THERMODYNAMICS APPLIED TO FERRO-ALLOYS SMELTING

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ABSTRACT

A review of thermodynamic information and models of slags, including associated software when available, is presented. The pertinence and accuracy of these models is discussed by comparison of their predictions for various slag thermodynamic properties with the available experimental data. Practical industrial applications will be illustrated by a literature review of the dephosphorization process of ferromanganese alloys and by the description of Ti behavior during silico-manganese alloys production. This latter example will show how the thermodynamic models have been used to propose a flotation treatment at low temperature to enhance TiC removal.

1. INTRODUCTION

During the past decades, efforts have been made to develop thermodynamic models for multi-component oxide systems. The aim of these models is to permit the calculation of phase diagrams and thermodynamic properties such as component activities, sulphide and phosphate capacities, etc.

These models contain a set of self-consistent parameters that have been calibrated against the available thermodynamic information, typically experimental phase diagrams, slag/gas and slag/metal partition experiments. Unfortunately, for some elements of utmost interest for the ferroalloy production, such as Ti, Cr, V or Nb, the information is often rare and disseminated. The first part of this paper, dedicated to the thermodynamic data, is mainly focused on information collected in the literature concerning these elements.

The presentation of the slag models proposed in the second part does not intend to be exhaustive. Presented here are mainly the models able to cope with multicomponent systems and that are either implemented in commercial software or whose mathematical expressions can be easily handled "manually".

The last part of this paper is devoted to two applications of thermodynamic concepts and models. The first concerns a literature review of the dephosphorization process of ferromanganese alloys (choice of slag composition, effect of the alloy composition and temperature). The second example is more focused on the potential contribution of thermodynamic models. It concerns the possibility of Ti removal during silico-manganese alloy production.

2. THERMODYNAMIC DATA

Slag Atlas [1] remains one of the best reference books for the user who desires quick access to condensed and reviewed information on the main thermodynamic data concerning metallurgical slags. Besides the oxides that are the main components of metallurgical slags such as SiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO for which the available information is quite complete and reliable, one can also find information on oxides of transition elements like chromium or vanadium which are of utmost interest for the ferroalloy industry. However, since few experimental studies have been devoted to these oxides, this information is often scarce or not always directly usable. For example, phase diagrams relative to chromium or titanium oxides have been, most of the time, established under oxidizing conditions where these elements have valence states quite different from those they have in slags during metallurgical treatments. Hereafter is a brief literature review on data concerning chromium, titanium niobium and vanadium where emphasis has been put on metal/slag partition data.

2.1 Chromium

Most of the phase diagrams concerning chromium have been established in air where chromium has the Cr^{3+} valence state and are reported in Slag Atlas. Chromium slag/metal partition coefficients have usually been measured in equilibrium with liquid iron, but also with Pt-Fe alloys under controlled atmosphere [2-4] and with liquid silver [5]. Activity measurements have also been performed by using an oxygen probe [6-8] or a Knudsen Cell [9].

These different techniques permit the study of slags with very different chromium and iron oxide contents:

- slags belonging to the SiO_2-Al_2O_3-CrO_x-MgO-CaO-CaF_2 system without iron oxides studied with the techniques not involving liquid iron [2-9] but also by equilibrium with a carbon saturated Cr ferroalloy [10,11],
- SiO_2-Al_2O_3-CaO slags with low iron oxide contents and with high and low chromium oxides contents and MgO contents up to 14% [12-14],
- SiO_2-FeO_x-MnO and SiO_2-FeO_x-CaO-MgO slags with high and low Cr-oxide contents [15-19].

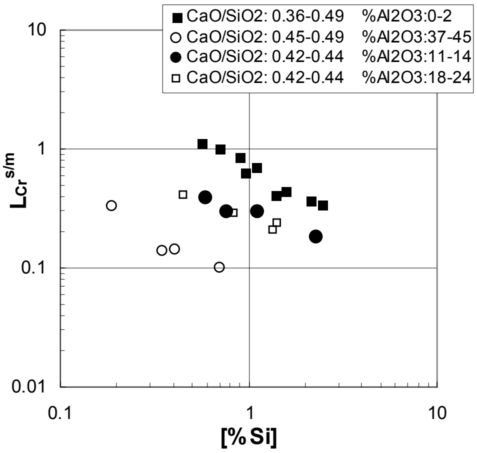

Figure 1. Experimental variation of the Cr slag/metal equilibrium coefficient with metal silicon content, slag basicity and alumina content [11].

