₂₂	/	/
CaO	<i>Parameter</i> ₁₃	<i>Parameter</i> ₂₃	<i>Parameter</i> ₃₃	/
MgO	<i>Parameter</i> ₁₄	<i>Parameter</i> ₂₄	<i>Parameter</i> ₃₄	<i>Parameter</i> ₄₄

Table 4. Optimized parameter values for current viscosity model.

	b_{11}	b_{12}	b_{22}	b_{13}	b_{23}	b_{33}	b_{14}	b_{24}	b_{34}	b_{44}
A	5 198.03	2 206.6	3 609.35	4 326.47	−942.38	1 387.21	393.78	8 486.02	1 851.68	1 984.58
	c_{11}	c_{12}	c_{22}	c_{13}	c_{23}	c_{33}	c_{14}	c_{24}	c_{34}	c_{44}
-3.1	1 996.27	5 215.92	−1 043.85	74.3	11 310.67	1 731.2	2 871.34	1 150.16	4 794.84	2 453.98

Fig. 3. Composition dependences of parameter *B* and *C*: (a) effect of SiO₂ on parameter *B*; (b) effect of Al₂O₃ on parameter *B*; (c) effect of CaO on parameter *B*; (d) effect of MgO on parameter *B*; (e) effect of SiO₂ on parameter *C*; (f) effect of Al₂O₃ on parameter *C*; (g) effect of CaO on parameter *C*; (h) effect of MgO on parameter *C*; and (i) relationship between parameter *B* and *C*. (Online version in color.)

$$\delta_i = \frac{|\eta_{i,\text{cal.}} - \eta_{i,\text{mea.}}|}{\eta_{i,\text{mea.}}} \dots\dots\dots (5)$$

The accuracy of the model was represented by the average relative error, Δ , for N measurements, which was calculated by

$$\Delta = \frac{1}{N} \sum_{i=1}^N \delta_i \times 100\% \dots\dots\dots (6)$$

It is found there is excellent agreement between the calculated and measured viscosities, with remarkable overall accuracy of 15.8% for 4 403 data, as shown in **Fig. 4**. Current model is based on more viscosity data, and obvious more accurate than other studies in these systems,^{3,4,7,16–20} where accuracies around 20% were reported. For each of the subsystems, current model also results in very high accuracy, with relative error lower than 20%, as shown in detail in **Fig. 5** and summarized in **Fig. 6**. More detailed comparisons between measured and calculated viscosity were also presented in **Figs. 8 to 10**.

In order to check the reliability of the model, the relationships between relative error and melt compositions, temperature and measured viscosity value were plotted, as present in **Fig. 7**. It is shown that there is no clear trend between relative errors and contents of SiO₂, Al₂O₃, CaO and MgO, and temperature, *e.g.* through **Figs. 7(a) to 7(e)**. It is more worth noting that, there is also no clear trend between relative errors and viscosity value. Under the condition of very low viscosity value, a small absolute error on the calculation of viscosity will result in a very large relative error. However, current model could calculate the viscosity with equally accuracy over very wide viscosity value range, *i.e.*, from 10⁻² to 10⁴ Pa·s, as shown in **Fig. 7(f)**. Therefore,

Fig. 4. Comparison between calculated and measured viscosity data for all systems. (Online version in color.)

current model could calculate the viscosity very reliably over the entire composition, temperature and viscosity value ranges studied in the work.

3.3. Composition Dependences of Viscosity

3.3.1. Binary Systems

Based on the current model, the composition dependences of viscosity for binary, ternary and quaternary systems were derived, as illustrated in **Figs. 8, 9 and 10** respectively. It should be noted that, the calculated curves may correspond to either thermodynamically stable molten liquid or thermodynamically unstable supercooled melt, depending on the liquidus temperature.

For binary SiO₂-M (M=Al₂O₃, CaO, MgO) systems (**Figs. 8(a) to 8(c)**), it is found the viscosities always decrease with decreasing SiO₂ content. SiO₂ is well known

Fig. 5. Viscosity calculation by current model for each system: (a) binary $\text{SiO}_2\text{-Al}_2\text{O}_3$ system; (b) binary $\text{SiO}_2\text{-CaO}$ system; (c) binary $\text{SiO}_2\text{-MgO}$ system; (d) binary $\text{Al}_2\text{O}_3\text{-CaO}$ system; (e) ternary $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ system; (f) ternary $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system; (g) ternary $\text{SiO}_2\text{-CaO-MgO}$ system; and (h) quaternary $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ system. (Online version in color.)

