Slag Modelling and Industrial Applications

H. Gaye, J. Lehmann, P. Rocabois, F. Ruby-Meyer

IRSID, Maizières-lès-Metz, France

(Received January 16, 2001)

ABSTRACT

A bibliographical review of the most recent developments in slag modelling approaches, published since the 5th International Conference on Molten Slags, Fluxes and Salts, is presented, and the trends in using this information in Computational Thermodynamics software/database packages are outlined. Industrial applications based on examples pertaining to various iron- and steelmaking reactors are discussed. These applications are made essentially with the IRSID slag model and the CEQCSI software. They concern metal refining or micro alloying by slag-metal reactions and inclusions control in steels.

INTRODUCTION

Models for the estimation of the thermodynamic properties of metallurgical slags and fluxes find their natural expression in Computational Thermodynamics software/database packages which have been developed in the last two decades. The most widely used commercially available packages, Thermo-Calc /1/, F*A*C*T /2/, ChemSage /3/, MTDATA /4/ and GEMINI2 /5/ combine computation codes for multiphase, multicomponent equilibria calculation and databases and have found extensive applications in the metallurgical, materials and chemical engineering industries.

At IRSID, a non-commercially available package called CEQCSI /6/, based in large part on the IRSID slag model /7/, has been developed for very specific applications in the field of iron and steelmaking. It is well adapted for calculations of slag crystallisation path, slag-metal equilibrium and inclusions precipitation in liquid steel and during solidification.

Texts published since the 5th International Conference on Molten Slags, Fluxes and Salts, concerning experimental determinations of slag thermodynamic properties, slag modelling, and Computational Thermodynamics packages are discussed. Industrial examples based essentially on the IRSID experience in iron and steelmaking applications are then presented.

EXPERIMENTAL DATA AND SLAG MODELLING

Recent experimental studies of slag thermodynamic properties

Although an exhaustive review of phase diagrams studies is outside the scope of this paper, a few studies are reported here, as they are instrumental in expanding the database for the F*A*C*T system. They concern systems containing PbO and ZnO /8,9/, and the effect of MgO and Al_2O_3 on the liquidus temperatures of the fayalite field in the Al_2O_3-MgO-"FeO"-CaO-SiO_2 system in equilibrium with metallic iron /10/. A study concerning the Al_2O_3-CaF_2-SiO_2 system /11/ of direct interest for steelmaking was also reported.

The determinations of oxide component activities in slag systems have been receiving sustained interest, with an approach possibly less systematic and more oriented towards previously unexplored domains than in the past decade. They concern, in particular, measurements of FeO activities in steelmaking ladle slags with low FeO content /12-16,19/ or BOF slags /21/, MnO activity in BOF /17,23/ and ladle slags /18-19/, P_2O_5 activities in various steelmaking slag systems /23-26/, Cu, Pb and minor elements solubility in iron-silicate slags /21-22/. A rather large number of studies concern slag systems containing Cr oxides /27-30/ or Ti oxides /21-34/.

Sulphide capacities have been the object of several studies with, in particular, very thorough investigations of subsystems of the "FeO"-Al_2O_3-CaO-MgO-MnO-SiO_2 system /35-40/.

Special mention has to be made of the studies performed by Suito *et al.* /19,41-42/. They have concluded a long list of investigations of slag activities measurements presented in the last decade by an exhaustive study of activities of SiO_2 and Al_2O_3, activity coefficients of Fe_tO and MnO, and MgO saturation in the CaO-SiO_2-Al_2O_3-MgO system /19/. In addition, their studies on deoxidation equilibria in liquid iron /41-42/ explain a long unresolved apparent discrepancy between solubility products of CaO (MgO) obtained from liquid phase measurements and thermodynamic estimations at infinite dilution in Ca (Mg) and O : there is a very sharp increase of apparent solubility product in the diluted composition range (%Ca + 2.51 %O < 0.005).

Recent developments in slag modelling

A good deal of effort has been devoted to expanding the databases covered by existing models, with perhaps fewer proposals for new models than in previous periods.

