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# CHALLENGES IN PROCESS METALLURGY

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## ABSTRACT

During the course of the years, with the rapid strides of advancement of technology, metallurgy has expanded to materials science and engineering, with the induction of process metallurgy into the same, covering, at the same time, the advances in physics, chemistry, mechanical engineering as well as computational techniques. In designing processes, it is extremely important to have a fundamental understanding of the various process steps, the chemical reactions, heat and mass transfer aspects as well as considerations with respect to the energy requirements and environmental impacts. The present paper will present some of the advances in the consideration of the thermochemical and thermophysical properties of metallic materials and slags towards an optimization of the processes. The property models developed with respect to the thermodynamics and viscosities of multi-component slags will be presented.

**Key words:** Thermodynamic model, Slag, molar volume, Sulphide capacity, Interfacial tension.

## INTRODUCTION

Modelling of Materials processes requires a fundamental understanding of the process phenomena based on thermodynamics, transport phenomena and kinetics of the steps involved. While a traditional thermochemical model often lacks the input from kinetics and transport phenomena, some computerised fluid dynamic (CFD) models lack a thermodynamic and kinetic basis. Further, CFD models need accurate input of thermophysical data, such as the viscosities of the various molten phases and the interfacial tensions, to generate reliable mapping of flow patterns in reactors.

Futuristic process models, referred to as "macro-models" should be structured using the reaction models that are part of the gross process. Such reaction models referred to as "micro-models" may be advantageously used as building blocks. The micro-models, in fact, are reaction descriptions based on experimental thermochemical and kinetic information. The latter needs to be complemented by thermophysical data, essentially to describe the heat- and mass transfer phenomena involved. The research programs in the present laboratory have been strategically structured and conducted stepwise along this line. The present work is to surmise the modelling studies carried out in the present laboratory in recent years. While emphasis is given to the micro-models, an example of using micro-models as building blocks in process simulation is also presented. In the case of thermodynamic modelling, only a brief discussion is given, since this topic is presented in our another paper.

## THERMOPHYSICAL PROPERTY STUDIES

### Viscosity[1,2]

Since viscosities of ionic melts are of great importance in metallurgical processes, great attention has been paid in the present laboratory to both modelling as well as experimental studies of the slag viscosities. A description of viscosities in the multicomponent system, $Al_2O_3$-CaO-$Cr_2O_3$-FeO-$Fe_2O_3$-MgO-MnO-$SiO_2$ is aimed at. In order to achieve this task, a Temkin-Lumsden type of model for estimating the viscosities of multicomponent slags has been developed [1,2] combining Eyring's description of viscosities. In line with Eyring approach, the model applies reaction rate theory to describe the slag viscosity which is described in Eq.1:

$$\eta = \frac{h\,N\,\rho}{M} \exp\left(\frac{\Delta G^*}{R\,T}\right) \qquad (1)$$

where h is Plank's constant, N is Avogadro's number, R is the gas constant, T is the temperature in Kelvin, and ρ and M are the density and molecular weight of the melt, respectively. The Gibbs energy of activation for viscosity in Eq.1 can be expressed as

$$\Delta G^* = \sum X_i \Delta G_i^* + \Delta G_{Mix}^* \qquad (2)$$

$\Delta G_i^*$ is the Gibbs energy of activation of the pure component i in liquid state and is usually a linear function of temperature. A series of experimental measurements of the viscosities of binary and ternary oxide melts in order to evaluate the model parameters for lower order systems. A comparison of the model predictions with experimental details presented in Fig. 1.

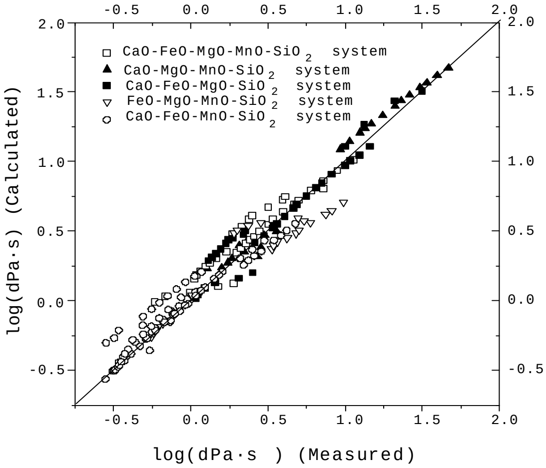

*Fig. 1. A comparison of calculated results with measured viscosity values in four quaternary and one quinary system*

### Surface and Interfacial Tension[3]

Slag/metal interfacial tensions have a marked influence on the efficiency of many metallurgical processes. This is an important factor in the case of metal refining operations. Measurements on surface and interfacial tensions have been carried out in the present laboratory using an X-ray sessile drop method. The surface tension of nickel as a function of temperature from the sessile drop measurements at KTH could be expressed as

$$\sigma\ (Nm^{-1}) = 1.810 - 0.3286 \times 10^{-3}\ (T - 1455^{o}C) \qquad (3)$$

This equation compares very well with the equations recommended for the surface tension of Ni combining the results from different measurements.

