RECENT DEVELOPMENTS IN PHYSICO-CHEMICAL CHARACTERISATION AND MODELLING OF FERROALLOY SLAG SYSTEMS

S. Jahanshahi, S. Sun and L. Zhang

CSIRO Minerals, Box 312 Clayton South, Victoria, 3169, Australia.
E-mail: Sharif.Jahanshahi@csiro.au, Shouyi.Sun@csiro.au, Ling.Zhang@csiro.au

ABSTRACT

Recent studies on the physico-chemical properties of molten slags and oxide solid solutions of interest is reviewed. The review covers redox and phase equilibria in slags, viscosity, diffusivity, electrical conductivity, kinetics of interfacial reactions between slags and CO-CO_2, interfacial properties and phenomena. Some highlights from ongoing work on modelling phase diagrams, component activity, viscosity and electrical conductivity of multi-component slags will be presented and results compared with published experimental data on slags with or without suspended solid phases.

1. INTRODUCTION

Over the past two decades considerable effort has been invested in studying the physical chemistry of metallurgical melts and their interactions with other phases that are present in smelting processes. These investigations have build up our fundamental knowledge and understanding of many simple and complex melts and allowed us to gain an insight into the reactions taking place in many pyrometallurgical processes. The present work will attempt to review the recent studies on redox and phase equilibria, transport properties such as viscosity, electrical conductivity and diffusivity in slags, and the interfacial properties and reactions that are relevant to production of ferroalloys. The primary focus of this review is on oxide melts or slags with some reference to behaviour of solid solutions and molten alloys.

Our improved knowledge and understanding of the high temperature behaviour of solution phases has allowed development of models for calculating some of the complex behaviour of metallurgical melts and making these available to researchers and plant metallurgists as a means of bridging gaps in our knowledge. For researchers these models allow a more efficient means of characterising behaviour of multi-component systems by directing the inherently difficult experimental studies. For plant metallurgists the models serve as an enabling tool for analysis and optimisation of performance of processes. While a review of recent developments in modelling metallurgical systems is beyond the scope of the present paper, some examples from an on-going work on one such model will be presented here and compared with recently published data on multi-component slags.

2. REDOX EQUILIBRIA

2.1 Iron

Redox equilibria in iron oxide containing slags has been well researched and the recent studies [1-3] on calcium silicate based slags containing alumina and/or magnesia were reviewed and presented elsewhere [3]. This review showed that the Fe^{3+}/Fe^{2+} ratio is strongly dependent on the oxygen activity (a_O, with standard state defined as unit CO_2/CO ratio) and basicity of slags. Unlike lime saturated calcium ferrite and silica saturated iron silicate slags, the multi-component slags showed departure from ideal behaviour with respect to the dependence of Fe^{3+}/Fe^{2+} ratio on oxygen activity. This indicates noticeable dependence of the ratio of activity coefficients of $FeO_{1.5}$ to FeO on the oxidation state of slags. Interesting enough for a given slag basicity, temperature has little effect on the dependence of Fe^{3+}/Fe^{2+} ratio on oxygen activity expressed as CO_2/CO ratio.

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This is somehow expected from the entropy change for the reaction:

$$FeO + \frac{1}{2}CO_2(g) = FeO_{1.5} + CO(g) \tag{1}$$

Another interesting finding is the insignificant dependence of Fe^{3+}/Fe^{2+} ratio on the iron oxide content (0.8 to 42 wt%) of these slags. This is illustrated in Figure 1 and according to Yang and Belton [3] the redox equilibria data could be represented by;

$$\log\left(\frac{Fe^{3+}}{Fe^{2+}}\right) = 0.45(\pm 0.02)\log\left(\frac{CO_2}{CO}\right) - 0.91(\pm 0.02) \tag{2}$$

for slags with CaO/SiO_2 ratios close to unity and at temperatures in the range of 1350 to 1500 °C. Similar correlations were obtained by Yang and Belton for slags with different basicity.

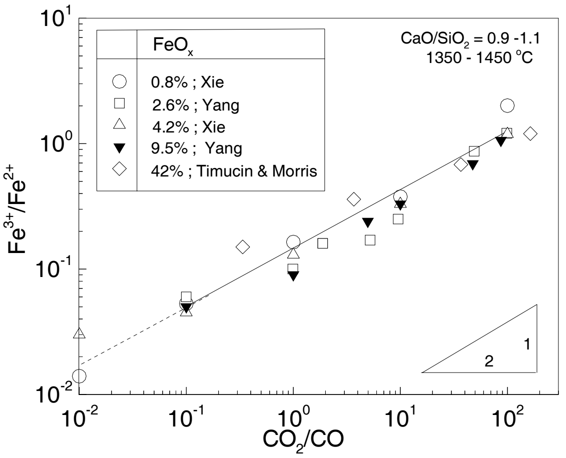

Figure 1. The equilibrium Fe^{3+}/Fe^{2+} ratio in calcium silicate based slags as a function of oxygen activity defined as p_{CO2}/p_{CO} in high and low iron slags [1-4].

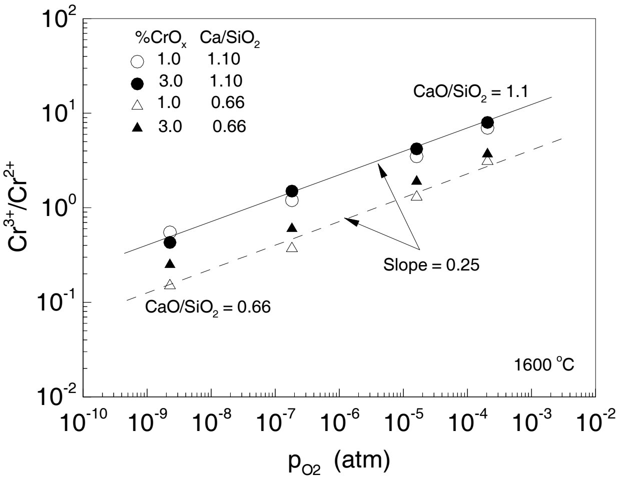

Figure 2. Variation of equilibrium Cr^{3+}/Cr^{2+} ratio with oxygen partial pressure (p_{O_2}) in calcium silicate slags with 1-3 wt% CrO_x and CaO/SiO_2 ratios of 1.10 and 0.66 at 1600 °C [8].

Compared to iron oxide containing slags, fewer investigations have been carried out on the redox behaviour of other transition metals in calcium silicate based slags. The reported data on chromium, manganese, vanadium and titanium tend to be similar to that of iron oxide and will be summarized below.

2.2 Chromium

Recent studies by Xiao and Holappa [5], Morita *et al.* [6,7] and Schwerdtfeger and Mirzayousef-Jadid [8] have quantified the dependence of oxidation state of chromium on oxygen partial pressure (p_{O_2}), slag basicity and chromium content of calcium silicate based slags at temperatures in the range of 1500 to 1600 °C. These studies covered broad ranges of p_{O_2} (10^{-14} to 0.21 atm) and CaO/SiO_2 ratio (0.2 to 1.5) and CrO_x content (1-75 wt%). In Figure 2 the variation of Cr^{3+}/Cr^{2+} ratio with p_{O_2} and CaO/SiO_2 ratio in slags with 1-3 wt% CrO_x are presented.

According to Figure 2, the dependence of Cr^{3+}/Cr^{2+} ratio on p_{O_2} is close to ideal behaviour for slags containing 1-3 wt% CrO_x. Extrapolation of data by Schwerdtfeger and Mirzayousef-Jadid to p_{O_2} of less than 10^{-11} atm indicates that the concentration of Cr^{3+} in these slags becomes small with Cr^{3+}/Cr^{2+} ratio of about 0.1. This value is considerably lower than those reported by Morita *et al.* [6,7] and Xiao and Holappa [5] for slags containing 4 to 50 wt% CrO_x. This difference could be partly attributed to the CrO_x content of these slag, as Morita *et al.* [7] showed that at a given temperature, p_{O_2} and CaO/SiO_2 ratio, the Cr^{3+}/Cr^{2+} ratio increases by about a factor of 3 as the chromium content of their calcium silicate slag was increased from 4 to 16 wt%.

Slag basicity has also an effect on the Cr^{3+}/Cr^{2+} ratio, with the redox ratio increasing with CaO/SiO_2 ratio at a given CrO_x content, temperature and p_{O_2} [5-8].

According to Schwerdtfeger and Mirzayousef-Jadid, under more oxidising conditions ($p_{O_2} > 10^{-2}$ atm) significant concentrations of Cr^{6+} exist in calcium silicate slags. The data on Cr^{6+}/Cr^{3+} shows relatively large scatter, presumably due to the errors in the wet chemical analysis technique used. Nevertheless, the Cr^{6+}/Cr^{3+} ratio shows strong dependence on p_{O_2} and slag basicity. Morita *et al*'s data on the dependence of Cr^{6+}/Cr^{3+} ratio on CaO/SiO_2 ratio in MgO-SiO_2-CaO slags saturated with $MgO.Cr_2O_3$ at 1600 °C in air shows a factor of 4 increase in Cr^{6+}/Cr^{3+} ratio as the CaO/SiO_2 was increased from about 2 to 10.