Fig. 6. Performances of current model in viscosity calculation for each system (S, A, C and M represent SiO_2 , Al_2O_3 , CaO and MgO respectively). (Online version in color.)

as a primary network “former” in silicate melts. Lower SiO_2 content indicates less polymerized melt, and thus result in lower viscosity. For binary $\text{Al}_2\text{O}_3\text{-CaO}$ system (Fig. 8(d)), the viscosity increases with increasing CaO at its lower contents, but then decreases at its higher contents. This is likely attributed to the charge compensation in Al^{3+} tetrahedral structure.⁷⁾ When Al_2O_3 forms tetrahedrally coordinated structure similar to SiO_2 , the charge compensation by Ca^{2+} is needed. Therefore lower content of CaO will mostly behave as charge compensator and promote the polymerization of the melt, and, hence, increase the viscosity. While at higher content of CaO , the Ca^{2+} is abundant enough, and part of the CaO will behave as network “modifier”, and then decrease the viscosity.

Fig. 7. Dependences of model error on various variables: (a) SiO₂ content; (b) Al₂O₃ content; (c) CaO content; (d) MgO content; (e) temperature; and (f) viscosity value. (Online version in color.)

3.3.2. Ternary Systems

For ternary systems, it is shown in Fig. 9 that over the entire composition ranges, the effects of components on viscosity are quite complex. However, within relative narrower range, the effects of the components can also be explained in a way consistent with binary systems according to the concept of network “former” and “modifier”. Similar to binary systems, the viscosity generally increases with increasing SiO₂ content (Figs. 9(a) to 9(c)), except when the contents of other components are very high. The CaO can behave as a charge compensator to Al³⁺ tetrahedral or network “modifier”, depending on melts compositions. For Al₂O₃-containing systems (Figs. 9(a) to 9(d)), the viscosity increases with increasing CaO at its lower content, because of the charge compensation effect discussed in last section. At higher content of CaO, it typically behaves as a network “modifier”, and thus the viscosity generally decrease with increasing CaO content. For Al₂O₃, it can be a network

“former” or “modifier” depending on the content of other components.²¹⁾ For example, at a high content of CaO, Al₂O₃ behaves mostly as a network “former”, and the viscosity increase with increasing Al₂O₃ content. However, at a high content of SiO₂, it will behave as a network “modifier”, and the viscosity decrease with increasing Al₂O₃ content. For MgO, it can also behave as network “former” or “modifier”.²²⁾ The viscosity generally decreases with increasing MgO content when there is enough network “formers”, *i.e.*, SiO₂ and Al₂O₃. However, the viscosity increases with increasing MgO at its high content, where the conventional network “formers” are insufficient.

3.3.3. Quaternary System

The iso-viscosity curves for SiO₂-Al₂O₃-CaO-MgO quaternary system at various content of MgO were presented in Fig. 10. By comparison with ternary SiO₂-Al₂O₃-CaO system (Fig. 9(a)), the trend of composition dependence is

Fig. 8. Composition dependences of viscosity for binary systems: (a) $\text{SiO}_2\text{-Al}_2\text{O}_3$ system; (b) $\text{SiO}_2\text{-CaO}$ system; (c) $\text{SiO}_2\text{-MgO}$ system; and (d) $\text{Al}_2\text{O}_3\text{-CaO}$ system. (Online version in color.)

Fig. 9. Composition dependences of viscosity for ternary systems: (a) $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ system; (b) $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system; (c) $\text{SiO}_2\text{-CaO-MgO}$ system; and (d) $\text{Al}_2\text{O}_3\text{-CaO-MgO}$ system. (Online version in color.)

Fig. 10. Composition dependences of viscosity for quaternary $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ system: (a) $\text{MgO}=5\%$; (b) $\text{MgO}=10\%$; (c) $\text{MgO}=15\%$; (d) $\text{MgO}=20\%$; (e) $\text{MgO}=25\%$; and (f) $\text{MgO}=30\%$. (Online version in color.)

clear: the viscosity of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ quaternary system decreases with increasing MgO content. Within studied composition range (up to 30%), MgO typically behaves as a network “modifier”, and thus decreases the viscosity. However, it should take care that the liquidus temperature generally increases with increasing MgO content,²³⁾ thus the low-viscosity high- MgO systems shown in Fig. 10 may be practically less useful. It is also revealed in Fig. 10 that the low viscosity area of quaternary system is much larger than ternary systems. It is accordant with the fact that industrial slags are mostly multi-compositional.

4. Conclusions

In summary, an accurate and simple viscosity model based on MYEGA model was established for $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ system and its subsystems. The model was calibrated by 4 403 non-graphite crucible viscosity data, which cover very wide compositions, temperature and viscosity value ranges. The following main conclusions can be drawn from this work:

(1) Current model calculates the viscosity with a remarkable overall accuracy of 15.8%. For each of the subsystems, current model also results very good accuracy, with relative error lower than 20%.

(2) The model could calculate the viscosity very reliably over the entire composition, temperature and viscosity value ranges studied in the work, even for viscosity value as low as 10^{-2} Pa·s.

(3) The composition dependences of viscosity for binary, ternary and quaternary systems were derived using established model. The effects of each component on viscosity can be interpreted based on the concept of network “former” and “modifier” and the charge compensation effect of Ca^{2+} on the tetrahedral-coordinated structure of Al^{3+} .

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