### Thermal Diffusivities of Slags and Mould Fluxes[4,5]

The thermal diffusivities of synthetic slags as well as proprietary mould flux slags used in Swedish continuous casting practice were measure using a Laser-Flash technique. A three layer method was adopted for the measurements. The results show that the thermal diffusivities are strongly temperature-dependent. Further, in the case of mould fluxes, the thermal diffusivities are dependent of the extent of crystallisation, which is, once again structure dependent.

## THERMODYNAMIC STUDIES

Thermodynamic studies relevant to steelmaking processes carried out in the present laboratory have been focused on the oxide activities and sulphide capacities of multicomponent slags.

### Thermodynamic Model for Multicomponent Oxide Solutions[6,7]

In the model for slags developed in the present group [8-10], a silicate melt is considered as an oxygen matrix with different cations including $Si^{4+}$ distributed in it as suggested by Lumsden [11]. The thermodynamic properties of the solution can be formulated by the consideration of the next- nearest neighbour interactions, namely the interactions between the cations when oxygen ions are present. As an example of the model calculations, the effect of the replacement of $SiO_2$ by CaO on the activities of alumina in the case of BF, EAF and LF slags is illustrated in Fig. 2. It seen that an increase of the mass pct CaO/mass pct $SiO_2$ ratio leads to a considerable decrease of the alumina activity, irrespective of the type of the slag.

### Molar Volumes[8]

It has been known that, in the case of binary metallic systems, molar volumes are related to the relative affinities between the two component metal atoms. Since both relative molar enthalpies of mixing and relative molar volumes could directly be correlated to the bondings between the nearest and next-nearest neighbor ions in the system, these two properties can be expected to have a direct correlation. By examining a number of binary silicate systems, a relationship between the two properties was arrived at. This is represented in Eq.4.

$$\frac{V^{M}}{\sum_{i} x_i V_{m,i}} = \lambda \frac{H^{M}}{RT} \qquad (4)$$

where $V^{M}$ is the relative integral molar volume and $\sum x_i V_{m,i}$ represents the average molar volume. $\lambda$ is a constant, $H^{M}$ the relative integral molar enthalpies for mixing, R the gas constant and T is the temperature. The constant $\lambda$ may be evaluated for the binary systems from the literature data for molar volumes and the enthalpies of mixing that can be evaluated from ThermoSlag software® described in the earlier section.

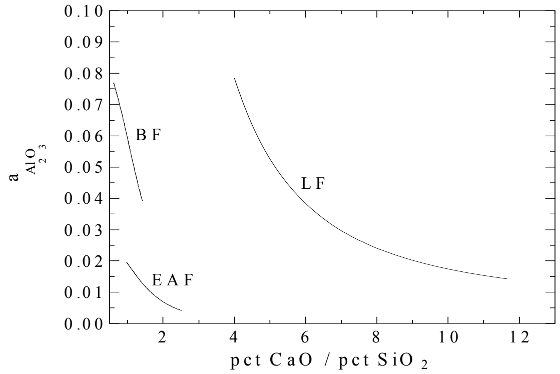

*Fig. 2. The activities ofbAl$_2$O$_3$ of some typical slag compositions in BF, EAF and LF.*

Using Gibbs-Helmholtz equation, the enthalpies of mixing, can be calculated from the integral molar Gibbs energies of mixing obtained from the thermodynamic module by the following relationship:

$$H^M = \frac{\partial\left[f\left(T, y_{Si^{4+}}\right)/T\right]}{\partial\left(1/T\right)} + \frac{\partial}{\partial\left(1/T\right)}\left[\sum_{i=1,m-1}\left(\sum_{j=i+1,m} y_{Ci} y_{Cj} \Omega^{Ci,Cj(O)}\right)/T\right] \qquad (5)$$

The integral molar volume, $V^M$, can be estimated when combining Eq.4 and 5. The $\lambda$ values for the different binary systems have been evaluated with experimental density data.

Model calculations were carried out for the eight binary systems where the results could be compared to experimental data. The model deviation from experimental data in these systems is maximum two percent, typically much less. It should be pointed out that experimentally uncertainties for density measurements are about ± 2% [12]. The model calculation in the case of Al$_2$O$_3$-FeO-MgO-SiO$_2$ system is given in Fig. 3. The molar volume estimated for blast furnace slags is presented in Fig. 4.