Thus, the database for the F*A*C*T system has been largely increased by critical assessment of various binary, ternary and quaternary oxide systems /43-45/ and liquid Fe-Ni-Cu-Co-S mattes /46-47/, leading to the construction of a complete database for copper smelting and refining /48/. In this database, the slag, matte and alloy phases are treated as different phases, all described by the modified quasichemical model, and the sulphide solubility in the slag is predicted by the Reddy-Blander model, as modified by Pelton. The modelling of matte and slag as one oxisulphide phase has been announced as being the subject of future work.

One of the important developments of the Thermo-Calc database is the assessment of the Ca-Fe-O-Si system /49/. In this assessment, both liquid metal and CaO-FeO-Fe_2O_3-SiO_2 slag system are described with the ionic two-sublattice model, with a single set of parameters. Other developments at the KTH concern the use of a previously proposed model /50/ for the description of the measured sulphide capacities in multicomponent slag systems, and the elaboration of a new mathematical model to predict the thermochemical and thermophysical properties of multicomponent slags using only information from the binary subsystems /51/.

At IRSID, the cell model for oxides and diluted sulphur was applied to describe the behaviour of Ti oxides in multicomponent slags /52/. It is presently used for calculations in the system SiO_2-TiO_2-Ti_2O_3-Cr_2O_3-Al_2O_3-Fe_2O_3-CrO-FeO-MgO-MnO-CaO-CaF_2-S. The oxysulphide model /53/ has also been consolidated for the system SiO_2-Al_2O_3-Fe_2O_3-FeO-MgO-MnO-CaO-S. In these cell models, the multicomponent systems are described using only binary parameters.

Mogutnov *et al.* /54/ have developed an associated-solution model of liquid slags and silicates, based on Prigogine's theory, and have applied it with success to ternary and quaternary compositions of the CaF_2-CaO-Al_2O_3-SiO_2-MnO-Ca_3P_2 system.

The Lin and Pelton /55/ structural model has recently been reactivated and extended by Serrano and Pelton /56/ to the ternary systems SiO_2-MnO-MgO, SiO_2-FeO-MnO and SiO_2-FeO-MgO. Further studies are announced to describe more complex silicates such as SiO_2-FeO-CaO in which a random mixing of Fe^{2+} and Ca^{2+} cannot be assumed, and to incorporate S^{2-} in partial substitution for O^{2-}. The same model has also been applied for alkaline binary and ternary silicates /57/.

Another novel approach is the use of molecular dynamics simulations to describe the behaviour of diluted oxides and fluorides in the CaO-CaF_2 system /58/.

Very little has been published recently concerning the use of optical basicity in slag modelling and process control. A user friendly software package has however been developed, with the purpose of providing an access to the Optical Basicity Databank for technological applications and for the purposes of scientific evaluation /59/.

A comparative study of various models has been made for MnO-containing slags relevant to ferromanganese melting /60/. In this study, the UIPM (unified interaction parameter model), regular solution model, associated solution model, two-sublattice model, polymerisation model, modified quasichemical model and cell model were considered, and their applicability to metal and slag phases was assessed. The final choice was to select the UIPM model for the metal phase, and the cell model for the slag phase, with however revised values of the parameters originally proposed at IRSID for a better fit in the composition domain concerned.

TRENDS IN COMPUTATIONAL THERMODYNAMICS.

A recent update of the current status of the main commercial computational thermodynamics packages has been presented at the last IUPAC Conference (Jülich, April 2000).

A strong trend is increased cross-breeding of the contributions of the various teams. Developments in data assessments and solution models had previously been widely shared on a scientific basis; some software products are now developed in common. It has thus been announced /61/ that the F*A*C*T and ChemSage groups were proposing common packages called FACTSage and ChemApp with enlarged database platforms and improved user friendly access.

Another trend is the increased coupling of purely thermodynamic packages with kinetic models. For instance, the coupling of Thermo-Calc and DICTRA /62/ provides a unique commercial software which can precisely simulate diffusion-controlled phase transformations in various materials.