Using the measured variations of Cr^{3+}/Cr^{2+} and Cr^{6+}/Cr^{3+} with p_{O_2} in low CrO_x calcium silicate slags at 1600 °C, Schwerdtfeger and Mirzayousef-Jadid [8] derived a series of mathematical expressions for representing the fractions of Cr^{2+}, Cr^{3+} and Cr^{6+} as function of p_{O_2} and slag basicity. In Figure 3 the results obtained from their model are presented for slags with CaO/SiO_2 ratios of 0.66 and 1.1. This Figure illustrates the pronounced effect of slag basicity on stabilising the higher oxidation states of chromium in such slags. For example at p_{O_2} of 10^{-7} atm, the fraction of Cr^{2+} increases from 0.43 to 0.69 as the CaO/SiO_2 is reduced from 1.1 to 0.6. This Figure also shows that the Cr^{3+}/Cr_{total} ratio reaches its maximum value at p_{O_2} of $4x10^{-3}$ and $3x10^{-2}$ atm in slags with CaO/SiO_2 ratios of 1.1 and 0.6, respectively. The other interesting trend relates to the stability of Cr^{6+} and according to this model the concentration of hexa-valent chromium becomes significant at p_{O_2} of greater than 10^{-2} atm.

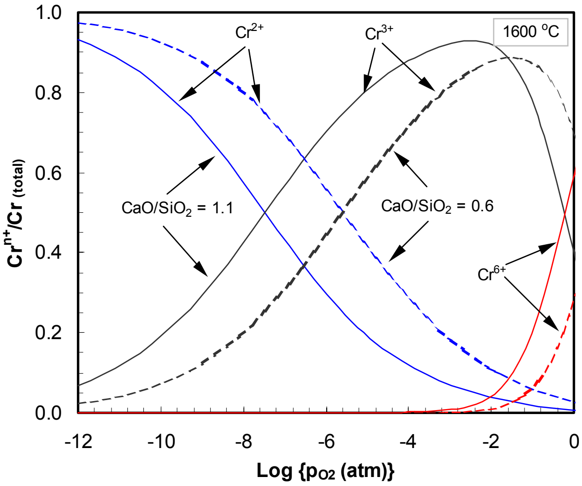

Figure 3. Variations of the calculated fractions of Cr^{2+}, Cr^{3+} and Cr^{6+} with oxygen partial pressure (p_{O_2}) of calcium silicate slags containing 1-3 wt% CrO_x according to a model by Schwerdtfeger and Mirzayousef-Jadid's [8].

As mentioned earlier the published data on chromium redox equilibria indicates that apart from p_{O_2} and slag basicity, the total chromium content of slags (Cr_{total}) appears to affect the oxidation state of chromium in slags. Thus the above predicted values are only valid for slags with 1-3 wt% Cr_{total}.

2.3 Manganese

At high temperatures, the higher oxidation states of Mn are considerably less stable than Mn^{2+}. Published studies by Tamura *et al.* [9] and Tran [10] show that significant concentration of Mn^{3+} could be measured at p_{O_2} of greater than 10^{-6} atm in CaO-MgO-SiO_2 slags at 1400 °C. As shown in Figure 4, the Mn^{3+}/Mn^{2+} ratio increases with increasing CO_2/CO ratio with the dependence being close to ideal behaviour, i.e.;

$$\left(\frac{Mn^{3+}}{Mn^{2+}}\right) \propto \left(\frac{CO_2}{CO}\right)^{\frac{1}{2}} \tag{3}$$

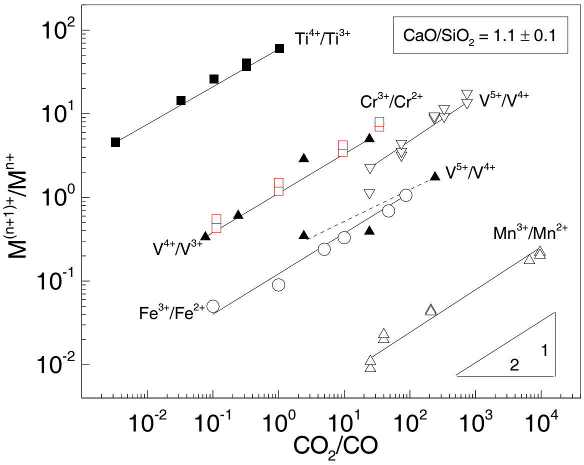

Figure 4. Comparison of the equilibrium redox ratio $(M^{n+}/M^{2n-1)+})$ for Ti [8,14,15], V [11,12, 13], Fe [2, 9], Mn [9] and Cr [8] as a function of oxygen activity (p_{CO_2}/p_{CO}) in calcium silicate slags.

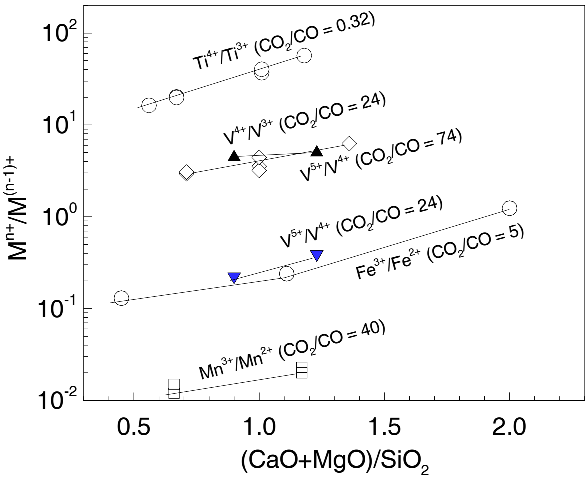

Figure 5. Comparison of the equilibrium redox ratio $(M^{n+}/M^{2n-1)+})$ for Ti [14,15], V [11,12,13], Fe [9], Mn [9] and Cr [8] as a function of slag basicity defined as (CaO+MgO)/SiO$_2$.

The effect of slag basicity on Mn^{3+}/Mn^{2+} ratio is similar to those observed for Fe^{3+}/Fe^{2+} and Cr^{3+}/Cr^{2+} ratios with the tri-valent form becoming more stable at higher CaO/SiO$_2$ ratios.

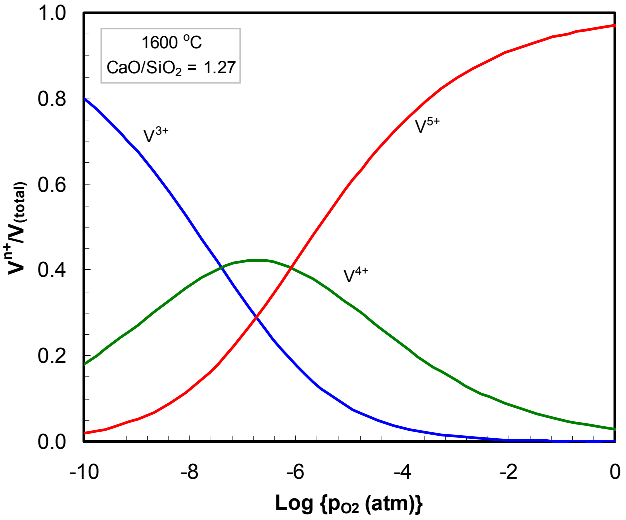

Figure 6. Variations of the calculated fractions of V^{3+}, V^{4+} and V^{5+} with oxygen partial pressure (p_{O_2}) of CaO-SiO$_2$-VO$_x$ slags according to Mittelstädt and Schwerdtfeger [11].

2.4 Vanadium

The effects of p_{O_2} and slag basicity on the redox equilibria of vanadium in calcium silicate based slags have been investigated by Mittelstädt and Schwerdtfeger [11] and Farah [12,13]. As shown in Figures 4 and 5, at similar oxygen activity, Farah's results for V^{3+}/V^{4+} ratio appear to be of similar value to Fe^{3+}/Fe^{2+} ratio, but her results were much lower than those reported by Mittelstädt and Schwerdtfeger for slags of similar basicity. Using the proposed model by Mittelstädt and Schwerdtfeger for calcium silicate slags, the variations of the fractions of V^{5+}, V^{4+} and V^{3+} with p_{O_2} were calculated and are presented in Figure 6. The transition from higher oxidation state to lower ones occurs more gradually than those shown in Figure 3 for chromium containing slags. Furthermore, at oxygen partial pressures corresponding to Fe/FeO equilibrium ($\sim10^{-9}$ atm) a significant fraction of vanadium exist as V^{4+} in these slags at 1600 °C.

2.5 Titanium

Recent measured redox equilibria data on CaO-SiO_2-TiO_x slags at temperatures between 1570 and 1600 °C [8, 14,15] show titanium is mostly present in the tetra-valent form with Ti^{4+}/Ti^{3+} ratio being much higher than for iron oxide in similar slags and oxygen activity (see Figure 4). The two sets of redox equilibria data are in close agreement with each other and show that at a given oxygen activity and temperature, the Ti^{4+}/Ti^{3+} ratio increases with increasing CaO/SiO_2 ratio.

3. LIQUIDUS BOUNDARIES AND PHASE DIAGRAMS

There have been a number of experimental investigations on phase diagrams and the liquidus of various slag systems in the interests of the ferroalloy smelting processes in recent years [16-23]. The details of composition and temperature range covered in the measurements were summarised in Table 1. These studies have significantly contributed to our knowledge on the effect of various oxide components on the phase relations in slag systems. In particular useful guides were provided for the smelting operation by those studies covering the composition ranges of the feeding materials [18-23].

In recent years, computer calculation of phase equilibria for complex multi-component and multi-phase systems is becoming increasingly more accessible. Some thermodynamic packages, for example FactSage [24], MTDATA [25] and CSIRO's multi-phase equilibrium (MPE) model [26], contain the major oxide components, such as MnO, CrO, Cr_2O_3, NiO, CaO, MgO, FeO, Fe_2O_3, Al_2O_3 and SiO_2 in the interests of the ferroalloy operations. These packages can be used to calculate multiphase equilibrium and component activities. However, it should be mentioned that the packages in general offer good levels of accuracy for relatively simple systems. The direct use of the packages for industrial systems is subject to the validity of the model descriptions in the temperature and composition ranges of interest.