In all these situations, chromium is present with two valence states Cr^{2+} and Cr^{3+} and the ratio Cr^{2+}/Cr^{3+} increases with decreasing oxygen activity and decreasing basicity. Figure 1 shows the effect of the Si content of a chromium alloyed liquid steel on the equilibrium chromium partition $L_{Cr}^{s/m}$, defined as $(\%Cr)_{slag}/\ [\%Cr]_{metal}$, for acid slag [11]. Hereafter, (%i) will stand for the weight percentage of i in the slag and [%i] for the weight percentage of i in the metal.

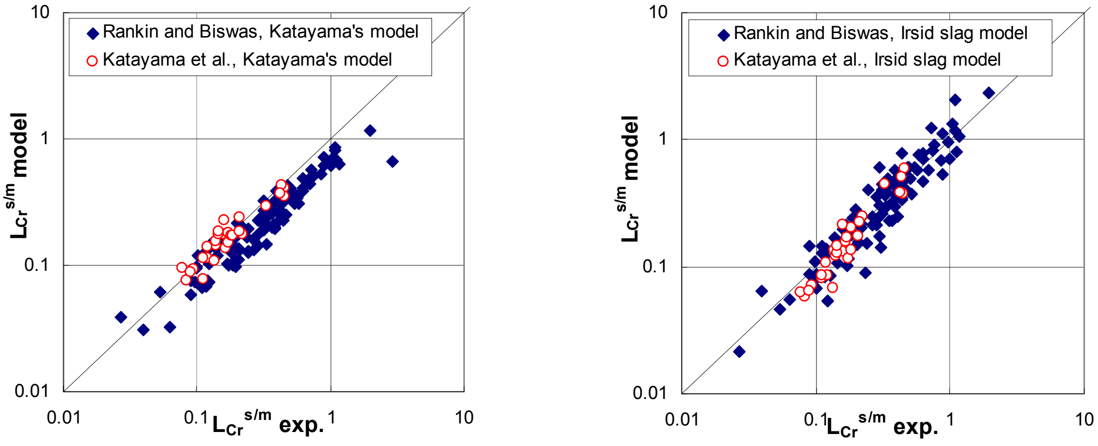

Figure 2. Comparison between experimental data [11,14] and values calculated with Katayama's and Irsid model of the Cr equilibrium partition coefficient.

Katayama et al. [11] propose a useful expression of the Cr partition coefficient as a function of slag and metal composition and of temperature:

$$\log L_{Cr}^{s/m} = 0.843 \log N_{CrO} - 0.035[\%Cr] + 0.106\left(N_{CaO} + 0.1N_{MgO} - 0.8N_{Al_2O_3} - N_{SiO_2}\right) + \frac{195}{T} + 0.884 \quad (1)$$

where N_i is the mole fraction of oxide i. Total chromium oxide content in the slag is expressed as CrO. The quality of this relation is illustrated on Figure 2 . The accuracy of the prediction is all the more interesting since it is valid over a wide slag composition range: up to 70% SiO_2, 23 to 51% Al_2O_3, up to 40% CaO, up to 38% Cr_2O_3 and up to 10% FeO. Nevertheless, the predictions of Irsid slag model that will be described in section 0, appear to be somewhat better for the large Cr partition coefficients, i.e. for relatively oxidizing conditions. For these points, even though Irsid's prediction seems to be a little more scattered than Katayama's, it doesn't deliver a systematically underestimated value as seems to be the case for Katayama's relation.

2.1 Titanium

As for chromium, most of the phase diagrams concerning titanium have been established in air and, in these conditions, titanium is present as Ti^{4+} [20-22]. They are also reported in the Slag Atlas. Uncertainties remain concerning the Ti_2O_3-TiO_2 phase diagram. The version proposed by Eriksson and Pelton [23] based, in particular, on the Brauer and Littke data [24], is recommended.