Several industrial applications involving the coupling of CFD codes and thermodynamic models have been proposed. For instance, a two-dimensional fluid dynamic model accounting for the steel, slag and argon phases has been incorporated with the thermodynamic model of desulphurisation developed at the KTH to study sulphur removal in a gas-stirred steel ladle /63/. Another application concerns the coupling of a CFD code of the steel ladle and thermochemical softwares (MTDATA and ChemSage) in order to understand the individual mechanisms that take place during inclusion generation, their interaction with steel, refractories, slag and atmosphere, and their removal from or retention in the steel /64/. Other applications concern the coupling of CEQCSI with a nucleation and growth model to study the kinetics of inclusions precipitation during steel solidification /65/, and a very ambitious, albeit somewhat simplistic approach, using ChemSage for the simulation of an LD-converter process /66/.

INDUSTRIAL APPLICATIONS: SLAG-METAL REACTIONS

One of the most obvious uses of Computational Thermodynamics packages in extractive metallurgy is the evaluation of the equilibrium distribution of elements between various phases, and the definition of appropriate conditions for optimal metal purification.

A very significant example is the application of the F*A*C*T thermodynamic computing system for the thermodynamic modelling of lead and zinc distribution among matte, slag, liquid copper and gas phases during copper smelting and converting /67-68/. This required calculations in the 8-component system Zn-Pb-Cu-Ca-Fe-Si-O-S. Model evaluations were compared with available experimental data, and predictions have been proposed in situations where experimental data are difficult to obtain.

In the field of steelmaking, a very detailed analysis of ladle steel desulphurisation on thermodynamic grounds has recently been made /69/. Various models to express the slag sulphide capacity, and evaluate the oxygen activity at the slag-metal interface from the Al/Al_2O_3 equilibrium were tested. The best agreement was obtained by combining the KTH model for sulphide capacity /38/, and the expression of Al_2O_3 activity recently proposed by Ohta and Suito /19/.

This example is a very convincing demonstration of the usefulness of industrial data to confirm thermodynamic estimations. Some care has however to be taken in order to eliminate a possible bias that can occur from kinetic limitations and a cross-check of different means to evaluate a given quantity, as well as an estimation of time required to reach equilibrium, should be made, whenever possible. For example, Figure 1 indicates the results of a calculation using slag and metal analyses of samples taken at six time intervals during a ladle vacuum treatment /70/. The oxygen activities at the slag-metal interface evaluated for the Si/SiO_2 and Mn/MnO are in relatively good agreement for all samples and decrease essentially on account of the temperature decrease, whereas the activity evaluated from the Al/Al_2O_3 equilibrium is much lower in the first sample and progressively comes to agreement with the other estimations. Indeed, sample 1 was taken rather early after a late Al addition to the metal, and complete oxidation of the excess Al was effective only in samples 5 and 6. Note that oxygen activities that can be measured with a probe immersed in the metal are usually higher than the activities at the interface: oxygen in the metal is buffered by the strongest deoxidising element and its pure oxide (in general Al/Al_2O_3), as there is a constant oxygen intake from the lining, and even locally from the probe itself.

Besides metal refining, slag-metal treatments can be used for accurate and smooth micro-alloying of the metal, in conditions that will prevent artefacts arising from local supersaturations when the alloying element comes in contact with the metal. Such treatments in the case of Ti transfer from slag to metal have been recently analysed at IRSID /71/. The main conclusion is that the titanium equilibrium distribution ratio between reduced ladle metallurgy slags and steel depends essentially on the oxygen potential, that is on metal Al content, whereas moderate variations of slag composition or temperature have smaller effects. This is illustrated on figure 2 in which the lines represent model calculations for slag compositions 5% and 10% TiO_2, 10% MgO, $\%CaO/\%Al_2O_3$ = 1.4 at 1500°C and 1600°C, and the experimental points represent industrial data for slag compositions somewhat scattered around these values. In this diagram, the Ti oxide content of the slag is expressed as % TiO_2, although the calculation takes into account Ti^{3+} and Ti^{4+}.