3.1 Ferromanganese

As shown in Table 1 the new data covered some base systems, i.e., ternary [16-17] and quaternary systems [18-20] as well as industrial slags [21]. The MnO-Al_2O_3-SiO_2 ternary system can be considered as the base system for the ferromanganese smelting. However, the previous published phase diagram showed many uncertain areas drawn by dashed lines [27]. Very recently, the work by Roghani *et al.* [16] has determined the phase relations and liquidus surface between 1100 to 1500°C. Corrections were made to the previous published phase diagram in the phase regions below 1500°C. These included the position of the liquidus and the primary fields of various phases. Furthermore, the same authors have conducted measurements on the MnO-CaO-Al_2O_3-SiO_2 quaternary system, covering a broad composition range under conditions as indicated in Table 1 [19-20]. This work provided a comprehensive set of data that covers phase regions directly related to the ferromanganese smelting processes.

Table 1. Liquidus studies of various slag systems.

System/alloy type	Temperature	Composition	References
MnO-Al_2O_3-SiO_2 **(FeMn)**	1100-1500°C (~50°C steps)	MnO: 10-75; Al_2O_3: 0-40; SiO_2: 10-80 wt%; Mn-Si alloy saturation	[16]
	1550°C	SiO_2 saturation	[17]
CaO-MnO-Al_2O_3-SiO_2 **(FeMn)**	1300, 1350 and 1450°C	6 and 12 wt% MnO addition to the CaO-Al_2O_3-SiO_2(30-40) slags at CaO/Al_2O_3: 2.1, 1.4 and 0.96; Mn-Si alloy saturation	[18]
	1150-1500°C (~50°C steps)	Al_2O_3/SiO_2: 0.41, 0.55,0.65; MnO and CaO: 0 to (Ca,Mn)O saturation;	[19-20]
CaO-MgO-MnO-Al_2O_3-SiO_2 **(FeMn)**	1300-1380°C	MnO: 5-30; CaO: 20-35; MgO: 5-15; Al_2O_3: 5; SiO_2: 27-58 wt%	[21]
CrO_x-MgO-Al_2O_3-SiO_2 (FeCr)	1600 and 1700°C	MgO/Al_2O_3=2; SiO_2, spinel and forsterite saturations	[22]
FeO-MgO-Al_2O_3-SiO_2 **(FeNi)**	1450-1600°C	0, 2 and 3 wt% Al_2O_3 addition to the MgO-"FeO"-SiO_2(sat) slags	[23]

3.2 Ferrochromuim

The slag systems in the ferrochromium smelting are based on the CrO-Cr_2O_3-MgO-Al_2O_3-SiO_2 system. The phase diagram and liquidus data on this system and the sub-systems are very limited partly due to the relatively high melting temperatures. Degterov and Pelton [28] reported a thermodynamic assessment of the quaternary system CrO-Cr_2O_3-Al_2O_3-SiO_2. The paper presented a series of predicted phase diagrams including some sub-systems under different oxygen partial pressures.

Based on their experimental findings, Konstantin and Olsen [22] have proposed tentative liquidus curves of 1600 and 1700°C for the SiO_2-CrO_x-MgO-Al_2O_3 slags saturated with metallic Cr and at a fixed ratio of MgO/Al_2O_3=2.0. The solid phases in equilibrium with liquid were identified as spinel (Cr,Mg) $(Al,Cr)_2O_4$, olivine $(Cr,Mg)_2SiO_4$ and silica. As mentioned earlier the CSIRO MPE model [26] contains most oxide components of industrial slags, such as SiO_2, Al_2O_3, Cr_2O_3, TiO_2, Ti_2O_3, Fe_2O_3, FeO, CaO, MgO, MnO, CrO, PbO, NiO, CoO, ZnO, Na_2O, Cu_2O. To show an example, the calculated phase relations in the SiO_2-CrO_x-MgO-Al_2O_3 slags saturated with metallic Cr and at fixed ratios of MgO/Al_2O_3=2.0 and (MgO+Al_2O_3)/CrO_x=1.0 are presented in Figure 7. The tentative liquidus compositions proposed by Konstantin and Olsen at 1600 and 1700°C were also shown as a comparison. The model calculations agree well with the proposed primary phase fields of spinel and silica. Furthermore, the calculated diagram provides not only information on the primary solid phase, but also the secondary and third solid phases and their stability regions. Such information would require extensive amount of measurements to cover. On the other hand the accuracy of the model predictions is yet to be validated by measurements.

3.3 Ferronickel

The work by Chen *et al.* [23] investigated the effect of addition of Al_2O_3 on the liquidus temperatures in the FeO-MgO-SiO_2 system in the silica primary phase field. The system is directly relevant to the Cerro Matoso (South America) ferronickel smelting slags. The study found that there is a decrease in liquidus upon the addition of Al_2O_3 to the systems saturated with silica.

4. THERMODYNAMIC ACTIVITY

The recent experimental studies on component activities of ferroalloy type slags [5,17,29-33] was summarised in Table 2. The activities of MnO, CrO and Cr_2O_3 have been determined in the industrially relevant slags as well as some sub-systems.

Table 2. Activity studies of various slag systems.

System/alloy type	Temperature	Composition	References
MnO-Al_2O_3-SiO_2 **(FeMn)**	1550°C	a_{MnO} in entire liquid region	[17]
MnO-MgO-SiO_2 **(FeMn)**	1600°C	a_{MnO} in slag saturated with (Mn,Mg)O	[29]
CaO-MgO-MnO-Al_2O_3-SiO_2 **(FeMn)**	1500°C	a_{MnO} for Al_2O_3: 5; and various CaO/MgO and (CaO+MgO)/SiO_2	[30]
CrO_x-CaO-SiO_2 **(FeCr)**	1600°C	a_{CrO} and a_{Cr2O3} in entire liquid region	[5,31-32]
CrO_x-MgO-Al_2O_3-SiO_2 **(FeCr)**	1600 and 1700°C	a_{CrO}, a_{Cr2O3} and a_{mgO} in entire liquid region at MgO/Al_2O_3=2	[33]

The activity studies by Cengizler and Eric [30] investigated the influence of basicity ratio (in wt%, BR=CaO+MgO/SiO_2) and CaO/MgO ratio on MnO activities in the CaO-MgO-MnO-Al_2O_3(5 wt%)-SiO_2 system at 1500 °C. It was found that the MnO activity, a_{MnO} increases with increasing MnO content and BR values. The effect of the CaO/MgO ratio was not so significant, though a_{MnO} tends to increase slightly as the CaO/MgO ratio increases. The measured a_{MnO} at three BR values with CaO/MgO=0.2-0.28 are shown in Figure 8. The curves were calculated results by the MPE model using the same slag chemistry except at a constant value of CaO/MgO=0.24. It is shown that close agreement between the experimental data and the calculated values has been achieved.

It should be mentioned that at the experimental conditions of 1500°C the MPE model predicted regions where slag was in fact in equilibrium with solid phases, such as olivine $(Ca,Mg,Mn)_2SiO_4$ and halite (Ca,Mg,Mn)O as indicated in Figure 8. Unfortunately, the presence of the solid phases was not mentioned in the study by Cengizler and Eric [30]. Nevertheless, the close fit to the activity data may suggest the model predicted reasonable phase relations. The compositions of the slags saturated with solid phases as calculated by the model should be similar to those of the measurements.

5. VISCOSITY OF SLAGS

The viscosity data in multi-component slag systems of direct fit to the ferroalloy smelting processes are still limited though the data for some sub-systems, such as ternary or quaternary systems can be found in the recent edition of the Slag Atlas [27]. A recent study by Bi *et al.* [34] reported their measurements of viscosity in the ferromanganese making blast furnace slags of CaO(38-44.5)-MgO(3-9.5)-MnO(9-11)-Al_2O_3(8.8-14.9)-SiO_2(25.6-30.6)–CaF_2(0.5-6.4wt%). The temperature range covered was about 1325-1475 °C. They were aimed to determine the so-called ‘free running’ temperatures (at which the viscosity is 2.0 Pa.s) for their slag samples based on viscosity versus temperature plots.

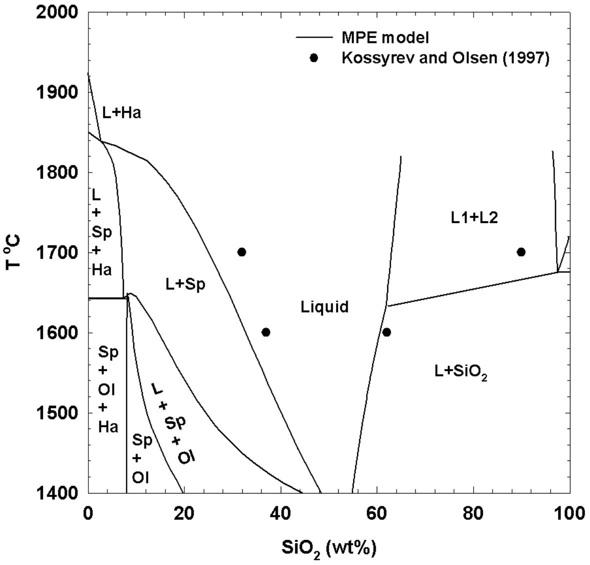

Figure 7. Phase relations in the CrO_x-MgO-Al_2O_3-SiO_2 system saturated with metallic Cr at $MgO/Al_2O_3=2$ and $CrO_x/(MgO+Al_2O_3)=1$ (Ha: halite (MgO);Sp:spinel $(Mg,Cr^{2+})(Al,Cr^{3+})_2O_4$; Ol: olivine $(Mg,Cr^{2+})_2SiO_4$; L: liquid; L1: liquid 1 and L2: liquid 2).

