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A structurally-based quasi-chemical viscosity model has been developed for the Al₂O₃–CaO–‘FeO’–MgO–SiO₂ system. The model links the slag viscosity to the internal structure of melts through the concentrations of various anion/cation Si₀.₅O, Mn²⁺/H₂O and Mn⁺/Si₀.₂₅O viscous flow structural units. The concentrations of structural units are derived from the quasi-chemical thermodynamic model.

The focus of the work described in the present paper is the analysis of experimental data and the viscosity models for fully liquid slags in the Al₂O₃–CaO–MgO, Al₂O₃–MgO–SiO₂ and CaO–MgO–SiO₂ systems.

KEY WORDS: slag viscosity; viscosity model; Al₂O₃–CaO–MgO–SiO₂.

1. Introduction

The present paper is the second in a series describing the development of the structurally-based quasi-chemical viscosity (QCV) model for the Al₂O₃–CaO–‘FeO’–MgO–SiO₂ system. A structurally-based viscosity model for fully liquid silicate slags applied to the Al₂O₃–CaO–‘FeO’–MgO–SiO₂ system at metallic iron saturation has previously been developed by authors.1 The present series of papers describes further extension of the model for the Al₂O₃–CaO–‘FeO’–MgO–SiO₂ system to incorporate an effect of MgO. In the first of this series of papers2 the QCV model was described and viscosity predictions were provided for the MgO, CaO–MgO, Al₂O₃–MgO and MgO–SiO₂ subsystems. The present paper focuses on the viscosities in the ternary subsystems Al₂O₃–CaO–MgO, CaO–MgO–SiO₂ and Al₂O₃–MgO–SiO₂.

The Al₂O₃–MgO–SiO₂, CaO–MgO–SiO₂ and Al₂O₃–CaO–MgO slag systems are important as they form the basis of the quaternary Al₂O₃–CaO–MgO–SiO₂ system. A new process for the production of iron has been developed using MgO additions to the slag to provide improved sintering properties. This process has been used to produce iron from low-grade iron ores. The development of a viscosity model for the Al₂O₃–MgO–SiO₂ system is important for pyrometallurgical treatment of radioactive wastes.3

Briefly, the methodology used in developing the QCV model in the present study involves the following stages: 1) collect and carefully analyse all the experimental data available for the slag systems under investigation; 2) exclude unreliable experimental datasets from the model optimisation (using analysis of phase equilibria and trends in the activation and vaporisation energies obtained from experimental viscosity data); 3) evaluate the variability (internal scatter) of experimental data; 4) analyse the trends in the concentrations of structural units obtained from the quasi-chemical thermodynamic model; 5) calculate the masses and volumes of the structural units using mass balance and available ionic radii data; 6) optimise the model coefficients for the whole compositional range of the slag systems including all unary, binary, ternary etc sub-systems by repeating optimisation cycles from low- to high-order systems; 7) analyse the model parameters obtained during optimisation to understand general trends and dependencies; 8) repeat steps 6 and 7 until the agreement between model predictions and experimental data is comparable to the data variability over the whole range of conditions.

2. Comparisons between QCV Model Predictions and Experimental Data

2.1. Al₂O₃–CaO–MgO

The viscosities of liquid slags in the Al₂O₃–CaO–MgO system have not been systematically investigated experimentally to date: only two experimental studies have been found in the literature. Bakhvalov et al.3 used a “vibra-
"or oscillating-type of the rheometer and did not report any additional information on the technique/materials used. Shalimov and co-workers\textsuperscript{4,5)} reported viscosity measurements undertaken using the rotational bob method, which is believed\textsuperscript{6)} to be not as accurate as the oscillating (or vibrational) rheometer for relatively low viscosities in the range of 0.01–0.1 Pa·s.

Figure 1 shows the liquidus isotherms in the Al\textsubscript{2}O\textsubscript{3}–CaO–MgO system predicted by FactSage\textsuperscript{7,8)} and the experimental compositions studied in Bakhvalov\textsuperscript{3)} and Shalimov\textsuperscript{4,5)} Experimental information\textsuperscript{3–5)} is available only for low-MgO compositions (below \(\sim 12\) wt\%) close to the Al\textsubscript{2}O\textsubscript{3}–CaO binary. Comparison of the reported temperatures and compositions with the phase equilibria information predicted with FactSage indicates that some of experimental data were obtained at conditions below the liquidus.