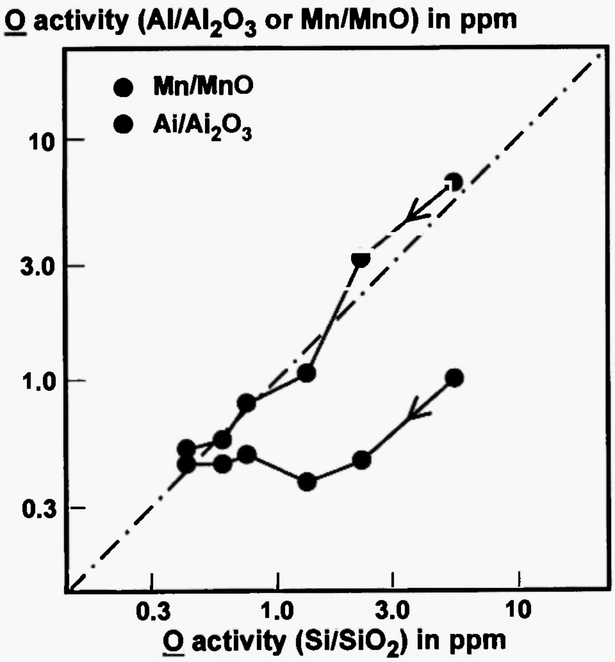

Fig. 1: Evolution of the oxygen activity calculated for the Si/SiO_2, Al/Al_2O_3 and Mn/MnO equilibria for six successive slag and metal samples taken during a ladle treatment under vacuum.

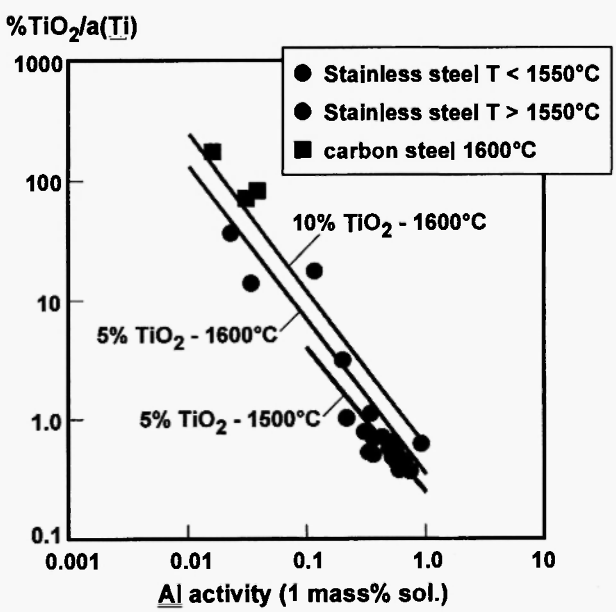

Fig. 2: Evolution of Ti equilibrium distribution ratio between slag and metal, as computed with the CEQCSI software, and comparison with industrial data of ladle treatments under vacuum on carbon and stainless steels.

INDUSTRIAL APPLICATIONS: METAL-REFRACTORIES INTERACTIONS

Laboratory experiments in crucibles containing 1 kg of steel were made at IRSID /71/ to study the effect on inclusions of the reduction of MgO-based refractory containing silicates by Al-Ti- deoxidised steels. Metal samples were taken every two to five minutes by suction in silica tubes and rapidly cooled. The samples were then analysed, and observations and micro analyses of inclusions were performed.

The evolution of steel composition and nature of inclusions depend on Al and Ti initial contents. For two extreme cases, the results are as follows :

- for an initial composition 0.03% Al, 0.04% Ti, there is first a continuous decrease in Al only, and the Ti content starts decreasing only when the Al content reaches about 0.006%. The inclusions consist of a mixture of alumina inclusions and spinels.
- for an initial composition 0.006% Al, 0.08% Ti, both Al and Ti contents decrease all along the experiment. Two types of inclusions were observed : spinels and a phase rich in Al_2O_3 and TiO_2.

In Figure 3, we have plotted the evolution of metal composition, superimposed on the phase diagram for the system Fe-0.12 %Mn-0.03 %Si-Al-Ti-O at 1580°C, as calculated using the slag model. This diagram indicates the nature of the first oxides formed as a function of dissolved Al and Ti contents, and the values of the oxygen activities at equilibrium between these oxides and the metal. When traces of Mg are added to the metal, the calculation indicates that, upon reaching oxygen saturation, the first oxide formed is a spinel $(Mg,Mn)O-Al_2O_3$ which coexists with either Al_2O_3 or liquid oxides. The calculation with the CEQCSI software of equilibrium inclusions composition from the elementary analysis of the metal samples is also in good agreement with the observations.

