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Evaluation of viscosity of mold flux by using neural network computationM.HANAO *et al.*

A new estimation method of viscosity or solidification temperature of mold fluxes was proposed by applying the neural network computation. In this evaluation system, the viscosity and the solidification temperature of mold fluxes can be evaluated from the analytical compositions in multi-component systems of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO-Na}_2\text{O-F-T.Fe-ZrO}_2\text{-TiO}_2\text{-BaO-MnO-B}_2\text{O}_3\text{-S-C}$ without any conversion of S or F to sulphide or fluoride. It was found that the calculated results of the dependence of viscosity on temperature and composition agree with the experimental results more precisely than some conventional physical models for viscosity. Furthermore, viscosity of mold fluxes can be estimated precisely in the wide range of SiO_2 content.

(cf. *ISIJ Int.*, 46 (2006), 346)**Viscosities of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-(R}_2\text{O or RO)}$ melts**S.SUKENAGA *et al.*

The effect of adding R_2O (R=Li, Na and K) or RO (R=Ba, Mg) on the viscosities of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ ($\text{CaO/SiO}_2=0.67, 1.00$ or 1.22 , $\text{Al}_2\text{O}_3=20$ mass%) melts has been measured by rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by ^{27}Al and ^{29}Si MAS-NMR spectra.

The viscosities of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ quaternary melts decreased with increasing the additive content of Li_2O or Na_2O . However, the viscosity of the melts increased with increasing the additive content of K_2O . In the case of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-RO}$ quaternary melts, the viscosities of the melts with $\text{CaO/SiO}_2=0.67$ decreased with increasing the additive content of BaO or MgO , however, the viscosities of the melts with $\text{CaO/SiO}_2=1.00$ and 1.22 increased with increasing the additive content of BaO .

In the case of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$, the analysis of ^{27}Al MAS-NMR spectra and ^{29}Si MAS-NMR spectra indicated that the degree of polymerization of silicate anions in the glasses decreased with the addition of Li_2O or Na_2O , and that the degree of polymerization of aluminosilicate anions in the glasses increased with the addition of K_2O . It was estimated from the results that the increase in viscosities of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$ melts was dependent on increase of aluminosilicate anions in the melts with the addition of K_2O .

In the case of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-RO}$, the analysis of ^{27}Al MAS-NMR spectra and ^{29}Si MAS-NMR spectra indicated that the degree of polymerization of silicate and aluminosilicate anions in the glasses decreased with the addition of MgO . The degree of polymerization of aluminosilicate anions in the glasses increased with the addition BaO . It was estimated from the results that the increase in viscosities of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-BaO}$ melts was dependent on increase of aluminosilicate anions in the melts with the addition of BaO .

(cf. *ISIJ Int.*, 46 (2006), 352)**Development of a quasi-chemical viscosity model for fully liquid slags in the $\text{Al}_2\text{O}_3\text{-CaO-FeO-MgO-SiO}_2$ system. Part 1. Description of the model and its application to the $\text{MgO, MgO-SiO}_2, \text{Al}_2\text{O}_3\text{-MgO}$ and CaO-MgO sub-systems**A.KONDRATIEV *et al.*

A structurally-based quasi-chemical viscosity model for fully liquid slags in the $\text{Al}_2\text{O}_3\text{-CaO-FeO-MgO-SiO}_2$ system has been developed. The model links the slag viscosities to the internal structures of the melts through the concentrations of various $\text{Si}_{0.5}\text{O}$, $\text{Me}_{2/n}^{n+}\text{O}$ and $\text{Me}_{1/n}^{n+}\text{Si}_{0.25}\text{O}$ viscous flow structural units. The concentrations of these structural units are derived from a quasi-chemical thermodynamic model of the system. The model described in this series of papers enables the viscosities of liquid slags to be predicted within experimental uncertainties over the whole range of temperatures and compositions in the $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ system.

(cf. *ISIJ Int.*, 46 (2006), 359)**Development of a quasi-chemical viscosity model for fully liquid slags in the $\text{Al}_2\text{O}_3\text{-CaO-FeO-MgO-SiO}_2$ system. Part 2. A review of the experimental data and the model predictions for the $\text{Al}_2\text{O}_3\text{-CaO-MgO, CaO-MgO-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-MgO-SiO}_2$ systems**A.KONDRATIEV *et al.*

A structurally-based quasi-chemical viscosity model has been developed for the $\text{Al}_2\text{O}_3\text{-CaO-FeO-MgO-SiO}_2$ system. The model links the slag viscosity to the internal structure of melts through the concentrations of various anion/cation $\text{Si}_{0.5}\text{O}$, $\text{Me}_{2/n}^{n+}\text{O}$ and $\text{Me}_{1/n}^{n+}\text{Si}_{0.25}\text{O}$ 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 $\text{Al}_2\text{O}_3\text{-CaO-MgO, Al}_2\text{O}_3\text{-MgO-SiO}_2$ and CaO-MgO-SiO_2 systems.

