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Research article

Viscosity model for oxide melts relevant to fuel slags. Part 3: The iron oxide containing low order systems in the system SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O–FeO–Fe_2O_3

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ABSTRACT

The viscosity model recently developed for the fully liquid system SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O is further extended to describe the viscosity of the iron oxide containing low order systems in the Newtonian range. The different structural roles of Fe^{2+} and Fe^{3+} to the viscosity are captured by the associate species. Using the monomeric associate species in combination with some specific larger structrual units, the model is capable of describing the viscosity of the melts FeO, FeO–SiO_2, FeO–Al_2O_3, Fe_2O_3–CaO, Fe_2O_3–MgO, Fe_2O_3–Na_2O, and Fe_2O_3–K_2O over the whole range of compositions as well as a wide range of temperatures and oxygen partial pressures using only one set of model parameters. A new mechanism is proposed to describe the local viscosity maximum around the fayalite composition in the FeO–SiO_2 melt. The model shows that the presence of the local viscosity maximum is dependent on the temperature and oxygen partial pressure. Moreover, the viscosity maximum caused by Al^{3+}- or Fe^{3+}-induced charge compensation is presented and a good agreement between the calculated viscosities and experimental data is demonstrated.

1. Introduction

Among the major components in industrial silicate melts, iron oxide has a unique feature, existing in ferrous (FeO) and ferric (Fe_2O_3) forms under most conditions. The Fe^{3+}/Fe^{2+} ratio in iron oxide containing melts is not simply equal to the ratio of initial bulk composition $FeO_{1.5}$/FeO. It varies with composition, temperature, and pressure and is also strongly dependent on oxygen partial pressure [1,2]. Furthermore, the structural roles of FeO and Fe_2O_3 are different in multicomponent oxide melts. FeO behaves as a network modifier such as CaO or MgO, whereas Fe_2O_3 plays an amphoteric role as Al_2O_3 does. However, the determination of the structural role of iron oxide is very complex, since it is strongly dependent on the nature of silicate melts. The structure-dependent viscosity therefore is a complicated function of Fe^{3+}/Fe^{2+} ratio. As reported by Dingwell [3], an increase in Fe^{3+}/Fe^{2+} ratio results in a greater viscosity. In contrast, Wright and Zhang [4] stated that an increasing Fe^{3+}/Fe^{2+} ratio leads to a small decrease in viscosity. It is also possible that a viscosity maximum occurs with increasing Fe^{3+}/Fe^{2+} ratio [5]. Because of such complex behaviors the early viscosity models [6–13] cannot sufficiently describe the viscosity of iron oxide containing melts, even for binary melts such as the FeO–SiO_2 melt. For example, Zhang and Jahanshahi [9] proposed a structure-based model to describe the viscosity of the CaO–MgO–MnO–FeO–Fe_2O_3–SiO_2 melt, in which the composition dependence of viscosity is described as a function of concentrations of bridging and free oxygens. It should be noted that these model parameters for the melts FeO–SiO_2 and Fe_2O_3–SiO_2 are assumed to be the same. Another similar model, describing the composition dependence of viscosity by a fourth-order polynomial equation of the bridging oxygen concentration was developed by Reddy and Hebbar [10] for the FeO–SiO_2 melt, in which Fe_2O_3 is also treated as FeO. In these models, which do consider the influence of iron oxide on viscosity, however, the different structural roles of Fe_2O_3 and FeO are ignored and the induced viscosity change therefore cannot be soundly captured, for instance, the local viscosity maximum around the fayalite composition (Fe_2SiO_4) in the FeO–SiO_2 melt [14–17]. Using these models to calculate the viscosity for relevant higher order systems by way of extrapolation could lead to a significant deviation under certain conditions, especially for high iron oxide containing slags. As presented by Zhang and Jahanshahi [9], the calculated viscosities for the CaO–MgO–FeO–Fe_2O_3–SiO_2 melt exhibit large deviations compared to experimental data. The same generally occurs for coal ashes and biomass ashes, since the Fe_2O_3 content of

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them can reach up to 27.8 wt.% and 36.27 wt.%, respectively [18,19]. To eliminate the large deviations, for example, Hurst et al. [20] employed different separate models for different FeO contents, in which different sets of model parameters are required and moreover the model parameters are constrained with respect to temperature. The predictive power of such a model is therefore strongly limited. That is, using numerical fitting models, the viscosity cannot be predicted over the whole range of compositions and a wide range of temperatures.

Since the early viscosity models cannot handle the local viscosity maximum in the FeO–SiO_2 melt, which is a fundamental system for further development of a reliable viscosity model of iron oxide containing multicomponent melts, a new viscosity model based on structure for iron oxide containing melts is therefore needed. A recently developed structure based model [21,22] is further extended to describe the viscosity for the SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O–FeO–Fe_2O_3 melt. In the new model, the viscosity is linked to the internal structure of oxide melts. The internal structure is then described by relying on the associate species distribution calculated from a self-consistent thermodynamic database [23–27]. Each associate species here, which is a stoichiometric species employed to describe the Gibbs energy of oxide melts, represents one kind of structural unit [21]. The structural treatment of iron oxide is described by using the associate species distribution. A new mechanism for the local viscosity maximum in the FeO–SiO_2 melt is proposed, and the existence of such viscosity maximum is then soundly explained. The iron oxide containing melts such as FeO, FeO–SiO_2, Fe_2O_3–CaO, and Fe_2O_3–Na_2O are the focus of the present paper. In Part 4 of this series, the model of iron oxide containing slags will be extended from lower to higher order systems.