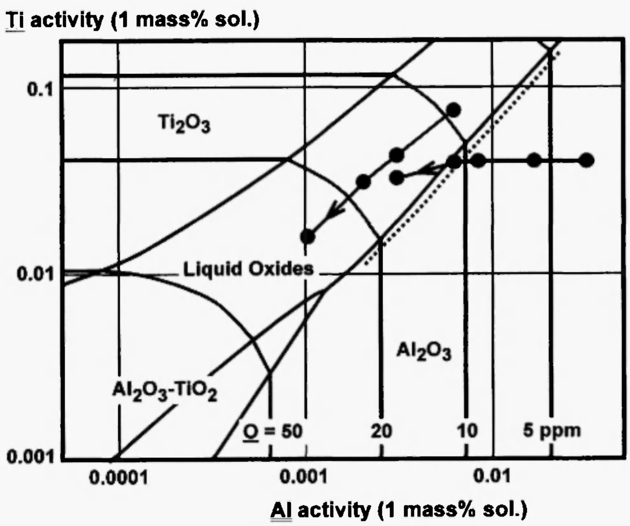

Fig. 3: Evolution of metal composition during two oxidation treatments in the laboratory, plotted on the computed equilibrium diagram for the system Fe-0.12%Mn-0.03%Si-Al-Ti-O at 1580°C.

INDUSTRIAL APPLICATIONS : INCLUSIONS CONTROL IN STEELS.

The procedure used in the CEQCSI software to calculate, from the overall elementary steel analysis, the sequence of precipitation of inclusions at equilibrium is applied by steps from the temperature of liquid steel treatment, to subsequent temperature evolution, during cooling and solidification of the steel. In this last situation, an original method has been developed /72/ in which the micro-segregation equations for elements dissolved in liquid metal, with or without diffusion in solid metal, and the equilibrium conditions between liquid steel and oxide, sulphide, nitride, or carbide precipitates are treated simultaneously. The calculation also gives the liquidus temperature of the oxide inclusions and their crystallisation path during cooling.

Various applications, in particular concerning semi-killed steels in which the formation of liquid oxide inclusions is required, and calcium treatments of Al-killed steels have been discussed in detail /73/. The example presented here concerns free-cutting steels and illustrates the use of the oxysulphide model. In these steel grades with high S contents, two main objectives are sought :

- obtain a good distribution of MnS precipitates to limit the chips length,
- protect the tool from hard abrasive oxides (Al_2O_3, spinels...) by preventing their formation or embedding them in sulphides.

In addition, for high-speed machining, it is advantageous to harden some of the sulphides that will then form protective films on the tool. One way to do this is to add calcium to form (Ca,Mn)S; another way is to obtain oxysulphides in which the hardening effect is created by the partial substitution of S by O. This last solution is applied for free-cutting steels.

Calculations were made to predict the nature of oxide, oxysulphide and sulphide phases precipitating in liquid steel and during solidification, in a base steel of composition 0.07 %C-1.35 %Mn-0.014 %Si containing minute amounts of tramp elements Al, Ca and Mg resulting from the ladle treatment, as a function of oxygen content (20 to 120 ppm). The calculated sequence of inclusions precipitation for an oxygen content of 60 ppm, which maximises the amount of oxysulphides and minimises the amount of harmful oxides is shown in Figure 4. This oxygen content was indeed found optimal in practice.