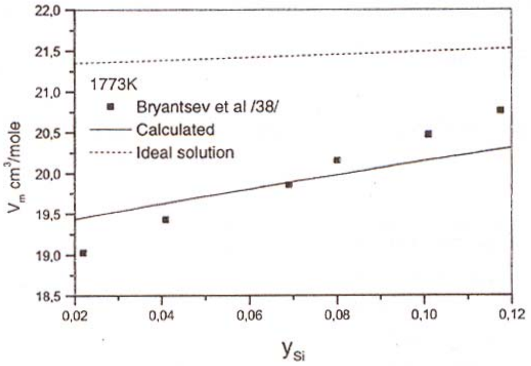

*Fig. 3. Comparison of calculated and measured molar volume values for the Al$_2$O$_3$-FeO-MgO-SiO$_2$ system for a base slag containing 30 FeO , 20 MgO and 50 SiO$_2$* (mass %).

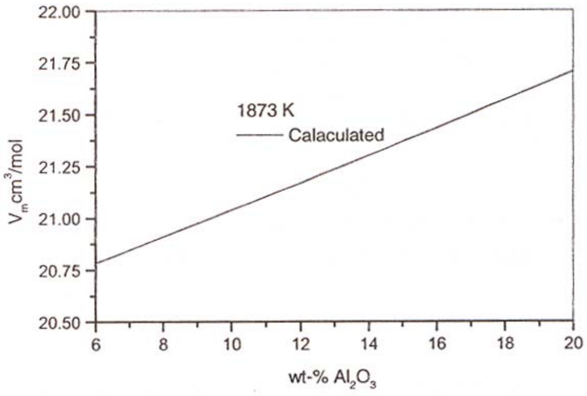

*Fig. 4. Calculated molar volume values for blast furnace slag*

## Sulphide Capacity Model[9,10]

In order to quantify the desulphurizing power of slags, an effort is currently being made at the Division of Metallurgy to get a reliable description of sulphide capacities in the multicomponent system, $Al_2O_3$-CaO-$Cr_2O_3$-FeO-$Fe_2O_3$-MgO-MnO-$SiO_2$, which covers most of the slags used in the pyrometallurgical industries. A sulphide capacity model has been developed [9]. According to this model, the sulphide capacity of an oxide melt can be expressed as:

$$C_S = \exp\left(\frac{-\Delta G^0}{RT}\right)\left(\frac{a_{O^{2-}}}{f_{S^{2-}}}\right) = \exp\left(\frac{-\Delta G^0}{RT}\right)\exp\left(-\frac{\xi}{RT}\right) \qquad (6)$$

where $\Delta G^0$ is the Gibbs energy change of the following reaction:

$$\frac{1}{2}S_2(g) + O^{2-}(slag) = S^{2-}(slag) + \frac{1}{2}O_2(g) \qquad (7)$$

A comparison of the model predictions with experimental data is presented in Fig. 5.

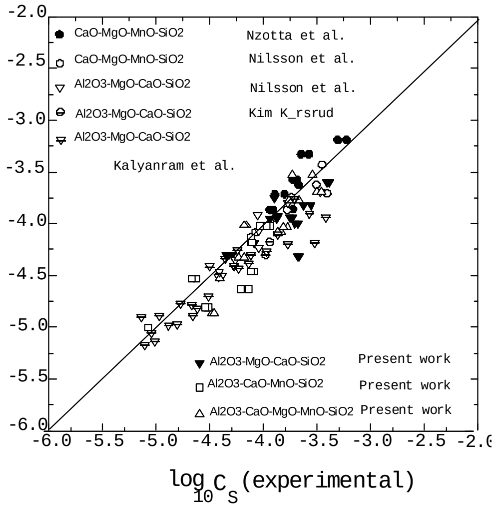

*Fig. 5. A comparison between the model prediction and the experimental data for a number of quaternary and quinery systems*

## KINETIC STUDIES

In order to incorporate the thermodynamic information into the CFD models, the kinetic factors need to be considered. Some examples of kinetic studies along this line are presented in this section.

## INTERFACIAL PHENOMENA IN SOME SLAG - METAL REACTIONS

The change of interfacial tension at metal-slag interface for sulphur transfer between molten iron, slag and gas phases was monitored by X-ray sessile drop method in dynamic mode in the temperature range 1830 - 1891 K[3]. The experiments were carried out with pure iron samples immersed partly or fully in the slag phase. The latter consisted of 30 wt % CaO, 50 wt % $Al_2O_3$ and ca 20 wt % $SiO_2$ (alumina saturated at the experimental temperatures) with additions of 'FeO'. The metal and the slag phases contained in alumina crucibles were exposed to a gas mixture of $CO$-$CO_2$-$SO_2$-Ar with defined oxygen and sulphur partial pressure and the change of the shape of the metal drop was followed as a function of time.