Figure 2 shows selected results of Bakhvalov\textsuperscript{3)} and liquidus temperatures calculated by FactSage\textsuperscript{7,8)} It can be seen that in all cases a sharp increase of slag viscosity (resulting in inflection points in the logarithm viscosity vs. reciprocal temperature line) is observed at temperatures corresponding to the predicted liquidus. This figure clearly demonstrates that careful analysis of phase equilibria (for example, using such software as the FactSage computer package) should be used for the experimental data in order to exclude possible heterogeneous viscosity measurements.

Comparison between Bakhvalov’s\textsuperscript{3)} and Shalimov’s\textsuperscript{4,5)} results at the same composition (Al\textsubscript{2}O\textsubscript{3}/CaO/MgO=41/53/6 wt\%) is presented in Fig. 3. The temperatures of the liquidus and phase field boundaries predicted by FactSage are also indicated in this graph by small arrows. It can be seen that there is a correlation between these temperatures and inflection points on the viscosity–temperature curves. Again rapid increases of the viscosity measurements with decreasing temperature are believed to be directly related to the crystallisation of the slag. According to Fig. 3 solidification of the slag sample in Shalimov’s work\textsuperscript{4,5)} appeared to occur at a higher temperature (\(\sim 1450\)°C) compared to that reported by Bakhvalov\textsuperscript{3)} (\(\sim 1300\)°C). The difference in these temperatures could be related to temperature measurements, thermal history, slag composition and/or experimental design and procedure.

Figures 4(a)–4(f) show the predicted iso-SNNB (second-nearest-neighbour bonds\textsuperscript{2}) concentrations in the Al\textsubscript{2}O\textsubscript{3}–CaO–MgO system at 1600°C for real and metastable liquid slag; these concentrations were predicted using the optimised thermodynamic database for this system and the FactSage computer package.\textsuperscript{7,8)} It can be seen from the concentration lines from this figure that Al\textsuperscript{3+} cation in this system preferentially forms (Al–Mg) and (Al–Ca) SNNB from (Al–Al), (Ca–Ca) and (Mg–Mg) SNNB (similar to the behaviour of the Si\textsuperscript{4+} cation in SiO\textsubscript{2}-containing systems). At intermediate composition ranges the concentrations of the (Al–Ca) and (Al–Mg) are significant, and only at high Al\textsubscript{2}O\textsubscript{3}, CaO or MgO compositions over \(\sim 70\) wt\% the sum of the (Al–Ca) and (Al–Mg) concentrations is less than 0.7 mol fraction.

The optimised values of the molar activation and vapourisation energies for all corresponding unary and binary subsystems have been given in previous publications.\textsuperscript{1,2)} The corresponding partial activation energies/vapourisation energy coefficients in this ternary system have been extrapolated from the corresponding unary and binary systems. Only one small ternary parameter expressing effect of the (Al–Mg) concentrations on the activation energy of viscous
flow\(^2\) was required to better describe viscosities in the \(\text{Al}_2\text{O}_3–\text{CaO}–\text{MgO}\) system and higher-order \(\text{SiO}_2\)-containing systems.

Figure 5 shows iso-viscosity lines [Pa·s] predicted by the present QCV model for liquid slags at 1 600°C. The viscosities of the slags in this \(\text{Al}_2\text{O}_3–\text{CaO}–\text{MgO}\) system are low (\(<\;0.2\,\text{Pa} \cdot \text{s}\)) and are significantly smaller than the viscosities observed in \(\text{SiO}_2\)-containing ternary slag systems (e.g. see Figs. 9 and 17).

2.2. \(\text{CaO}–\text{MgO}–\text{SiO}_2\)

Eleven experimental studies\(^9\)–\(^{19}\) of slag viscosities are reported for the \(\text{CaO}–\text{MgO}–\text{SiO}_2\) system. Sipp\(^6\) reported viscosity measurements for low temperatures (\(\leq 1 050\,\text{K}\)) using the uni-axial compression method described elsewhere.\(^{16}\) These results are related to the “metastable” glasses and were not included in the current model optimisation.