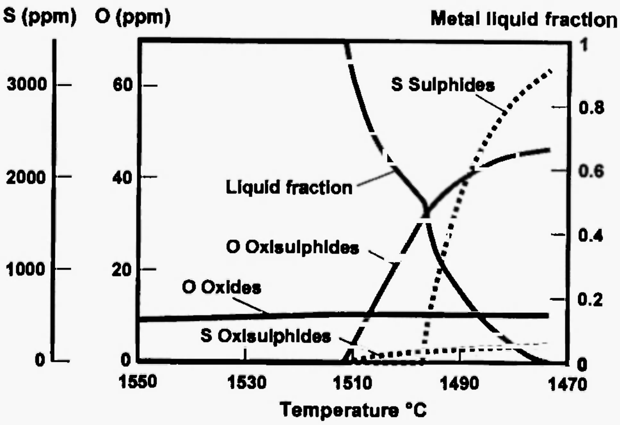

Fig. 4: Computed equilibrium sequence of precipitation of oxide, oxysulphide and sulphide inclusions during steel solidification (amounts of O and S trapped in these inclusions) in a free cutting steel grade containing 60 ppm O.

CONCLUSIONS

Intensive efforts have been made in the last few years to use established slag models for the appropriate description of more and more complex systems, and incorporate them in Computational Thermodynamics software/database packages. It is expected that the use of these models and confrontation with industrial results will help in defining the specific domains in which further experimental investigations of slag thermodynamic properties are needed and avoid duplication of studies in domains in which the data is fairly well established.

At this time, it does not seem that new slag modelling concepts that would substantially change the picture in the next few years have come to fruition.

An ever increasing number of industrial applications in the fields of metallurgical, materials and chemical engineering industries, that take full advantage of the models and of the accessibility of powerful calculation codes, have been proposed and they generally show very encouraging results. More and more, the opportunity of coupling thermodynamic codes and CFD or kinetic codes is put into effect for a better understanding of processes and materials design.

References

1. B. Sundman, B. Jansson and J.-O. Andersson, *Calphad* 9, 1985, pp. 153-90.
2. C.W. Bale, A.D. Pelton and W.T. Thompson, (F*A*C*T), CRCT, Ecole Polytechnique, Montreal, Canada, 1995.
3. G. Eriksson and K. Hack, *Metall. Trans B*, **21B**, 1990, pp. 1013-23.
4. A.T. Dinsdale, S.M. Hodson, T.I. Barry and J.R. Taylor, in *Computer Software in Chemical and Extractive Metallurgy*, Pergamon Press, New York, NY, 1989, pp. 59-74.
5. B. Cheynet, in *Computer Software in Chemical and Extractive Metallurgy*, Pergamon Press, New York, NY, 1989, pp. 31-44.
6. C. Gatellier, H. Gaye, J. Lehmann and Y. Zbaczyniak, *Revue de Metallurgie-CIT*, 1992, pp. 887-8.
7. H. Gaye and J. Welfringer, *2nd Int. Symp. on Slags and Fluxes*, Met. Soc. AIME, 1984, pp. 357-75.
8. E. Jak, N. Liu and P.C. Hayes, *Metall. Mater. Trans. B*, 1998, **29B**, pp. 541-53.
9. E. Jak, B. Zhao, N. Liu and P.C. Hayes, *Metall. Mater. Trans. B*, 1999, **30B**, pp. 21-7.
10. B. Zhao, E. Jak and P.C. Hayes, *Metall. Mater. Trans. B*, 1999, **30B**, pp. 597-605 and 1017-26.
11. S. Ueda and M. Maeda, *Metall. Mater. Trans. B*,