Available equilibrium experiments between a slag and one or several other phases have been performed under more reducing conditions where titanium is present with two valence states Ti^{4+} and Ti^{3+}. These other phases are:

- a gas phase [25]. In this case, only the ratio Ti^{4+}/Ti^{3+} and the activity coefficients ratio $\gamma_{TiO2}/\gamma_{Ti2O3}$ have been measured for the system SiO_2-TiO_x-CaO.
- a solid metallic phase, iron crucible or Pt-Mn alloy, or liquid silver or copper, and a controlled atmosphere. The relatively oxidizing conditions prevailing during these experiments (corresponding to an oxygen activity higher than 0.03 in the 1 wt% reference state) have permitted the study of sub-systems of SiO_2-Al_2O_3-TiOx-FeO_x-MnO-CaO [26-33].
- a liquid metallic phase (copper, nickel, steel and stainless steel) imposing more reducing conditions for the study of the TiO_x-Al_2O_3-CaO system [34-37] and the SiO_2-TiO_x-CaO system [38,39].
- a graphite crucible in a controlled atmosphere for the SiO_2-TiO_x-Al_2O_3-MgO-CaO system [40-42].

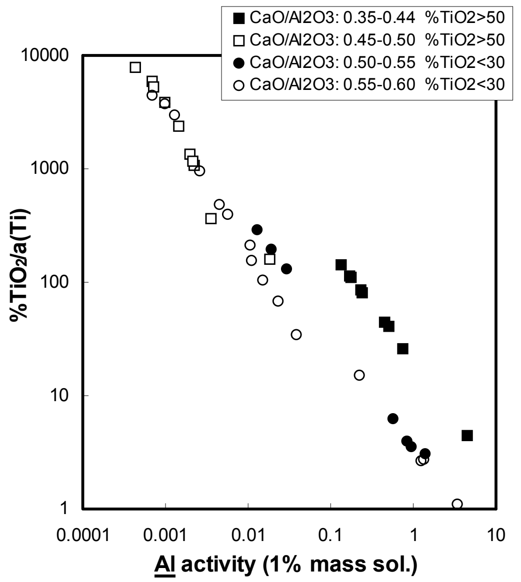

Figure 3. Experimental values of Ti equilibrium distribution ratio between slag and metal [34-37].

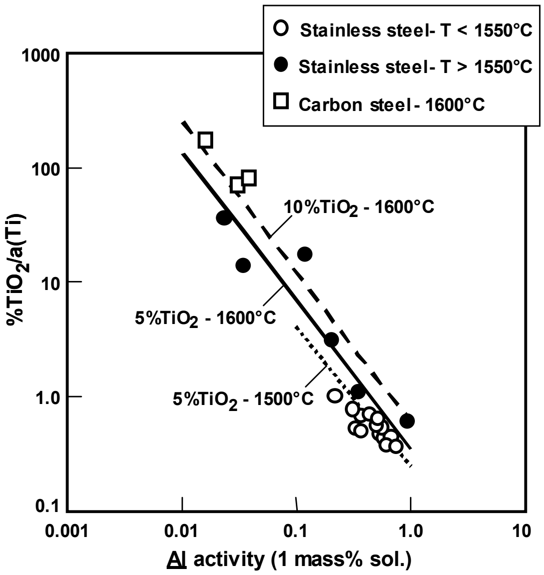

Figure 4. Comparison between Ti equilibrium distribution ratio between slag and metal computed with Irsid slag model (lines) and industrial data of vacuum ladle treatment (points).

For the first type, as well as in the last two types of experiments, the partition Ti^{3+}/Ti^{4+} has been chemically analyzed.

As for chromium, laboratory experiments show that the titanium equilibrium distribution ratio between slag and metal depends mainly on the oxygen potential, that is, in the case of Ca aluminate slags illustrated on Figure 3 [34-37], on metal Al activity. This ratio increases with decreasing $\%CaO/\%Al_2O_3$ ratio but this dependence is much more pronounced for slags with high titanium oxide content. In this figure, the steel characteristics are expressed with the Ti and Al activities, to combine information on carbon and stainless steels. For carbon steels, the activities are practically equal to the contents in weight %, whereas they are substantially different in the case of stainless steels ($a_{\underline{Al}}$ ~ 3 to 4 times %Al, and $a_{\underline{Ti}}$ ~ 7 to 8 times %Ti for the grades considered).

This tendency has been confirmed by industrial results, as shown in Figure 4, concerning ladle treatments of carbon and stainless steels [43] performed with slags having a higher CaO content than those investigated experimentally. For these ladle slags with less than 10% TiO_2, a variation of $\%CaO/\%Al_2O_3$ has relatively little effect on the distribution ratio, whereas an increase in the TiO_2 content or temperature induces an increase in the distribution ratio. On the figure, the lines represent calculations made with Irsid slag model (cf. § 3.3) 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 the industrial data for slag compositions somewhat scattered around these values. Although the titanium oxide content of the slag is expressed as $\%TiO_2$, the calculation takes into account Ti^{3+} and Ti^{4+}.