(cf. *ISIJ Int.*, 46 (2006), 368)**Development of a quasi-chemical viscosity model for fully liquid slags in the $\text{Al}_2\text{O}_3\text{-CaO-FeO-MgO-SiO}_2$ system. Part 3. Summary of the model predictions for the $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ system and its sub-systems**A.KONDRATIEV *et al.*

A structurally-based quasi-chemical viscosity model for fully liquid slags in the $\text{Al}_2\text{O}_3\text{-CaO-FeO-MgO-SiO}_2$ system has been developed. The focus of the work described in the present paper is the analysis of the experimental data and viscosity models in the quaternary system $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ and its sub-systems.

A review of the experimental data, viscometry methods used and viscosity models available in the $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ and its sub-systems is reported. The quasi-chemical viscosity model is shown to provide good agreement between experimental data and predictions over the whole compositional range.

sitional range.

(cf. *ISIJ Int.*, 46 (2006), 375)**Viscosity and surface tension measurements of $\text{RE}_2\text{O}_3\text{-MgO-SiO}_2$ ($\text{RE=Y, Gd, Nd and La}$) melts**F.SHIMIZU *et al.*

The effect of RE_2O_3 ($\text{RE=Y, Gd, Nd and La}$) on the viscosity and the surface tension of 45.2MgO-54.8SiO_2 (mol%) melts have been investigated with rotating crucible viscometer and ring method, respectively. Additionally, structural characterizations of these quenched vitreous samples have been investigated with Infra-Red spectrometer.

The viscosities of $\text{RE}_2\text{O}_3\text{-MgO-SiO}_2$ melts were found to decrease with increasing the content of any rare-earth additions, which suggests that rare-earth oxide behaves as a network modifier of complex silicate anions in high temperature melts. The viscosities decreased in the order of cationic radius of rare-earth; from Y_2O_3 , Gd_2O_3 , Nd_2O_3 to La_2O_3 . The surface tension of MgO-SiO_2 binary melts were found to increase with increasing the content of any rare-earth additions. The surface tensions obviously increased in the order of cationic radius of rare-earth, which the change of with rare-earth addition is direct antithesis of that of viscosities.

The decrease of the absorption band of $\text{RE}_2\text{O}_3\text{-MgO-SiO}_2$ glasses at 1060 cm^{-1} ($\text{Si}_4\text{nO}_{9\text{n}}^{2\text{n}-}$) with the attendant increase of the absorption band at 930 cm^{-1} ($\text{Si}_2\text{O}_6^{6-}$). These variations with rare-earth oxides content means that the degree of polymerization of complex silicate anions become smaller with rare-earth oxide additions.

The viscosity of rare-earth containing silicate melts linearly increases with cationic field strength of RE^{3+} . The surface tension of rare-earth containing silicate melts linearly decreases with cationic field strength, except Y_2O_3 additives.

(cf. *ISIJ Int.*, 46 (2006), 388)**Measuring and modeling of viscosity and surface properties in high temperature systems**L.HOLAPPA *et al.*

In order to be able to understand and model the kinetics of heterogeneous reactions and transport phenomena it is necessary to have experimental data of physical properties like viscosity, surface energy and interfacial energy. In this study viscosity of high-melting slags containing chromium oxides were measured. Central results and observed relationships and modelling are described. The results showed that addition of chromium oxide into the slag decreases the viscosity but the influence becomes weaker at high CrO_x contents. The viscosity-composition relation was evaluated by a modified Lida's model and a good agreement between the experimental and calculated results was observed.

Interfacial phenomena between liquid metal and slag with gas bubbles entering through the metal-slag interface were investigated by X-ray transmission technique. Bubble behaviour at metal-slag interface and dispersion of metal droplets into the slag were measured as a function of interfacial tension, gas bubble size and slag viscosity. The effect of different parameters on metal entrain-

ment is discussed.

(cf. *ISIJ Int.*, **46** (2006), 394)

Evaluation of surface tension of molten ionic mixtures

T. TANAKA et al.

A thermodynamic model was derived to evaluate the surface tension of molten ionic mixtures by considering the ratio of the radius of cation to that of anion. The present model reproduces the following characteristics of the composition dependence of molten alkaline-halide ionic mixtures precisely.

- almost linear change with the composition in common cation systems;
- large concave of the composition dependence in common anion systems.

The present model can be applied to evaluate the surface tension molten ionic mixtures with complex anion such as sulfate as well as molten SiO₂ based binary systems considering effective ionic radii for complex anions.