In recent years there have been a number of models developed for the calculation of slag viscosities as reviewed by Mills *et al.* [35]. Some models can be used to estimate viscosity values for slags related to ferroalloy smelting processes, for example, the CSIRO viscosity model for silicate melts developed by the present authors [26]. The model covers most oxide components (14 oxides) of industrial slags for various processes, such as iron and steel making, non-ferrous and coal ash type slags. Furthermore, the viscosity model has been incorporated in the MPE model to calculate viscosity for both liquid and solid containing melts. The details of the viscosity model and the MPE model are available in a previous publications [26]. The capability of the MPE model in predicting viscosity values for the ferromanganese type slags in the CaO-MgO-MnO-Al_2O_3-SiO_2 system over the temperature range of 1200-1500°C was demonstrated in Figure 9. In order to make comparison with the measurements, two sets of data by Rakitina *et al.* [36] were also shown. The compositions of the slag samples are given in Table 3. The main difference between Slag A and Slag B is MgO content of the two samples. The measurements show that Slag B with high MgO content has higher viscosity values than Slag A at a given temperature below 1450°C. Such increase was expected to be caused by the presence of the solid phase in Slag B. As predicted by the MPE model the liquidus temperatures are 1310 and 1490°C for Slag A and Slag B respectively as shown in Figure 9. The solid phase in equilibrium with the slag was found to be halite (Ca,Mn,Mg)O. It is generally expected that viscosity-temperature curves will show a discontinuity below the liquidus temperature. As the amount of solid phase increases, the viscosity rises much more rapidly than in liquid phase. It can be seen that the model predictions are close to the measurements. The agreement for values in the liquid region was better than in the solid containing melts. The reason for the uncertainties in the two phase region can be attributed to factors such as the size, shape and morphology of the solid particles which may not have been accounted for by the viscosity model for melts containing solid particles. In addition there could be uncertainty associated with the amount of solid phase predicted by the thermodynamic models. Nevertheless, the MPE model has shown to be able to provide useful guide in the ferroalloy smelting processes.

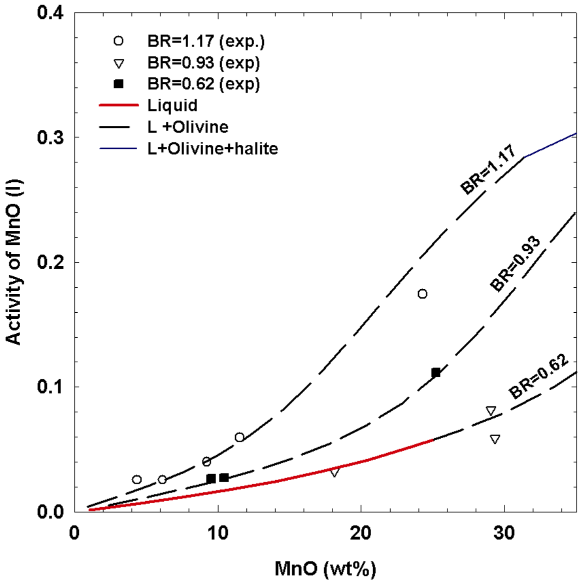

Figure 8. Activities of MnO (liquid standard state) in the CaO-MgO-MnO-Al_2O_3 (5wt%)-SiO_2 system at 1500°C and various basicity ratios (BR =(CaO+MgO)/SiO_2). Symbols are the experimental data by Cengizler and Eric [30] at CaO/MgO=0.20-0.28. Lines are calculated activities at CaO/MgO=0.24 by using the MPE model.

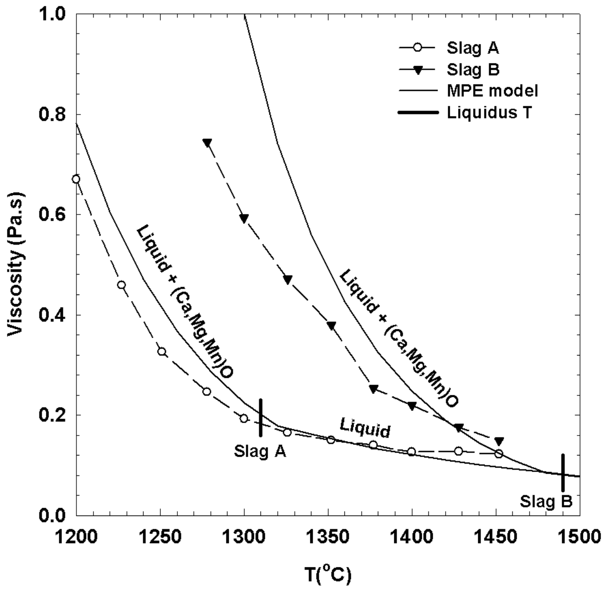

Figure 9. Viscosity-temperature curves for ferromanganese slags. The experimental data are from Rakitina *et al.* [36].

Table 3. Slag compositions of viscosity measurements by Rakitina *et al.* [36].

Sample No	Composition wt%				
	MnO	CaO	SiO_2	Al_2O_3	MgO
Slag A (melt No9)	49.01	18.19	26.71	4.16	1.93
Slag B (melt No11)	46.43	15.81	23.93	4.92	8.91

Information on the liquidus temperatures of the slag samples was not available in the study by Rakitina *et al.* [36]. However, the rapid increase in measured viscosity suggested the presence of solid phases. It should be mentioned that the effect of MgO on viscosity is caused by stabilising the halite phase at much higher temperature for Slag B than for Slag A. It is the presence of the solid phase which resulted in higher viscosity values in Slag B below 1490°C. It is useful to distinguish the effect on viscosity by the presence of solid phases from addition or substitution of a particular oxide component in homogenous liquids. The notion of three types of oxide species proposed by Urbain *et al.* [37] is very useful in analysing viscosity behaviour in the homogenous silicate melts. These are namely network former (SiO_2), modifier (metal oxide such as (Ca,Mg,Mn)O) and amphoteric (Al_2O_3) oxide. However as temperature decreases, the effect of the increasing amount of solid phases on viscosity will override the strong effect by the network former.

6. DIFFUSIVITY IN SLAGS

One of the principal reactions in production of ferroalloys is removal of oxygen from the molten slag, which results in extraction of valuable metals in the form of a molten alloy phase. Thus rate processes such as diffusion/mass transfer in the slag, chemical reactions at interfaces and transport of reaction products from the reaction interface should play important roles in determining the kinetics and efficiency of overall reduction process. Depending on the relative rates of the above processes and reactions, one can set up concentration gradients of species across the slag to the reaction interface. In this case the chemical diffusivity of oxygen in the molten slag, under the imposed concentration/activity gradient becomes a key property in controlling the reduction rate of transition metal oxides from the slag. Most published studies on diffusion in slags have been focused on determination of self-diffusivity rather than chemical diffusivity. Mills [38] compiled and reviewed most published data on self-diffusivity in various slags, thus the reader is referred to this comprehensive review. The present review is focused on chemical diffusivity of oxygen in molten slags and it will highlight a few interesting behaviours associated with the effects of transition metal oxides in slags.

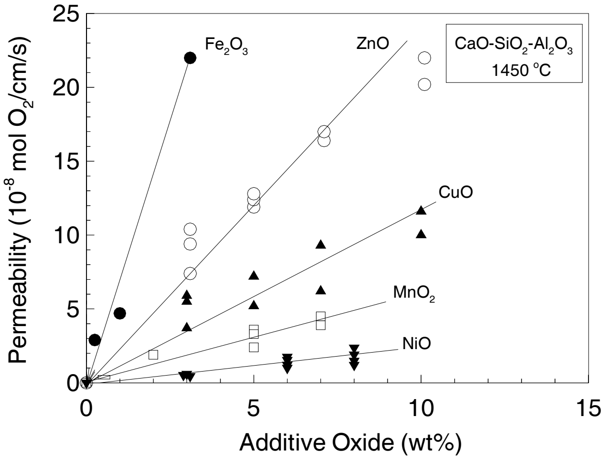

Figure 10. Effects of additives on the oxygen diffusion rate through CaO-40%SiO_2-20%Al_2O_3 slags at 1450 °C, according to Sasabe and Asamura [39].

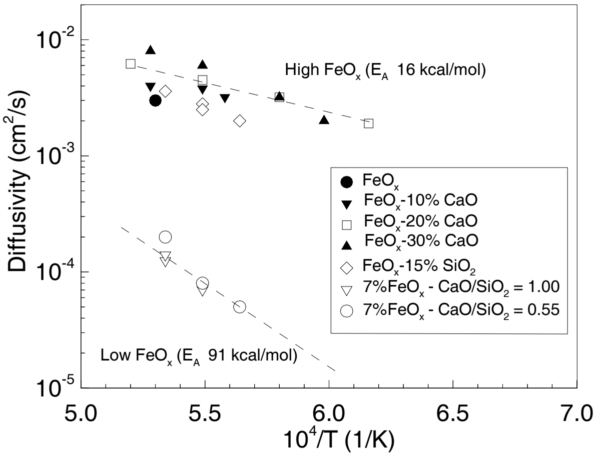

Figure 11. Variation of the interdiffusivity with temperature in slags with 7 to 100% FeO_x according to Sayad-yaghoubi *et al.* [41-43].