2.2 Niobium

Thermochemical data for niobium are scarcer than for chromium or titanium. The few available phase diagrams concern the valence state Nb^{5+} and only two ternary diagrams are reported in Phase Equilibria Diagrams [44], i.e. CaO-SiO_2-Nb_2O_5 and CaO-TiO_2-Nb_2O_5.

In metallurgical conditions, niobium also exists under two valence states Nb^{5+}, Nb^{4+} [45]. Among the available data on slag/metal equilibrium partition coefficients, few studies are relevant for the chemical systems of metallurgical interest:

- one on the system SiO_2-NbO_x-FeO_t-MnO-MgO [46,47],
- two on the system SiO_2-NbO_x-Al_2O_3-CaO [45,48].

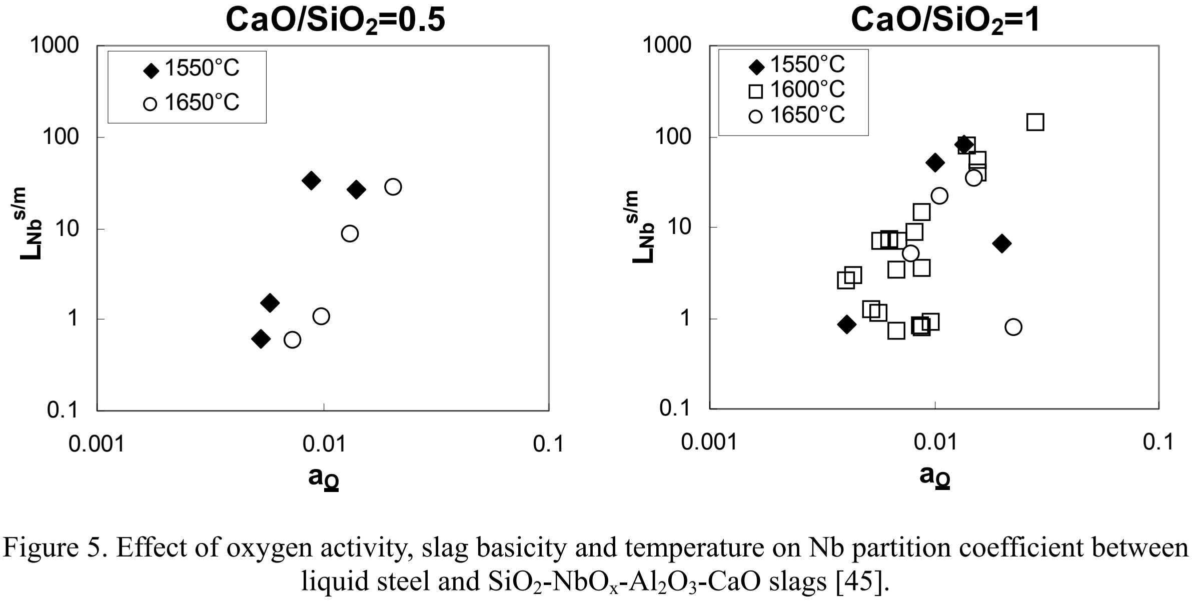

Figure 5. Effect of oxygen activity, slag basicity and temperature on Nb partition coefficient between liquid steel and SiO_2-NbO_x-Al_2O_3-CaO slags [45].

Even if they concern very limited composition range, they provide at least qualitative information on the effect of several key parameters such as oxygen activity, slag basicity and temperature. For example, the data represented on Figure 5, concerning SiO_2-NbO_x-Al_2O_3-CaO slags with Al_2O_3 contents varying between 30 and 45% [45], show quite clearly the effect of the slag basicity (its increase leads to an increase of the Nb partition ratio), but the experimental scatter prevents discerning a temperature effect

The other studies are mainly kinetic experiments on niobium removal from pig iron and cannot be used as a source of equilibrium data [49-55].