(cf. *ISIJ Int.*, **46** (2006), 400)

Influence of slag composition on slag-iron interfacial tension

H. SUN et al.

Interfacial tensions between liquid iron and slag were examined for CaO-SiO₂ binary and CaO-SiO₂-Al₂O₃ ternary slag systems. The influences of FeO, MgO, B₂O₃, TiO₂, BaO and ZrO₂ in slag on the interfacial tension were also investigated by varying these oxides from 1–30 wt% in the CaO-SiO₂ binary or CaO-SiO₂-Al₂O₃ ternary slag systems.

The interfacial tensions were determined by the sessile drop technique under argon atmosphere at 1853 K. An X-Ray radiographic technique was employed to image the profile of molten iron drop in a slag bath and the interfacial tensions between slag and iron were obtained from the drop shape analysis.

In examining the effect of slag composition on the interfacial tension, the oxygen in liquid iron and its impact on the interfacial tension was taken into consideration. The interfacial tension was found slightly increased with increasing CaO/SiO₂ ratio in CaO-SiO₂ slag, and with increasing MgO content in the slag. A decrease of interfacial tension was found with increasing FeO in slag. Only minor changes in the interfacial tension were observed with varying the slag composition in the CaO-SiO₂-Al₂O₃ ternary slag system and the influences of B₂O₃, TiO₂, BaO, and ZrO₂ in slag on the interfacial tension were found insignificant.

(cf. *ISIJ Int.*, **46** (2006), 407)

Lattice and radiation conductivities for mould fluxes from the perspective of degree of crystallinity

S. OZAWA et al.

The lattice and radiation conductivities have been determined for commercial mould fluxes in glassy and partially crystalline states as functions of the degree of crystallinity to confirm whether or not more crystallisation of mould fluxes is always effective in slow cooling in continuous casting. Lattice conduc-

tivities, refractive indices and absorption/extinction coefficients were measured on glassy and partially crystallised samples from commercial mould fluxes. The lattice conductivities of mould fluxes increased with increasing the degree of crystallinity at temperatures around 773 K and more prominent increase was observed where the degree of crystallinity exceeded about 20%, which would be due to the contact between crystal grains precipitated. However, fluxes having higher degrees of crystallinity showed negative temperature coefficients in the lattice conductivities, particularly at higher temperatures, and thus there was a case where the lattice conductivities decreased with increasing the degree of crystallinity at higher temperatures. On the other hand, the radiation conductivities tended to decrease with increasing the degree of crystallinity and became almost constant where the degree of crystallinity exceeded about 15%. As a consequence of this, more crystallisation does not always lead to slow cooling in continuous casting: the degree of crystallinity should be controlled to be about 15% where the partially crystalline phase exists around 773 K.

(cf. *ISIJ Int.*, **46** (2006), 413)

Thermal conductivity of the CaO-Al₂O₃-SiO₂ system

Y. KANG et al.

Thermal conductivity of the CaO-Al₂O₃-SiO₂ system, which is one of the most important silicate systems in iron- and steel-making processes, was measured using non-stationary hot wire method in the range from liquidus temperature to 1873 K. Measurements were carried out at various compositions, and iso-thermal conductivity line of the CaO-Al₂O₃-SiO₂ system was drawn in iso-thermal sections at 1673 K, 1773 K, and 1873 K. Thermal conductivity decreased with basicity increase, when CaO/SiO₂ ratio is smaller than unity, whereas it showed constant value when CaO/SiO₂ ratio is larger. In case Al₂O₃ content was varied at constant CaO/SiO₂ ratio of 0.39 and 0.90, thermal conductivity showed maximum at 15–20 mass% Al₂O₃, suggesting that Al₂O₃ behaves as an amphoteric oxide. In the temperature range of interest, the thermal conductivity of each composition decreased as temperature rises. Temperature dependence showed deviation from linearity with the reciprocal of absolute temperature, which was considered to be due to the thermally-induced depolymerisation of the silicate structure at higher temperature. Also, thermal conductivity was found to conform to an exponential function of 1/T during depolymerization with the apparent activation energy.

(cf. *ISIJ Int.*, **46** (2006), 420)

Application of square-wave pulse heat method to thermal properties measurement of CaO-SiO₂-Al₂O₃ system fluxes

K. NISHIOKA et al.

The square-wave pulse heat method was improved to measure thermal properties of vitreous samples by considering radiation heat transfer between the front and back faces of the samples, and the measurement accuracy of the method was exam-

ined.

Thermal properties of CaO-SiO₂-Al₂O₃ samples were measured by the method. Thermal diffusivities of the crystalline 40CaO-40SiO₂-20Al₂O₃ (mol%) sample are about 1.5–2.5 times larger than those of the vitreous sample. Specific heat of the crystalline and vitreous samples shows almost the same temperature dependency, except the highest measurement temperature due to crystallization of glass.

Finally, we investigated the reason that the thermal conductivity values measured by the improved square-wave pulse heat method differ from those by the line source method. As a result, crystallization of glass during the measurements would cause the difference of the temperature dependencies of the values measured by the two methods.