A theoretical model was developed to enable the computation of the sulphur content of the metal as a function of time on the basis of the sulphur diffusion in the slag and metal phases as well as surface tension-induced flow on the metal drop surface. Fig. 6 shows the calculated change of sulphur concentration in the bulk of metal as a function of time.

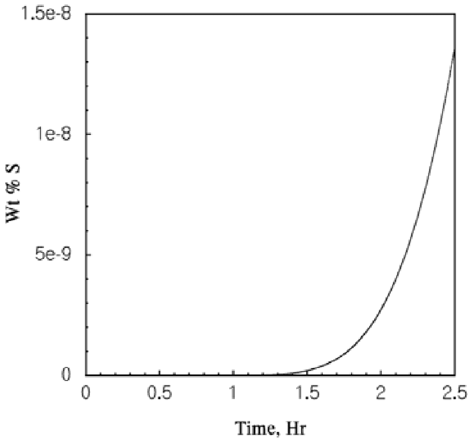

*Fig. 6. Calculated change of sulphur concentration in the bulk of metal as a function of time*

Dynamic sessile drop experiments were carried out in order to study the erosion of refractories by liquid iron containing oxygen. The results show the variation in contact angle with time indicating the reactions at micro level[13].

### Incorporation of the micromodels in process models[14]

By incorporating micromodels in CFD calculations a more realistic model of a process can be made. One example of that approach is the modeling of slag/metal reactions, which take place during ladle treatment [14]. Sulphur refining is taken as an example. The two-film theory has been used for many decades to describe the slag/metal reactions. When using this theory, a mass-transfer coefficient is calculated for the overall reaction between slag and metal, which for practical conditions is only valid for a very well defined system. Furthermore, an artificial interfacial area is calculated assuming that the surface between slag and metal is flat. However, it is well known that in most steel making processes when gas-stirring is applied, liquid metal becomes entrapped in the slag phase, forming a slag/metal mixing zone [14]. The total interface area between slag and metal in this mixing zone is enormous in comparison with the area calculated using to the two-film theory.

In the new approach, micromodels are incorporated into a CFD model. More specifically, the thermodynamic conditions during desulphurization have been incorporated in the two-dimensional three- phase model of a gas-stirred ladle. Thermodynamic equilibrium is expected to be established dynamically in the slag/metal mixing zone. By considering the volume of mixing between slag and metal and the thermodynamic equilibrium in the two-phase zone, the calculations of interfacial area and the mass-transfer coefficients for different elements are avoided. This way, the combined effect of fluid-flow and thermodynamics can be predicted from fundamental transport equations.

In the model calculation, the viscosity and sulphide capacity of the slag were evaluated using the above-mentioned viscosity and sulphide capacity models, while the $Al_2O_3$ activity in the slag was calculated using IRSID model. The activities of various elements in the liquid metal were calculated using the dilute-solution model.

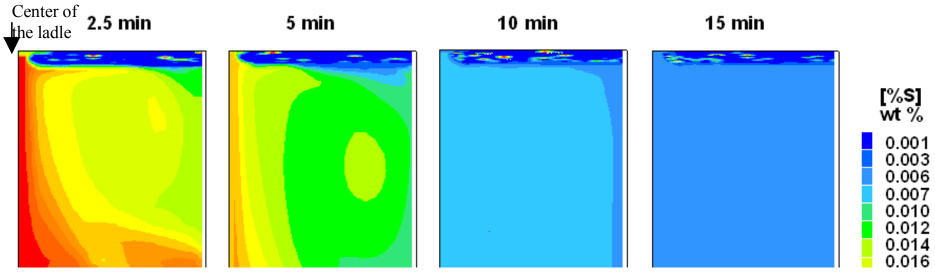

*Fig. 7. Change of sulphur content in steel as a function of refining time*

Fig. 7 shows the change of sulphur concentration in steel during refining, when 80 l/min argon gas is injected into 100 ton of steel. The predicted sulphur content in the steel for this case is 0.007 wt % to 0.008wt % after 15 minutes of gas-stirring. Actual plant data for a 15 minutes gas-stirring period with the same gas flow gives a sulphur content of 0.005 wt% to 0.010 wt%. The comparison shows that by incorporating micromodels into a CFD model of a gas-stirred ladle, it is possible to predict desulphurisation with acceptable accuracy.

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