2.3 Vanadium

Very few phase diagrams are available for vanadium oxide bearing systems. In these studies, as in the case of titanium, niobium and chromium, vanadium is in its higher valence state V^{5+}. Only one binary CaO-V_2O_5 and part of a ternary Na_2O-SiO_2-V_2O_5 are reported in the Slag Atlas. Some others are proposed in Phase Diagrams for Ceramists but, for most of them, their drawing is at least partly hypothetical.

Studies on slag-metal vanadium partition have been conducted mainly to optimize vanadium extraction from hot metal.

They have been therefore performed under rather oxidizing conditions by equilibrating slags:

- with solid steel foils [56, 57],
- with liquid iron [58,59] or
- in vanadium crucibles under controlled atmosphere [60].

Vanadium valence state under these conditions remains quite controversial. According to Werme [57], three valences can be found; V^{3+}, V^{4+} and V^{5+}. The effect of addition of CaO, Na_2O, MgO, Al_2O_3 and TiO_2 in FeO_x-SiO_2 [56,57] has, for example, been investigated. Except for TiO_2, all these additions lead to a decrease of vanadium partition coefficient. Na_2O bearing slags have also been studied such as Na_2O-CaO-CaF_2-SiO_2 slags doubly saturated with CaO and $2CaO.SiO_2$ by Tsukihashi et al. [61] or Na_2O-SiO_2 slags by Werme et al. [56]. Selin [62,63] proposes a graphical representation of vanadium iso-partition coefficients for CaO-FeO_x-SiO_2 slags saturated with MgO (Figure 6). The same graphics can be used without any correction for slags containing Al_2O_3 up to 14% and TiO_2 up to 13% as long they remain saturated with magnesia.

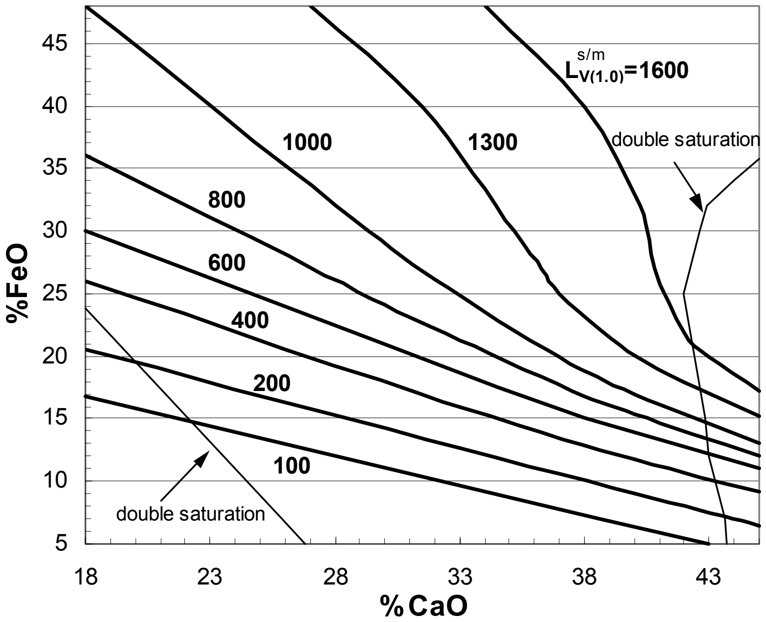

Figure 6. Equilibrium vanadium partition coefficient $L^{s/m}_{V(1.0)}$ between CaO-FeO_x-MgO_{sat}-SiO_2-1.0 wt% V slags and liquid iron at 1600°C [62]. For slags containing higher vanadium contents, use the formula: $L^{s/m}_{V} = L^{s/m}_{V(1.0)}.10^{-0.0368+0.0395.(\%V)-0.00273(\%V)^2}$

3. THERMODYNAMIC SLAG MODELS AND COMPUTER SOFTWARE

In order to be conveniently exploited and as safely as possible extrapolated, these data have been used to assess mathematical models. These models have been incorporated into computer programs in order to cope with complex metallurgical problems requiring calculations involving for example, besides the liquid slag phase, a liquid metallic phase and possibly one or several solid phases. A short review of these models is presented here along with their application range in terms of slag composition and, when available, the computer software in which they have been implemented.

3.1 Regular solution models

In these models, the activity coefficients of the oxides are developed as quadratic polynomials of the component molar fractions. For instance, expressions of the oxide activities based on this formalism are proposed for SiO_2-Fe_tO-CaO slags by Ban-ya et al. [64,65] or of the P slag/metal partition coefficient in SiO_2-P_2O_5-Fe_tO-MgO-CaO slags [66].