(cf. *ISIJ Int.*, **46** (2006), 427)

Estimation of heat transfer of a front-heating front-detection laser flash method measuring thermal conductivity for silicate melts at high temperatures

H. OHTA et al.

The thermal conductivity of silicate melts at high temperatures was determined by applying a differential three-layered laser flash method. In this method, the correction for radiative heat transfer was indispensable to obtain accurate thermal conductivity of the melts at high temperatures because, at 1500 K, the uncorrected values are 20 to 40% larger than the corrected ones; further, the corrected values strongly depend on the absorption coefficient of silicate melts. Recently, we applied the front-heating front-detection laser flash method using a short initial time period immediately after laser pulse irradiation for silicate melts. This method was considered to be unaffected by the radiative heat transfer. However, the amount of the radiative effect on thermal conductivity was not estimated. On the basis of heat transfer theory, the temperature responses of this method were numerically calculated by considering radiative heat transfer. The result revealed that the radiative effect is less than 4.4% even at 1743 K.

(cf. *ISIJ Int.*, **46** (2006), 434)

Crystallization of CaO-SiO₂-TiO₂ Slag as a candidate for fluorine free mold flux

H. NAKADA et al.

The time-temperature-transformation diagram (TTT diagram) of CaO-SiO₂-TiO₂ slag has been determined by using differential thermal analysis (DTA) in order to investigate the crystallization of the slag as a candidate for fluorine free mold flux. The incubation time of CaOSiO₂TiO₂ in CaO-SiO₂-TiO₂ slag is as small as that of cuspidine (3CaO₂SiO₂CaF₂) in commercial mold fluxes. This finding indicates that the CaOSiO₂TiO₂ crystallizes rapidly in the slag film between the mold and the steel in the continuous casting machine, similar to cuspidine in commercial mold fluxes. CaOSiO₂TiO₂ in CaO-SiO₂-TiO₂ slag is substituted for cuspidine in commercial mold fluxes. The thickness of the crystalline layer of CaOSiO₂TiO₂ is smaller than that of cuspidine. In order to improve the heat transfer control of CaO-SiO₂-TiO₂ slag, it is necessary

to decrease the incubation time of $\text{CaOSiO}_2\text{TiO}_2$ at high temperature.

(cf. *ISIJ Int.*, **46** (2006), 441)

The ability of slags to absorb solid Oxide inclusions

M. VALDEZ et al.

The capture rate of solid oxide-inclusion particles from molten steel by molten slag depends on the rate of steel film drainage (which occurs at certain particle velocities), interfacial separation, and dissolution into the slag. In this study the capture of common oxide inclusions of sizes 2.5–200 μm and with velocities ranging from their terminal velocities to $0.3 \text{ m} \cdot \text{s}^{-1}$ approaching the interface between molten iron and slags with chemistries corresponding to ladle, tundish and mold slags are investigated. Calculations, based on a model available in literature, show that film drainage (when applicable) is rapid enough to be ignored. A sensitivity analysis based on the slag properties show that the interfacial ener-

gy between slag and inclusion is the most pertinent property that could hinder interfacial separation. However, the interfacial tension needed to achieve this has to be a minimum of 0.41 N/m which is unreasonable for the case of common oxide inclusions such as Al_2O_3 , MgO , ZrO_2 and MgAl_2O_4 . The final step of dissolution was found based on studies with Confocal Scanning Laser Microscope experiments, to be significantly slower than the other steps. For a 100 μm particle, in the slags/inclusions investigated a correlation between slag viscosity, η [$\text{Pa} \cdot \text{s}$] and super saturation, ΔC [$\text{kg} \cdot \text{m}^{-3}$] with inclusion dissolution time, τ [s] was shown to be, $\tau = 2.04 \cdot 10^{-2} / (C/\eta)$.

(cf. *ISIJ Int.*, **46** (2006), 450)

Dynamic oxidation of the Ti-bearing blast furnace slag

L. ZHANG et al.

The effects of the dynamic oxidation on the physical chemical characteristics of the Ti-bearing blast

furnace slag, on the selective enrichment, precipitation and growth of the Ti component and the drop of metallic Fe from the slag have been investigated. Air was blown into the molten slag as oxygen resource through a lance during the dynamic oxidation process. It was found that the TiC, TiN, (Ti_2O_3) , Fe and (FeO) in the slag were oxidized, and the temperature of slag increased and the viscosity of slag decreased. These were not only in favour of the selective enrichment of the Ti component into the perovskite phase, but also in favour of the precipitation and growth of the perovskite phase, meanwhile promoted the coalescence, growth and drop of the metallic Fe droplets in the molten slag under an air agitation condition.

(cf. *ISIJ Int.*, **46** (2006), 458)