Most of the researchers\(^{12}–^{17},^{19}\) have used Pt or Pt/Rh materials for both the container and sensor, which is the most suitable in the temperature range investigated (1 523–1 873 K). However, Kawai\(^{10}\) used the graphite crucibles and bobs for viscosity measurements up to 1 700°C. According to the analysis by Gul’tyai,\(^9\) who also used graphite, this material starts reacting with \(\text{SiO}_2\) in the slag at temperatures higher than 1 500°C (intensive reaction occurs for \(T \geq 1 650\,\text{°C}\)) and therefore during experiments temperatures should not exceed 1 600–1 650°C. This condition was not satisfied in the experiments carried out by Kawai\(^{10}\) and might be the reason for a systematic deviation of his results from others. Kozu and Kani\(^{11}\) reported neither materials of crucible and bob used nor other details of experiments; it is not possible therefore to evaluate reasons for the deviation of their results from others.

The rotational cylinder viscometry technique was used in a number of studies\(^9,^{11},^{15},^{17}–^{19}\); this method is considered to be one of the most accurate in the investigated range of viscosities (\(~0.1–10\,\text{Pa} \cdot \text{s}\)). Some researchers\(^{12}–^{15}\) used the oscillating bob method, which is also suitable for these viscosities. Gul’tyai\(^9\) did not publish a full description of the apparatus used, except it was reported to be a rotational viscometer.

Since the composition and state of the slag can change during viscosity experiments it is important to carry out the post-experimental analysis of the quenched slag samples to verify the composition and to ensure that samples are homogeneous and bubble-free. Only a few researchers reported that such an analysis was carried out: Scarfe\,et\,al.,\(^{15}\) Sykes\,et\,al.,\(^{17}\) and Urbain\,et\,al.;\(^{18}\) these results were therefore given a higher weight in the model optimisation.

The widest compositional range in the \(\text{CaO}–\text{MgO}–\text{SiO}_2\) system was investigated by Gul’tyai,\(^9\) while a number of researchers reported only one composition measured (usually the composition of diopside—\(\text{CaMgSi}_2\text{O}_6\), which is of geological interest). The widest investigated temperature range was reported by Urbain and co-workers\(^{18}\) for the composition close to diopside.

Figure 6 shows the liquidus isotherms calculated by FactSage and experimental compositions investigated by a number of researchers.\(^9,^{11},^{12},^{15},^{17}\) Most of the experimental measurements were undertaken in the compositional areas in which the liquidus temperatures are predicted to be below 1 600°C. Careful analysis of the experimental data showed that some of the results by Gul’tyai\(^9\) at lower \(\text{SiO}_2\) concentrations, and by Kawai,\(^{10}\) were carried out below the liquidus.

Agreement between the experimental\(^9,^{11},^{12},^{15},^{17}\) and predicted viscosities as a function of reciprocal temperature at or close to the composition of diopside (\(\text{CaMgSi}_2\text{O}_6\)) is shown in Fig. 7. All the cited researchers except Licko\(^{12}\) used the rotational viscometry technique; the experimental procedures were similar, except in the studies by Gul’tyai.\(^9\) Most of the data are consistent with each other, except the
data by Kozu and Kani. The latter authors did not report experimental details, and it is not possible to evaluate reasons for such deviation from the rest of the results. The present model agrees well with the measurements reported by most of the authors.9,12,15,17)

The iso-concentrations (0.1, 0.2, ..., 0.9 mol fr) of the SNNB in the CaO–MgO–SiO₂ system at 1500°C are shown in Figs. 8(a)–8(f). The concentrations of the Si–Si SNNB (Fig. 8(a)) are not sensitive to the CaO/MgO weight ratio but decreases rapidly towards values close to zero with a decrease of SiO₂ concentration below 40 wt%. Both X⁻Ca–Si (Fig. 8(d)) and X⁻Mg–Si (Fig. 8(e)) have maximum values at orthosilicate compositions (2MgO·SiO₂ and 2MgO·SiO₂, respectively) and similar distributions across the ternary system: the “maxima” extended towards opposite binary joins (the CaO–SiO₂ for Mg–Si and the MgO–SiO₂ for Ca–Si SNNB, respectively). The concentrations of non-silicate SNNB X⁻Ca–Ca, X⁻Mg–Mg and X⁻Ca–Mg (see Fig. 8(b), 8(c), 8(f)) approach values that have a significant effect on the viscosity trends only at low SiO₂ concentrations (less than 30 wt%).

Figure 9 shows iso-viscosity curves [Pa·s] and liquidus calculated by FactSage at T=1500°C. It can be seen that viscosities slightly increase with increasing of the CaO concentration along iso-SiO₂ lines. Slag viscosities increase rapidly with increasing SiO₂ concentration.