1999, **30B**, pp. 921-5.
12. Y. Taniguchi, K. Morita and N. Sano, *ISIJ Int.*, 1997, **37**, pp. 956-61.
13. H. Fujiwara, M. Kitou, T. Matsui and E. Echise, *Metall. Mater. Trans. B*, 1997, **28B**, pp. 243-50 and 1999, **30B**, pp. 419-27
14. K. Matsuzaki, Y. Higano and K. Ito, *ICST/ Ironmaking Conf. Proc.*, 1998; pp. 1471-6.
15. L. Yang and G.R. Belton, *Metall. Mater. Trans. B*, 1998, **29B**, pp. 837-45.
16. S.-H. Kim and B. Song, *Metall. Mater. Trans. B*, 1999, **30B**, pp. 435-42.
17. A. Sobandi, H.G. Katayama and T. Monomo, *ISIJ Int.*, 1998, **38**, pp. 953-8.
18. N. Sano and K. Morita, *Alex McLean Symp. Proc.*, 1998, Iron & Steel Society, pp. 3-9.
19. H. Ohta and H. Suito, *Metall. Mater. Trans. B*, 1998, **29B**, pp. 119-29.
20. S. Ueda, K. Morita and N. Sano, *ISIJ Int.*, 1998, **38**, pp. 1170-9.
21. H.G. Kim and H.Y. Sohn, *Metall. Mater. Trans. B*, 1998, **29B**, pp. 583-90.
22. M. Kudo, E. Jak, P.C. Hayes, K. Yamaguchi and Y. Takeda, *Metall. Mater. Trans. B*, 2000, **31B**, pp. 15-24.
23. A.T. Morales and R.J. Fruehan, *Metall. Mater. Trans. B*, 1997, **28B**, pp. 1111-7.
24. A. Sobandi, H.G. Katayama and T. Monomo, *ISIJ Int.*, 1998, **38**, pp. 781-8.
25. W.H. Van Niekerk and R.J. Dippenaar, *Metall. Mater. Trans. B*, 1998, **29B**, pp. 147-53.
26. L.-F. Li, M.-F. jiang, C.-J. Jin, W.-Z. Wang and Z.-P. Chen, *Metall. Mater. Trans. B*, 1999, **30B**, pp. 451-7.
27. A.M. Garbers-Craig and R.J. Dippenaar, *Metall. Mater. Trans. B*, 1997, **28B**, pp. 619-24.
28. Y. Okabe, I. Tajima and K. Ito, *Metall. Mater. Trans. B*, 1998, **29B**, pp. 131-36.
29. M. Hino, K.-I. Higuchi, T. Nagasaka and S. Ban-Ya, *Metall. Mater. Trans. B*, 1998, **29B**, pp. 351-60.
30. K. Morita, M. Mori, M. Guo, T. Ikagawa and N. Sano, *Steel Research*, 1999, **70**, pp. 319-24.
31. K. Matsuzaki and K. Ito, *ISIJ Int.*, 1997, **37**, pp. 562-5.
32. M. Ito, K. Morita and N. Sano, *ISIJ Int.*, 1997, **37**, pp. 839-43.
33. M. Ohta and K. Morita, *ISIJ Int.*, 1999, **39**, pp. 1231-8.
34. Y. Morizane, B. Ozturk and R.J. Fruehan, *Metall. Mater. Trans. B*, 1999, **30B**, pp. 29-43.
35. M.M. Nzotta, R. Nilsson, Du Sichen and S. Seetharaman, *Ironmaking and Steelmaking*, 1997, **24**, pp. 300-5.
36. E. Drakaliysky, Du Sichen and S. Seetharaman, *Can. Metall. Quart.*, 1997, **36**, pp. 115-20.
37. M.M. Nzotta, *Scand. J. Metall.*, 1997, **26**, *ISIJ Int.*, pp. 169-77.
38. M.M. Nzotta, Du Sichen and S. Seetharaman, *ISIJ Int.*, 1998, **38**, pp. 1170-9 and 1999, **39**, pp. 657-63.
39. M.M. Nzotta, Du Sichen and S. Seetharaman, *Metall. Mater. Trans. B*, 1999, **30B**, pp. 909-20.
40. J.-D. Seo and S.-H. Kim, *Steel Research*, 1999, **70**, pp. 203-8.
41. G. Li and H. Suito, *Metall. Mater. Trans. B*, 1997, **28B**, pp. 251-8 and 259-64.
42. H. Ohta and H. Suito, *Metall. Mater. Trans. B*, 1997, **28B**, pp. 1131-9.
43. S.A. Degterov and A.D. Pelton, *Metall. Mater. Trans. B*, 1997, **28B**, pp. 235-42.
44. E. Jak, S.A. Degterov, P. Wu, P.C. Hayes and A.D. Pelton, *Metall. Mater. Trans. B*, 1997, **28B**, pp. 1011-8.
45. E. Jak, S.A. Degterov, P.C. Hayes and A.D. Pelton, Can. Metall. Quart., 1998, **37**, pp. 41-7.
46. F. Kongoli, Y. Dessureault and A.D. Pelton, *Metall. Mater. Trans. B*, 1998, **29B**, pp. 591-601.
47. F. Kongoli and A.D. Pelton, *Metall. Mater. Trans. B*, 1999, **30B**, pp. 443-50.
48. S.A. Degterov and A.D. Pelton, *Metall. Mater. Trans. B*, 1999, **30B**, pp. 661-9.
49. M. Selleby, *Metall. Mater. Trans. B*, 1997, **28B**, pp. 563-76 and 577-96.
50. Du Sichen, R. Nilsson and S. Seetharaman, *Steel Research*, 1995, **66**, pp. 458-62.
51. J. Björkvall, Doctoral Thesis, KTH, March 2000.
52. J. Lehmann and H. Gaye, *82nd Steelmaking Conf. Proc.*, 1999, pp. 463-70.
53. H. Gaye and J. Lehmann, *Proc. 5th Int. Conf. on Molten Slags, Fluxes and Salts*, Sydney, Australia,