Addition of transition metal oxides to silicate slags can have very marked effects on the diffusivity of oxygen. This behaviour was demonstrated by Sasabe and Asamura [39] through their studies on oxygen permeability in $CaO-SiO_2-Al_2O_3$ slags at 1450 °C. Their data are represented in Figure 10, which shows small additions of iron oxide to the slag resulted in considerable increases in the transport rate of oxygen. Other oxides such as ZnO, CuO, MnO_2 and NiO showed similar effects.

Recent studies by Sayad-yaghoubi *et al.* [41-43] on chemical diffusivity of oxygen in a range of iron oxide containing slags has demonstrated some orders of magnitude difference between the diffusivity in low and high iron oxide slags. As shown in Figure 11 the temperature dependence or activation energy for oxygen diffusion is also affected by the iron oxide content of slags.

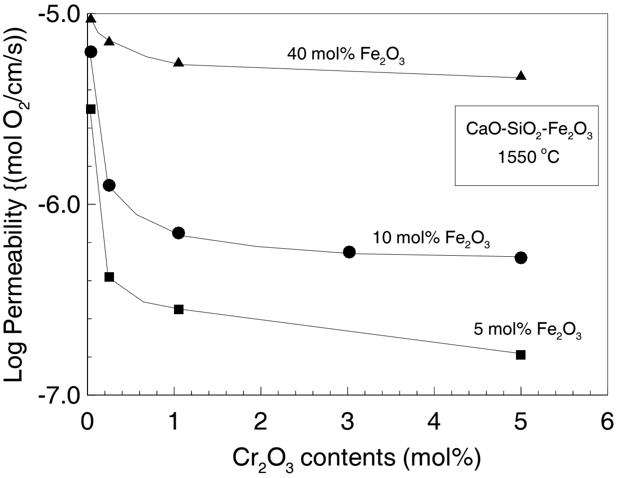

Figure 12. Effects of Cr_2O_3 and Fe_2O_3 additions to $CaO.SiO_2$ on the oxygen permeability through the slag at 1550 °C, according to Sasabe and Asamura [39].

Another interesting behaviour shown by Sasabe and Asamura [39] is on the combined effects of Fe_2O_3 and Cr_2O_3 additions to slags. Their results (Figure 12) on calcium silicate based slags shows that while addition of Fe_2O_3 alone resulted in higher oxygen permeability, when Cr_2O_3 was added to these slags considerable decrease in the permeability of oxygen resulted. This decrease could be due to the effect of Cr_2O_3 on stabilising a spinel phase such as $[Fe,Cr]_3O_4$ and hence locking up the multivalent ions in a solid phase.

7. ELECTRICAL CONDUCTIVITY OF SLAGS

An extensive compilation of the conductivity data for molten oxide systems from single oxide to multicomponent slags containing Al_2O_3-CaO-FeOx-MgO-MnO-SiO_2 has been given by Mills [27]. It is generally observed that the conductivity of a given slag always tends to increase with temperature, unlike metals for which the conductivity decreases with temperature. It may also be observed that at a given temperature the conductivity of a slag generally increases with some measure of the slag's "basicity". Mills demonstrated [44] that the degree of depolymerisation (which, loosely speaking, relates to basicity) is the primary factor affecting the electrical conductivity of the melt, especially the SiO_2-rich slags.

The role of transition metals, such as Fe and Mn, may be two fold. As "basic" oxides, they contribute to the depolymerisation of the silicate slag and therefore can potentially increase the conductivity by increasing the density and the mobility of the cation charge carriers. However, as the transition metals may be present in various oxidation (valence) states, electronic conduction may occur through the charge transfer process such as:

$$Fe^{2+} \leftrightarrow Fe^{3+} + e^- \qquad (3)$$

The electrical conductivity of pure iron oxide (solid and liquid wustite) has been shown to behave like a semiconductor [45,46]. In other words the conduction is dominated by electrons or "holes" in the melt. In slags containing iron oxide, both ionic and electronic conductions are therefore expected. In fact, it has been shown that the current efficiency (a measure of the ionic contribution to the conductivity) for electrolysis in liquid "wustite" is very low [47,48]. Over 90 percent of the conduction is by electrons. As CaO or SiO_2 is added to the iron oxide slag, the current efficiency gradually increases, reflecting a diminishing contribution due to semiconduction [49]. Mirroring this trend, the net conductivity of the iron oxide-containing slags also shows a strong dependence on the level of iron oxide concentration in the melt, as exemplified by the results shown in Figure 13 [50]. According to Dickson and Dismukes [49], the electrical conduction at low levels of FeO can be essentially ionic in FeO-CaO-SiO_2 melts. However, the transition between ionic and electronic domination varies with the CaO/SiO_2 ratio, or slag basicity.

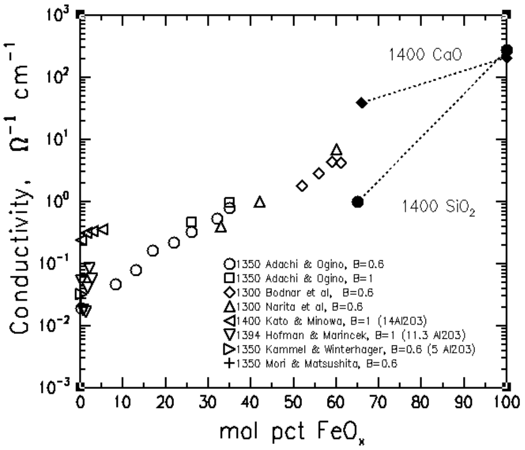

Figure 13. Electrical conductivity of iron-free and iron-containing CaO-SiO_2-Al_2O_3-MgO) slags at 1350 and 1400°C, liquid iron oxide, liquid calcium ferrite and liquid iron silicate at 1400°C.

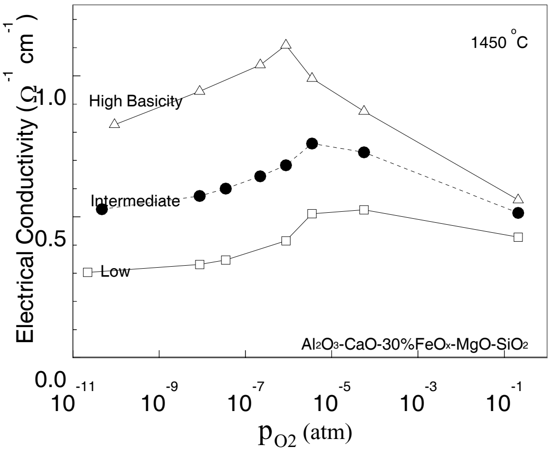

Figure 14. Variation of slag conductivity with basicity and oxidation state at 1450°C and 30wt% FeO_x.

For slags with sufficiently high levels of iron oxide and therefore substantial electronic contribution, the conductivity is shown to vary with the oxidation state. Recently the dependence on oxidation state within a wide range of p_{O_2} for slags containing SiO_2-Al_2O_3-MgO-CaO-FeO was studied [51]. The slags were of relevance to the smelting of platinum group metals (PGM). The conductivity for slags with 30% FeO at 3 levels of basicity at 1450°C is shown in Figure 14 as a function of the partial pressure of oxygen from near iron saturation to air. The conductivity goes through a maximum at some intermediate level of p_{O_2}.

There have been studies of the electrical conductivity of industrial manganese slags [52,53] and synthetic slags of CaO-MnO-SiO_2, CaO-MgO-MnO-SiO_2 and Al_2O_3-CaO-MgO-MnO-SiO_2 [54-56]. Similar to iron oxide, the addition of MnO to the slags or substitution of CaO by MnO in silicate slags leads to increased conductivity. The effect is most prominent with MnO above 50-60 mol%. Electronic conduction has also been suggested, which arises from electron hopping between the Mn^{2+} and the Mn^{3+} sites in the slag.

The effect of MnO is, however, not as strong as that of FeO. This may be largely due to the relative stability of MnO compared to the higher order oxides of manganese. For slags with a similar basicity at a given oxygen activity, the ratio of Mn^{3+}/Mn^{2+} is much lower than Fe^{3+}/Fe^{2+}, as shown earlier in this paper. No systematic study has been carried out on the dependence of conductivity on the oxidation state of MnO. However, under the prevailing reducing conditions in the smelting furnace, the manganese in slag is expected to be predominantly in the Mn^{2+} state. Electronic conduction may only have moderate contribution to the net conductivity.

The study of Cr_2O_3-containing slags is usually complicated by the low solubility of chromium or easy saturation by chromite phases. Liutikov and Tsylev [57] managed to obtain conductivity data for a wide range of composition in the Al_2O_3-MgO-SiO_2 slag with addition of up to 12% Cr_2O_3 at 1500 – 1800°C. Based on recent understanding of the phase equilibria in Cr-containing slag systems, the conduction behaviour of the slag may be qualitatively well accounted for by assuming that small addition of Cr_2O_3 to slags increases the conductivity as other transition metals do. But addition beyond the solubility range results in the formation of magnesio/ferro-chromite/ferrite solid phases, which tie up the conducting cations like Mg^{2+} and Fe^{2+}, leading to decreases in conductivity. For quantitative description, it follows that accurate depiction of the solid-liquid phase equilibria is needed.

There have been various efforts in modelling the electrical conductivity of molten oxide slags. Using data of Segers *et al.* [54,55], Jiao and Themelis [58] obtained the following empirical model for the conductivity of manganese slags with CaO of up to 47 mol%, MgO up to 20 mol%, MnO 8 – 56 mol% and SiO_2 35 – 50 mol% at 1500°C:

$$\kappa_{1500} = -\,3.34 + 6.41\,X_{CaO} + 6.75\,X_{MgO} + 8.06\,X_{MnO} \tag{4}$$

where X denotes mole fraction of the oxide species in the slag. Although good fit to the experimental data was obtained, the applicability of the model to industrial slags appears to be rather limited. The account for the effect of Al_2O_3 is rather awkward and for some industrial slags, a negative value of conductivity may result from the model.