2. Model discussion

As emphasized in the discussion of the recently developed viscosity model [21,22] for the fully liquid system SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O and its subsystems, the structural dependence of viscosity is of fundamental and essential significance. A comprehensive description of structural dependence of viscosity is therefore required too for iron oxide containing melts. In the current model, the viscosity is correlated with the internal structure of oxide melts by means of the associate species distribution calculated from a self-consistent thermodynamic database.

2.1. The iron oxide melt

In contrast to the oxide components in the SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O melt, the iron oxide due to the nature of the transition metal oxide produces some new challenges for the viscosity modeling. The structural feature in the FeO or Fe_2O_3 melt cannot be sufficiently described by using only the associate species FeO and Fe_2O_3. The variation of structure-dependent density, for instance, indicates additional necessary associate species. It is seen from Fig. 1 that a decelerated increase of molar volume results (here converted from the density data [28]) with respect to the $Fe^{3+}/\Sigma Fe$ ratio at temperatures from 1450 °C to 1525 °C for the iron oxide melt. Such variation of molar volume indicates the existence of a structural unit containing both Fe^{2+} and Fe^{3+}, in addition to isolated structural units FeO and $FeO_{1.5}$, otherwise, the variation should be linear. A structural unit with Fe_3O_4 stoichiometry reported by Virgo and Mysen [29] may exist in iron oxide containing melts. Such structural unit has been confirmed and employed to describe the iron redox reaction and volumetric properties [30,31]. Therefore, the structural unit $FeO_{1.3}^{-}$ is required to describe the structural change in the iron oxide melt, although this structural unit (i.e. the associate species Fe_3O_4) is not required to reproduce the existing thermodynamic data such as phase diagram and activities.

Since Fe_2O_3 is an amphoteric oxide, it can be possibly charge-compensated by FeO, which was also proposed by Dickenson and Hess [32]. Hereby, the associate species Fe_3O_4 is considered to be an

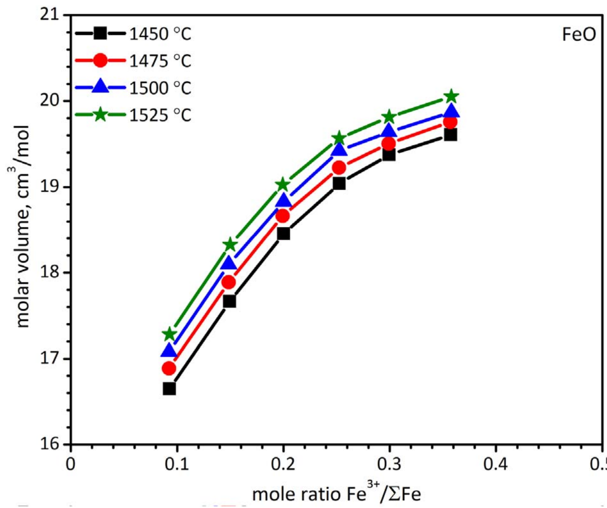

Fig. 1. The molar volume over the $Fe^{3+}/\Sigma Fe$ ratio in the FeO melt.

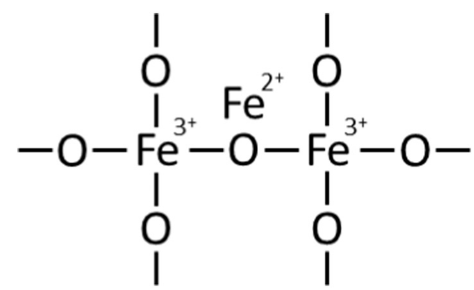

Fig. 2. Schematic representation of the associate species Fe_3O_4.

outcome of the charge compensation of two FeO_2^{-} by one Fe^{2+} (see Fig. 2), although the Fe^{3+} in the structural unit Fe_3O_4 may not all be tetrahedrally coordinated in oxide melts, possibly due to the inherited structural features from the solid Fe_3O_4. Analogous to the associate species $CaAl_2O_4$, the self-polymerization does not occur for Fe_3O_4. Therefore, the structural change in the iron oxide melt is described by using the associate species FeO, Fe_2O_3, and Fe_3O_4. The size of the basic structural units referring to these associate species is subject to the monomer-like scale, in which they behave like the other monomeric associate species, e.g. $CaSiO_3$ and $NaAlO_2$. The viscosity contribution can then be described in the framework of the ideal viscosity part, as defined in Part 1 of this series [21]. The viscosity of the iron oxide melt is described by:

$$\ln \eta = \ln \eta_{ideal} = \left(\sum_i X_i \cdot \ln \eta_i \right) \quad (1)$$

where: $\ln \eta_i = A_i + B_i/T$

η_{ideal} is the ideal viscosity part; X_i is the mole fraction of the monomeric associate species i; η_i is the viscosity contribution from the monomeric associate species i; A_i and B_i are the temperature and composition independent constants respectively for the ideal viscosity part; T is the absolute temperature.

2.2. The FeO–SiO_2 melt

The structural change in the iron oxide containing binary melts is more complex, especially for the FeO–SiO_2 melt. The Fe^{3+}/Fe^{2+} ratio in the FeO–SiO_2 melt varies not only with temperature and oxygen partial pressure but also with composition.

A monotonic decreasing Fe^{3+}/Fe^{2+} ratio occurs with increasing temperature (see Fig. 3(a)) or with decreasing oxygen partial pressure (see Fig. 3(b)). In contrast, the Fe^{3+}/Fe^{2+} ratio exhibits a non-