The experimental9,10,12,13) and calculated slag viscosities as a function of CaO/(CaO+MgO) weight ratio at 50 wt% SiO₂ for different temperatures are shown in Fig. 10. The
dashed lines connecting the experimental points are plotted to guide the reader to results reported by the different authors and different temperatures. The viscosities calculated by the present QCV model agree well with the experimental points. It can be seen from this figure that several points by Kawai\cite{10} have obvious deviation from the other results. Two points at weight ratio \(\text{CaO}/(\text{CaO}/\text{MgO}) = 0.64\) at 1500 and 1600°C were obtained below or close to the liquidus predicted by FactSage and were not included in the model optimisation. This is also the case for one point by Gul’tyai\cite{9} at 1400°C. Again, this point is not used in the optimisation. Data by Machin,\cite{13,14} Licko,\cite{12} Scarfe\cite{15} and Urbain\cite{18} were given preference during selection of model parameters.

Figure 11 shows the experimental\cite{9,12,15,18} and calculated slag viscosities as a function of wt \(\text{SiO}_2\) at wt \(\text{CaO}/(\text{CaO}/\text{MgO}) = 0.64\) for a range of temperatures in the system \(\text{CaO–MgO–SiO}_2\).

2.3. \(\text{Al}_2\text{O}_3–\text{MgO–SiO}_2\)

The \(\text{Al}_2\text{O}_3–\text{MgO–SiO}_2\) system is another example of a well-investigated slag system: there are viscosity data from 11 experimental studies\cite{14,18,20-28} available in the literature. Most of the researchers employed the rotational cylinders method and Pt (or Pt/Rh alloys)\cite{14,22,24-26} or Mo\cite{18,21,23,27,28} materials for the sensor and container. The use of molybdenum implies the use of neutral atmosphere (Ar, \(\text{N}_2\)), whilst Pt (or Pt/Rh alloys) can be used in air. The “torsional” rheometer used by Ermolaeva\cite{20} might not be suitable for the viscosities and temperatures investigated; as will be pointed out below these results have an obvious deviation from the other studies.

The majority of experimental viscosity measurements in the \(\text{Al}_2\text{O}_3–\text{MgO–SiO}_2\) were obtained by Lyutikov\cite{23} (for 50 slag compositions investigated), Toplis and Dingwell\cite{26} (22 compositions) and Zhilo\cite{27} (40 compositions). A large portion of these results were used in the model optimisation.

Toplis and Dingwell\cite{26} also reported measurements of the viscosity at lower temperatures (1094–1147 K) using the techniques only designed for measuring very high viscosities (\(\geq 0.9\) Pa·s). These results are related to the glassy state and were therefore not included into the model optimisation.

The highest temperatures achieved during viscosity measurements of fully liquid slags in the \(\text{Al}_2\text{O}_3–\text{MgO–SiO}_2\) system were reported by Urbain\cite{5} and Hofmaier\cite{21} to be approximately 2400 K. For such temperatures it is necessary to use a pyrometer for temperature measurements, which has a greater experimental uncertainty than the used of a thermocouple.

Figure 12 shows the liquid isotherms calculated by FactSage\cite{7,8} and compositions of experimental viscosity measurements in the \(\text{Al}_2\text{O}_3–\text{MgO–SiO}_2\) system.
were performed for partly crystallised slags. The arrows on this figure indicate the liquidus temperatures for each composition calculated by FactSage. It can be seen that in each case the liquidus predicted with FactSage approximately coincides with the inflection points on the viscosity–temperature curves (log $\eta$ vs. $1/T$) indicating that solid phases precipitated out of liquid slag were present during the experiments and had affected the viscosity measurements. The data reported by Ermolaeva\textsuperscript{20)} have two notable inflection points on the log $\eta$ vs. $1/T$ plot: the first higher temperature inflection point could be related to the beginning of crystallisation (primary phase field is mullite, Al$_6$Si$_2$O$_{13}$); the second one can be related to the temperature when another solid phase (spinel solid solution) starts to precipitate out. The points reported for temperatures below the liquidus were excluded from the optimisation.