For non-ferrous smelting slags, the authors [58] derived correlations between ln κ and the slag composition for 1400 and 1500°C and discussed the inclusion of the electronic contribution in modelling the electrical conductivity. Recently, an attempt [51] has been made to build the effect of oxidation state on the electronic conduction, as well as the temperature factor, coherently into a model describing the effect of the slag chemistry. The model gives close prediction of the conductivity over a wide range of slag chemistry and temperature with the conductivity extending from 0.01 to 300 S/cm, as shown in Figure 15. The effect of Cr_2O_3 in these slags was also modelled. Good fit was obtained for slags containing 0-8 wt% CrOx, where newly measured experimental data exists.

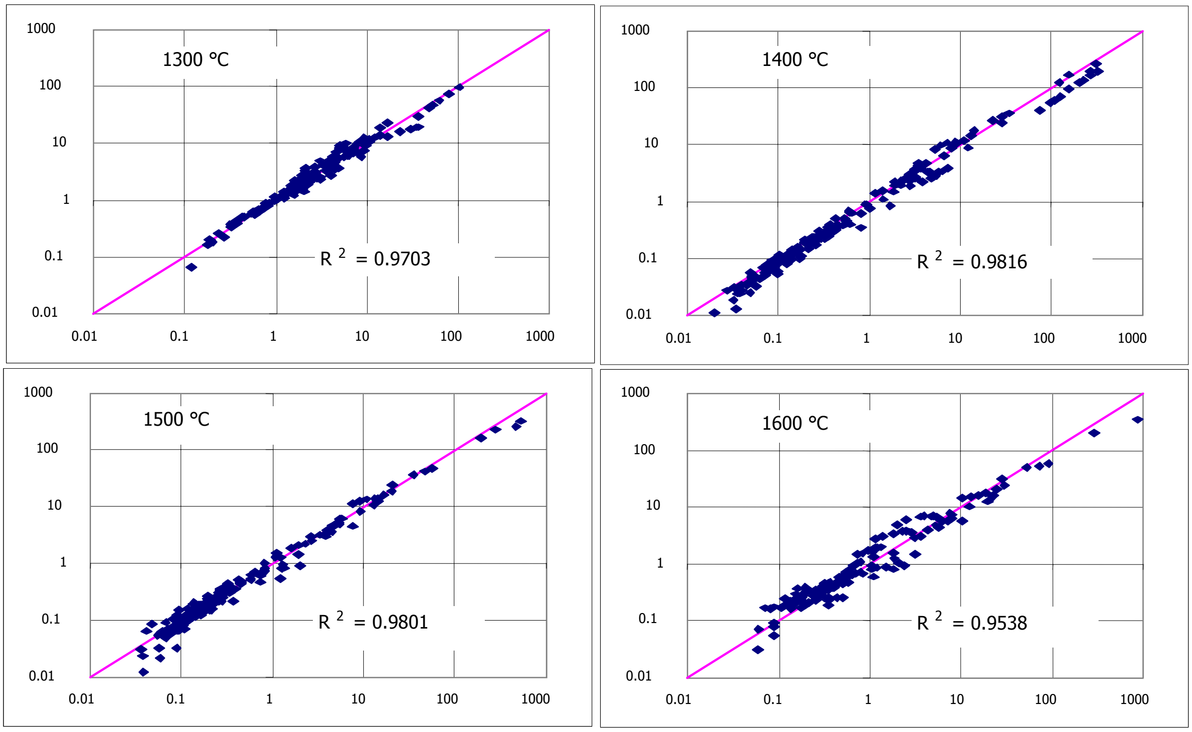

Figure 15. Fit of conductivity model (x-axis) to experimental data (y-axis) for Al_2O_3, CaO, FeO_x, MgO, SiO_2 containing slags. (All values are in $(\Omega.cm)^{-1}$; the value of the correlation coefficient R^2 is also shown).

8. INTERFACIAL PROPERTIES OF MELTS IN FERROALLOY SMELTING

High temperature interfacial phenomena in ferroalloy smelting are difficult to observe directly. Many of these phenomena are controlled or influenced by the interfacial forces. There have been many laboratory studies of the surface and interfacial tensions. A knowledge of these interfacial forces and how they respond to chemical changes is of value in understanding some aspects of the process behaviour.

Accurate determination of the surface tension of molten metals is very difficult. The experiments can often be plagued by impurities particularly of the VIA group elements (O, S, Se, and Te). Keene [59] has compiled and reviewed the surface tension data for pure liquid metals. The temperature dependence has also been presented where available. For liquid iron, chromium, manganese, nickel and silicon, the following values (in mN/m) are given:

$$\sigma_{Fe} = 1909 - 0.52\,(T - 1530) \qquad (5)$$

$$\sigma_{Cr} = 1642 - 0.20\,(T - 1860) \qquad (6)$$

$$\sigma_{Mn} = 1219 - 0.35\,(T - 1245) \qquad (7)$$

$$\sigma_{Ni} = 1834 - 0.376\,(T - 1455) \qquad (8)$$

$$\sigma_{Si} = 775 - 0.145\,(T - 1410) \qquad (9)$$

where T is in ^{o}C.

A review of the data for binary iron alloys is also given by Keene [60]. There is huge scatter among the data for Fe-Cr alloys. However, most data indicate that the addition of Cr to Fe slightly decreases the surface tension. Pure manganese has a surface tension value of 1000 to 1100 mN/m at 1550 ^{o}C. It is surface active in liquid Fe-Mn alloys. Addition of Mn to liquid iron reduces the surface tension, initially sharply and then more gently. Silicon is also surface active and the surface tension of liquid Fe-Si decreases approximately linearly with the atomic percent of Si over almost the entire composition range. Similarly, carbon in liquid Fe-C within the solubility range also decreases the surface tension.

Of particular interest is the strong surface activity of oxygen and sulphur. As shown in Figures 17 and 18 for liquid iron small addition of O or S can lead to drastic decreases in the surface tension of the liquid metal. Belton has shown that the behaviour of the surfactants may be well represented by the combined Gibbs-Langmuir adsorption isotherm [61]:

$$\sigma = \sigma^0 - R\,T\,\Gamma^0 \ln(1 + K\,a_i) \tag{10}$$

where σ^0 is the surface tension of the surfactant free liquid metal, R is gas constant, T temperature, a_i the activity of the surfactant and K the Langmuir adsorption coefficient. Similar behaviour is found for other metals and for liquid alloys. It has been shown for various reactions that the kinetics of the interfacial process is closely interweaved with the adsorption of the surfactants like O and S [61,62].

Limited surface tension data are available for slags used in ferroalloy smelting [27]. In $MnO-SiO_2$ and in $FeO-MnO-SiO_2$ slags, SiO_2 acts as surfactant, in other words, it reduces the surface tension of the melt. In $Al_2O_3-MnO-SiO_2$ and $CaO-MnO-SiO_2$, slags, the fluxes seem to be surface active. However, in $Al_2O_3-CaO-FeO-MnO-SiO_2$ slags, substitution of CaO by MnO while other components are kept constant reduces the surface tension at 1200 – 1350 °C. For $CaO-SiO_2$ slags with molar ratio of CaO/SiO_2 from 0.57 to 0.77, addition of a few percent of Cr_2O_3 reduces the surface tension at 1600 °C. Strong surfactants can also have influence the reaction at the interface [63].

There have been numerous studies on the interfacial tension between iron alloys and various slags. An extensive compilation of the interfacial tension data has been given by Mills [27]. Mills and Keene have also thoroughly reviewed interfacial tension data for liquid steel and BOS slags [64]. New measurements have been carried out on slag-steel systems in more recent years [65-67]. Effort has been spent in developing numerical models aimed at correlating data and predicting the interfacial tension for given metal-slag chemistry and temperature [68,69]. Of particular interest are developments in recent years of attaching models for interfacial tension to general thermodynamic packages. Tanaka and Hara [70] used this approach to calculate the surface tension of the alloys and slags by using the bulk thermodynamic properties evaluated in the CALPHAD method and by using the Girifalco-Good equation to calculate the interfacial tension between liquid iron alloys and slags. Good agreement between the predictions and the experimental data is reported.

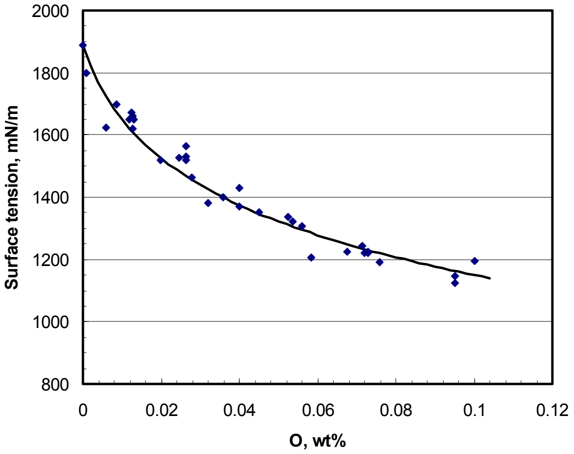

Figure 16. Effect of oxygen on the surface tension of liquid iron at 1550 and 1600°C [62].