1997, ISS, pp.27-34.
54. B.M. Mogutnov, A.I. Zaitsev and A.D. Litvina, 1998 *ICST/Ironmaking Conf.Proc.* pp. 1477-86.
55. P.L. Lin and A.D. Pelton, *Metall. Trans. B*, 1979, **10B**, pp 667-75.
56. A.R. Serrano and A.D. Pelton, *ISIJ Int.*, 1999, **39**, pp. 399-408.
57. F. Bennour, M. Gilbert, J. Rogez and J.C. Mathieu, *Metall. Mater. Trans. B*, 1999, **30B**, pp. 67-74.
58. D.K. Belashchenko, O.I. Ostrovski and Y.I. Utochkin, *ISIJ Int.*, 1998, **38**, pp. 673-9.
59. F. Mitchell, D. Sleeman, J.A. Duffy, M.D. Ingram and R.W. Young, *Ironmaking and Steelmaking*, 1997, **24**, pp. 306-20.
60. H.-J. Li, A.E. Morris and D.G.C. Robertson, *Metall. Mater. Trans. B*, 1998, **29B**, pp. 1181-91.
61. A.D. Pelton, C.W. Bale, G. Eriksson, K. Hack, S. Petersen and P. Koukkari, *10th IUPAC Conf.*, April 2000, Jülich, Germany, p. 77.
62. B. Sundman, J. Agren and P. Shi, *10th IUPAC Conf.*, April 2000, Jülich, Germany, p. 78.
63. L. Jonsson, Du Sichen and P. Jönsson, *ISIJ Int.*, 1998, **38**, pp. 260-7.
64. G.J. Hassall, K.C. Bain, R.W. Young and M.S. Millman, *Ironmaking and Steelmaking*, 1998, **25**, pp. 273-8.
65. H. Gaye, P. Rocabois, J. Lehmann and M. Bobadilla, *Steel Research*, 1999, **70**, pp. 356-61.
66. A. Traebert, M. Modigell, P. Monheim and K. Hack, *Scand. J. Metall.*, 1999, **28**, pp. 285-90.
67. S.A. Degterov and A.D. Pelton, *Metall. Mater. Trans. B*, 1999, **30B**, pp. 1033-44.
68. S.A. Degterov, Y. Dessureault and A.D. Pelton, *Can. Metall. Quart.*, 2000, **39**, pp. 43-54.
69. M.A.T. Andersson, P.G. Jönsson and M.M. Nzotta, *ISIJ Int.*, 1999, **39**, pp. 1140-9.
70. M. Faral and H. Gaye, *2nd Int. Symp. on Slags and Fluxes*, Met. Soc. AIME, 1984, pp. 159-79.
71. F. Ruby-Meyer, J. Lehmann and H. Gaye, *SCANMET I*, June 1999, Lulea, pp. 213-28.
72. M. Wintz, M. Bobadilla, J. Lehmann and H. Gaye, *ISIJ Int.*, 1995, **35**, pp. 715-22.
73. H. Gaye, C. Gatellier and P.V. Riboud, *Proc. E. T. Turkdogan Symp.*, ISS, 1994, pp. 113-124.