The SNNB concentrations predicted with FactSage\textsuperscript{7,8)} in the Al$_2$O$_3$–MgO–SiO$_2$ system at 1,700°C are presented in Figs. 14(a)–14(f). The SNNB concentrations in the regions below the liquidus temperatures are given for homogeneous metastable liquids. Concentrations of the Si–Si SNNB are not sensitive to the changing CaO/Al$_2$O$_3$ ratio but decreases rapidly to less than 0.5 mol fraction as the SiO$_2$ concentration decreases below 70 wt%. Both $X_{\text{Al-Si}}$ (Fig. 14(d)) and $X_{\text{Mg-Si}}$ (Fig. 14(e)) have maxima at orthosilicate (Al$_2$O$_3$, SiO$_2$ and 2MgO·SiO$_2$, respectively) compositions, but the maximum values are significantly different being $\sim$0.41 mol fraction of $X_{\text{Al-Si}}$ and $\sim$0.9 mol fraction of $X_{\text{Mg-Si}}$. These “maxima” are extended across the ternary systems. Only at low SiO$_2$ concentrations of $\sim$30 wt% the concentrations of non-silicate SNNB $X_{\text{Al-Al}}$, $X_{\text{Mg-Mg}}$ and $X_{\text{Al-Mg}}$ (Figs. 14(b), 14(c), 14(f), respectively) approach significant values that affect the viscosity trends.

Figure 15 presents the experimental\textsuperscript{20,23–25,28)} and calculated viscosities as a function of the Al$_2$O$_3$/(Al$_2$O$_3$/MgO) weight ratio at constant SiO$_2$ concentration of 50 wt% and different temperatures (1,500, 1,600, 1,700, 1,800, 1,900°C). Dashed lines indicate metastable liquid under the liquidus calculated by FactSage. It can be seen that significant deviation of the experimental results\textsuperscript{20,23–25,28)} from the model predictions is observed at compositions below the liquidus. Figure 15 also illustrates the fact that the slag viscosities as a function of the Al$_2$O$_3$/(Al$_2$O$_3$/MgO) weight ratio have slight non-linearity that could have resulted from the charge compensation effect. The deviation from the linearity towards maximum is less pronounced in this system compared to the Al$_2$O$_3$–CaO–SiO$_2$ system (the value of the charge compensation term $E_{\text{ch}}/c_{\text{AlCa}}$ of 1.90 is larger than the $E_{\text{ch}}/c_{\text{AlMg}}$ value of 1.29). The viscosities of the Al$_2$O$_3$–CaO–SiO$_2$ (dashed line) and Al$_2$O$_3$–FeO–SiO$_2$ (dot-dashed line) systems at 1,900°C are given in Fig. 15 for comparison. It can be seen that in all systems the trends of viscosity as a function of Al$_2$O$_3$/(Al$_2$O$_3$/MeO) (Me = Mg, Ca, Fe) at 50 wt% SiO$_2$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig13.png}
\caption{Examples of viscosity measurements in the Al$_2$O$_3$–MgO–SiO$_2$ system. (Dashed lines indicate the trend.)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig14.png}
\caption{Predicted SNNB iso-concentrations (FactSage) in the Al$_2$O$_3$–MgO–SiO$_2$ system at 1,700°C.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig15.png}
\caption{Liquid viscosities in the Al$_2$O$_3$–MgO–SiO$_2$ system as a function of wt Al$_2$O$_3$/(Al$_2$O$_3$/MeO) (Me = Mg, Ca, Fe) at 50 wt% SiO$_2$.}
\end{figure}
dicted slag viscosities as a function of wt% SiO₂ at 1 700°C and model optimisation. The uncertainties in the experimental data is very important for the Al₂O₃–MgO–SiO₂ this effect is predicted to be the least.

Figure 16 shows the experimental14,18,20,21,23,25,26 and predicted slag viscosities as a function of wt% SiO₂ at Al₂O₃/(Al₂O₃+MgO)=0.7 by weight (molar A/(A+M)=0.5) for different temperatures (1 500, 1 600, 1 700, 1 800, and 1 900°C); the liquidus calculated by FactSage is also available in the FactSage package. It can be seen from comparison of Fig. 14 and Fig. 17 that iso-viscosity curves follow the trends of the iso-SNNB curves and provide an accurate description of the experimental data for fully liquid slags.

3. Conclusions

A general structurally-based quasi-chemical viscosity model has been developed, which accurately describes slag viscosity in the Al₂O₃–CaO–MgO, CaO–MgO–SiO₂ and Al₂O₃–MgO–SiO₂ systems. The model links the slag viscosity to the structure of the liquid slag expressed in terms of the second nearest neighbouring bonds; the latter are extracted from the thermodynamic quasi-chemical model available in the FactSage package.

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REFERENCES

20) E. V. Ermolaeva: Ogneupory, 16 (1951), 162.