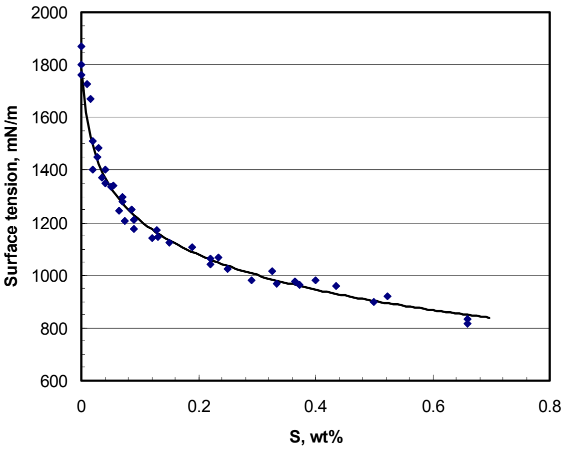

Figure 17. Effect of sulphur on the surface tension of liquid iron at 1550 and 1600°C [62].

In ferroalloy smelting droplets of reduced metal percolate through the charge bed and into the slag layer and finally settle to the metal bath in the hearth. In electrical field, electrocapillarity can modify the metal-slag interfacial tension. It has been demonstrated that for copper smelting, movement of copper metal and matte droplets in slags is influenced by the applied electrical field [71]. This may have an effect on the coalescence of drops and therefore the effective separation of the matte and the slag. Whether a similar effect occurs in the ferroalloy smelting is not clear.

9. KINETICS OF INTERFACIAL REACTIONS BETWEEN SLAGS AND CO-CO_2

The kinetics of interfacial reactions between CO-CO_2 gas mixtures and molten iron alloys as well as iron oxide containing slags has been extensively investigated by Belton and co-workers and reviewed recently [72,73,74].

Some of the key findings from the above studies could be summarised as:

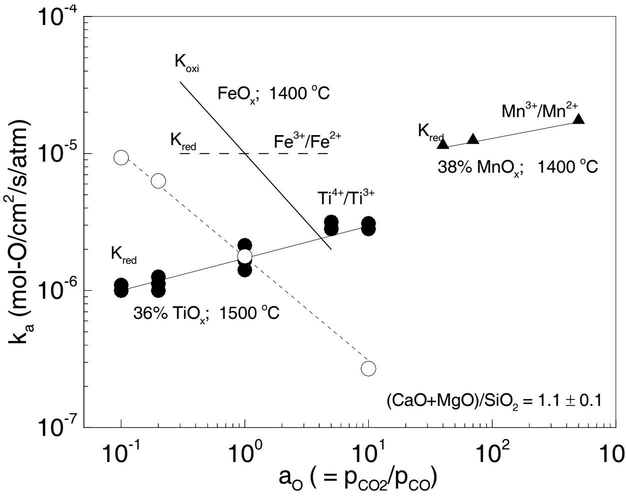

Figure 18. Dependence of the apparent first order rate constant for reduction and oxidation of MnO_x [10] and TiO_x [77] by CO-CO_2 gases, on the oxygen activity (a_O) defined as unit p_{CO2}/p_{CO} ratio as standard state.

- The apparent first order rate constant for reduction (k_a) of calcium silicate and calcium-alumino silicate slags containing more than 40 wt% FeO_x with CO-CO_2 gas mixture, increases with increases with slag basicity and virtually independent of iron oxide content at a given slag basicity and temperature.
- At lower iron oxide contents the rate constant decreases from $7x10^{-6}$ to 10^{-6} mol O/cm^2/s/atm with decreasing iron oxide until about 1 wt% FeO_x for slags with unit CaO/SiO_2 ratio at 1300 C. No noticeable decrease in the rate constant was observed at iron oxide contents of less than 1 wt%.
- In medium and low FeOx slags, the rate constant for reduction of slags is strongly dependent on the oxidation state of the slag and increases with increasing Fe^{3+}/Fe^{2+} ratio or oxygen activity (a_O).
- These observations are in accord with the proposed charge transfer model [75,76], i.e:

$$CO + O^{2-} = CO_2^{2-} \tag{11}$$

$$CO_2^{2-} + 2Fe^{3+} = 2Fe^{2+} + CO_2 \tag{12}$$

- Furthermore, parallel could be drawn between the effects of slag chemistry on the apparent constant and on the electrical conductivity of similar slags. This suggests that other transition metal oxides could have similar effect on enhancing the rate of oxygen exchange between slags and CO-CO_2 gas.

Tran [10] and Li [77,78] studied the effects of MnO_x and TiO_x on the rates of interfacial reactions between CO-CO_2 gas mixtures and calcium silicate based slags at 1400 and 1500 C. These measurements were made under conditions where mass transfer in the molten slag or gas phase was not rate limiting. Tran used CaO-SiO_2-MgO slags with (CaO+MgO)/ SiO_2 ratio of 1.2, MgO/SiO_2 ratio of 0.12 and 38 wt% MnO_x. First order rate constants were derived from initial state of reduction or oxidation of slag, which were pre-equilibriated under gas atmospheres of known a_O.

The results are plotted in Figure 18 and show the rate constant varies between 1 and 2 x 10^{-5} mol/cm^2/s/atm, increasing slightly with a_O. These values seem to be of similar magnitude to that for iron oxide slags but noticeably higher (by a factor of about 2).

This Figure also shows results by Li *et al.* [77,78] on the reactions between titania containing slags with CO-CO_2 gases. For an Fe-free slag containing 36% TiO_x, both oxidation and reduction rates were determined at 1500°C. The rate constants were found to follow very closely the reversibility criterion, as has been shown in the oxidation and reduction of liquid calcium ferrite [79,80] and low FeO_x slags by CO-CO_2. Li's data on the rate constant for reduction increased slightly with the oxidation state of Ti in the slag, or the a_O, roughly from $1x10^{-6}$ to $3x10^{-6}$ mol/cm^2/s/atm with a_O increasing from 0.1 to 10. At $a_O = 1$, the rate constant was an order of magnitude lower than for the reduction of iron oxide from slags with comparable composition. When iron oxide and titanium oxide coexist, the effect of TiO_x on the overall rate of reduction was found to be more complicated. TiO_x acted as a "basicity modifier" and increased the rate for slags with $CaO/SiO_2 = 0.7$ but decreased the rate for slags with $CaO/SiO_2 = 1.3$. These results indicate that at very low iron oxide contents in the slag, the interfacial rate of reactions is likely to play an important role in limiting the overall rate of reduction of titania slags.

10. CONCLUDING REMARKS

The above review has shown that recent experimental studies have made significant contributions to our knowledge based understanding and models of physico-chemical properties of ferroalloy type slags. However, there are still some key gaps in current knowledge on such systems that need to be filled and/or bridge through application of fundamentally based models. These include redox equilibria in slags containing more than one transition metal oxides and the thermodynamic behaviour of minor elements in slags, alloys and solid solutions.

Compared to the thermodynamic data, limited experimental data are available on transport and interfacial properties of multi-component slags and alloys. In particular data on diffusivity, thermal conductivity, surface and interfacial tension of slags and alloys are needed before some of the dynamic behaviour of smelting processes can be analysed and optimised through application of multi-phase reaction models.

Finally, the existing solution models for slags, solid solutions and alloys have allowed analysis of various processes with respect to phase equilibria and the effects of suspended solid phases on transport properties of multi-component metallurgical slags. Apart from extension of these models to cover kinetics of multi-phase reactions, linkage with fluid flow and heat transfer models will be the next logical step in development of advanced tools for simulation of chemical reactions, heat and mass transfer in electric furnaces.

11. ACKNOWLEDGEMENTS

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12. REFERENCES

[1] Xie, D.,: PhD dissertation, University of Newcastle, 1992.
[2] Yang, L.,: PhD dissertation, University of Newcastle, 1995.
[3] Yang, L., and Belton, G.R., : *Meta. Mat. Trans. B*, Vol.29B, 1998, pp.837-45.
[4] Timucin, M., and Morris, A.E.,: *Met. Trans B*, Vol.1, 1970, pp.3193-201.
[5] Xiao, Y., and Holappa, L., in Proceedings of 4th Intl Conference on Molten Slags and Fluxes, 1992, ISIJ, pp. 127-132.
[6] Morita, K., Shibuya, T. and Sano, N., *Tetsu-to-Hagane*, 1988, vol 74, pp. 632-639.
[7] Morita, K., Mor, M., Guo, M., Ikagawa, T, and Sano, N., *Steel Research*, 1999, Vol 70, pp. 319-324.
[8] Scwerdtfeger, K., and Mirzayousef-Jadid, A., in Proceedings of the Belton Symposium, 2000, AIME ISS, pp.108-119.
[9] Tamara, Y., Nakamura, S., and Sano, N., *Tetsu-to-Hagane*, 1987, vol. 73, pp. 2214-2218
[10] Tran, T.,: PhD dissertation, University of Melbourne, 1997.
[11] Mittelstadt, R., and Schwerdtfeger, K.,: *Metall. Trans B*, Vol.21, 1990, pp.111-.
[12] Farah, H.,: PhD dissertation, University of New South Wales, 1998.
[13] Farah, H. and Brungs, M.P., in press, *Journal of Materials Science* (2003).
[14] Trannel, G., : PhD dissertation, University of New South Wales, 1998.
[15] Trannel, G., Ostrovski, O., and Jahanshahi, S.,: the 5th International Conference on Molten Slags, Fluxes and Salts '97, Sydney, Jan. 6-8, 1997, pp. 501-506.
[16] Roghani, G., Jak, E. and Hayes, P., *Met. Mat. Trans. B*, 33B, 2002, pp827-838.
[17] Woo, D-H., Kang, Y-B. and Lee, H-G., *Met. Mat. Trans. B*, 33B, 2002, pp915-920.
[18] Rait, R. and Olsen, S.E., the 6th International Conference on Molten Slags, Fluxes and Salts, 12-17 June, 2000 Stockholm-Helsinki, CD-ROM.
[19] Roghani, G., Jak, E. and Hayes, P., *Met. Mat. Trans. B*, 33B, 2002, pp839-849.

[20] Roghani, G., Jak, E. and Hayes, P., in 4th Australian Melt Chemistry Symposium, 2002, Clayton, Victoria.
[21] Eric. R.H., Hejja, A.A. and Stange, W., *Minerals Eng*., 4(12), 1991, pp1315-1332.
[22] Konstantin, K.L. and Olsen, S.E., in 5th International Conference on Molten Slags, Fluxes and Salts '97, The Iron and Steel Society, 1997, Sydney, pp403-406.
[23] Chen, S., Jak, E. and Hayes, P., in 4th Australian Melt Chemistry Symposium, 2002, Clayton, Victoria.
[24] Bale, C.W., Chartrand, P., Degterov, S.A., Eriksson, G., Hack, K., Mahfoud, R.B., Melancon, J., Pelton, A.D. and Petersen, S., CALPHAD, 26(2), 2002, pp189-228.
[25] Davies, R.H., Dinsdale, A.T., Gisby, J.A., Robinson, J.A.J. and Martin, S.M., CALPHAD, 26(2), 2002, pp229-271.
[26] Zhang, L., Jahanshahi, S., Sun, S., Chen, C. Bourke, B., Wright, S. and Somerville, M., JOM, 2002, 54, pp51-56.
[27] Slag Atlas, 2nd Edition, Ed: Ed: Verein Deutscher Eisenhuttenleutte. Verlag Stahleisen GmbH, D-Dusseldorf, Germany, 1995.
[28] Degterov, S.A. and Pelton, A.D., , *J. Phase Equilibria*, 1996, 17(6), pp488-494.
[29] Geldenhuis, J.M.A., Pretorius, E.B. and Dippenaar, R.J., INFACON 6, Vol.2, Johannesburg, SAIMM, 1992, pp105-110.
[30] Cengizler, H., Eric. R.H., INFACON 6, Vol.2, Johannesburg, SAIMM, 1992, pp167-174.
[31] Xiao, Y. and Holappa, L., in 5th International Conference on Molten Slags, Fluxes and Salts '97, The Iron and Steel Society, 1997, Sydney, pp69-74.
[32] Xiao, Y., Holappa, L. and Reuter, M.A., *Met. Mat. Trans. B*, 33B, 2002, pp598-603.
[33] Kossyrev, K.L., Marushkin, K., Alikhonyan, A.S. and Olsen, S.E., the 6th International Conference on Molten Slags, Fluxes and Salts, 12-17 June, 2000, Stockholm-Helsinki, CD-ROM.
[34] Bi, X., Zhou, S., Wu, S. and Xi, G., *Ironmaking and Steelmaking*, 20(6), 1993, pp476-481.
[35] Mills, K.C., Champman, L., Fox, A.B. and S. Sridhar, The Sixth International Conference on Molten Slags, Fluxes and Salts, June 12-15, 2000, Stockholm-Helsinki, CD-ROM.
[36] Rakitina, N.I., Turkina, N.A., Morozov, A.A., Dashevskii, V.Ya., Karyazin, I.A. and Kashin, V.I., *Metally*, 1984 (1), pp26-30.
[37] Urbain, G., Cambier, F., Deletter, M. and Anseau, M.R., *Trans. J. Br. Ceram. Soc.*, 80, 1981, pp139-141.
[38] Slag Atlas (2nd Edition) Edited by Verein Deutscher Eisenhüttenleute (VDEh), Düsseldorf, Sept 1995.
[39] Sasabe, M., and Asamura, A, in proceedings of 2nd Int. Symposium on Metallurgical Slags and Fluxes, 1984, AIME TMS, pp. 651-67.
[40] Sayadyaghoubi, Y., Sun, S., and Jahanshahi, S.,: *Metall. Mater. Trans. B*, Vol.26B, 1995, pp.795-802.
[41] Sayadyaghoubi, S.,: PhD dissertation, University of Melbourne, 1995.
[42] Sayad-Yaghoubi, Y, Sun, S., and Jahanshahi, S.,: the 5th International Conference on Molten Slags, Fluxes and Salts '97, Sydney, Jan. 6-8, 1997, pp.839-44.
[43] Gaye, H., and Riboud, P.,: *C R Acad Sc Paris, C*, Vol.280, 1975, pp.1165-67.
[44] Mills, K.C., *ISIJ International*, 1993, vol.33 (1), pp.148-55.
[45] Inouye, H., Tomlinson, J.W., Chipman, J., *Trans Faraday Soc*, 1953, vol. 49, pp.796–801.
[46] Iwamoto, N., Kanayama, H. and Ogino, K., Proceedings ICSTIS, Suppl. Trans. ISIJ, 1971, vol.11, 491-94.
[47] Simnad, M.T., Derge, G., George, I., *Journal of Metals*, 1954, vol.6, pp.1386-90.
[48] Dancy, E.A. and Derge, G.J., *Trans Met Soc AIME*, 1966, vol.236, pp.1642–48.
[49] Dickson, W.R. and Dismukes, E.B., *Trans Met Soc AIME*, 1962, vol.224, pp.505-11.
[50] Sun, S. and Jahanshahi, S., in Proceedings 6th International Symp. Molten Salt Chem Tech., Ed. Chen, N. and Qiao, Z., Shanghai University Press, 2001, pp.308-13.
[51] Hundermark, R.J., Jahanshahi, S., and Sun, S., in Proceedings IMPC 2003, Cape Town, SA, 2003; Hundermark, R.J., Masters Thesis, University of Cape Town, 2003
[52] Min'ko N.I. and Nevedomskii V.A., *Melts*, 1991, vol.3(6), pp.359-64.
[53] Sun, S. and Davidson, R., unpublished work.
[54] Segers L., Fontana A. and Winand R., *Electrochimica Acta*, 1978, vol.23, pp.1281-86.
[55] Segers L., Fontana A. and Winand R., *Can Met Quart*, 1983, vol.22(4), pp.429-35.
[56] Woollacott L.C., Howat D.D. and Jochens P.R., INFACON 74 – proceedings of the 1st International Ferro-alloys Congress, Johannesburg, SAIMM, 1974, pp.227-32.
[57] Liutikov R.A. and Tsylev L.M., *Russian Mining and Metallurgy*, 1963, vol.2, pp.54-58.
[58] Jiao, Q. and Themelis, N.J., *Met Mat Trans B*, 1988, vol.19B, pp.133-40.
[59] Keene, B.J., *International Materials Reviews*, 1993, vol.38(4), pp.157-92.

[60] Keene, B.J., *International Materials Reviews*, 1988, vol.33(1), pp.1-37.
[61] Belton, G.R., *Can. Met. Quart.*, 1982, vol.21, pp.137-43.
[62] Belton, G.R., *Met. Trans. B*, 1993, vol.23B, pp.241-58.
[63] Sun, S. and Belton, G.R., *Met. Mat. Trans. B*, 1998, vol.29B, pp.137-45
[64] Mills, K.C. and Keene, B.J., *International Materials Reviews*, 1987, vol.32, pp.
[65] Chung, Y., Kim, D. and Cramb, A.W., Steelmaking Conference Proceedings 1998, pp.519-27.
[66] Sun, H., Yoneda, N., Nakashima, K. and Mori, K., *Tetsu-to-Hagane*, 1997, vol.83, pp.1-6.
[67] Xiao, F. and Mukai, K., *J. Iron and Steel Research International* (China), 2002, vol.9(1), pp.6-11.
[68] Cramb, A.W. and Jimbo, I., *Steel Research*, 1989, vol.60, pp.157-65.
[69] Sun, H., Nakashima, K. and Mori, K., *ISIJ International*, 1997, vol.37, pp.323-31.
[70] Tanaka, T. and Hara, S., *Z. Metallkd.*, 1999, vol.90, pp.348-55.
[71] Choo, R.T.C., Warczok, A. and Toguri, J.M., Copper 91 (Cobre 91), Ottawa, Ontario, Canada, 18-21 Aug. 1991, Pergamon Press Inc. (USA), (Vol. IV), 1992, pp.409-24.
[72] Belton, G.R.,: 4th Intern. Conf. on Molten Slags and Fluxes, ISIJ, 1992, pp.63-85.
[73] Belton, G.R., and Fruehan, R.J., : Turkdogan Symposium. Proc., 1994, pp.3-22.
[74] Sun, S., and Jahnashahi, S., *Metl Mat. Trans. B*, Vol. 31B, 2000, pp. 937-944.
[75] El-Rahaiby, S.K.,Sasaki, Y., Gaskell, D.R., and Belton, G.R.,: *Met. Mat. Trans. B*, Vol.17B, 1986, pp.307-16.
[76] Sun, S. and Belton, G.R, *Met. Mat. Trans. B*, Vol.29B, 1998, pp.296-98.
[77] Li, Y.,: PhD dissertation, University of Newcastle, 1999
[78] Li, Y., Lucas, Ratchev, I.P., Lucas, J.A., Evans, G.M., and Belton, G.R., in Belton Memorial Symposium Proceedings, ISIS, 2000, pp. 339-350.
[79] Sun, S.: PhD dissertation, University of Newcastle, 1988.
[80] S Sun, Y Sasaki and G R Belton: *Met. Mat. Trans. B*, Vol.19B, 1988, pp.959-65.