3.2 Sublattice models

The two sublattice model [67] for ionic solutions is an extension of the general sublattice model [68]. The liquid silicate phase is assumed to consist of two sublattices, one for the cations and one for the anions and neutral species. This model is implemented in Thermo-Calc [69], MTDATA [70] and GEMINI2 [71]. One of the most recent developments of this model proposed in Thermo-Calc is an assessment of the Ca-Fe-O-Si system [72,73]. In this assessment, both liquid metal and the CaO-FeO-Fe_2O_3-SiO_2 slag system are described with the ionic two-sublattice model, with a single set of parameters.

A new mathematical model has been developed by Björkvall [74]. It uses Temkin's description of the entropy of ionic melts coupled with Lumsden's [75] description of silicate and aluminate melts, where the ionic melts are considered as an oxygen-ion matrix with the cations distributed in it. Contrary to the two sublattice model, no neutral species is supposed to be present in the melt structure and only information from the binary subsystems is used to assess the parameters. This model has been applied to compositions in the Al_2O_3-CaO-MgO-MnO-SiO_2 system with a generally satisfactory agreement with experimental values, but also generated some disagreements which are judged as being indicative of the need for further reliable experimental information.

A model for prediction of the sulphide capacities, based on the same structure description, has also been developed at KTH [76]. The logarithm of the sulphide capacities is developed as a polynomial of the mole fractions of the different cations in the oxygen-ion matrix. It has been applied for the prediction of sulphide capacities in the "FeO"-Al_2O_3-CaO-MgO-MnO-SiO_2 slags [77,78].

Mogutnov et al. [79] 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.

3.3 Quasi-chemical models

This model category uses the quasi-chemical theory of Guggenheim [80] to take into account short range order in ionic melts. The modified quasichemical model [81] has been assessed for multicomponent systems containing different combinations of the components Al_2O_3, CaO, MgO, MnO, FeO, Na_2O, TiO_2, Ti_2O_3 and ZrO_2. This model is used in the FactSage software which results from the merger between F*A*C*T [82] and ChemSage [83]. The database for this package has been recently largely increased by critical assessment of various binary, ternary and quaternary oxide systems containing lead, zinc or chromium oxides [84-86]. In addition, the same model was used for the thermodynamic modeling of liquid Fe-Ni-Cu-Co-S [87] and Co-Fe-Ni-S [88] mattes, leading to the construction of a complete database for copper smelting and refining [89]. This database was subsequently extended for calculations in the Zn-Pb-Cu-Ca-Fe-Si-O-S system [90,91]. 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 modeling of matte and slag as one oxisulphide phase is announced as being the subject of future work.

IRSID's cell model for slags is also based on the quasi-chemical theory [92]. 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 [93]. Implementations of this model are available in Thermocalc [69] and FactSage [83] and in the non-commercially available package CEQCSI developed at IRSID. An extension of this model to the description of the oxy-sulphides model with a complete range of solubility between pure oxides and pure sulphides has also been consolidated for the system SiO_2-Al_2O_3-Fe_2O_3-FeO-MgO-MnO-CaO-S [94]. In this model, the multicomponent systems are described using only binary parameters.

3.4 Other models

Despite not being implemented in any commercial software, an adaptation of Flood and Grjotheim's model [95] gives very precise estimations of P, O, Mn and S partitions between liquid steel and basic refining slags [96,97]. It is based on the assumption of an ideal mixing of ionic species: cations Ca^{2+}, Mg^{2+}, complex anions SiO_4^{4-}, PO_4^{3-} and simple anions O^{2-}, S^{2}. Semi-empirical correlations are then used to estimate the deviation from ideality.

Some more prospective approaches, in particular based on molecular dynamics, are proposed [98-101] but, presently, their use is restricted to simple binary or ternary systems and future developments of this method for complex systems is quite uncertain.

3.5 Optical basicity

Several correlations are proposed in the literature to relate chemical properties of slags, such as sulphide or phosphate capacities, to their optical basicity, expressed as a linear combination of the optical basicity of each of its components. In Slag Atlas, one can find a review of useful relations for sulphide and phosphate capacities for oxygen, manganese, vanadium and water partition. Utochkin [102] proposes the same kind of correlation to estimate the nitride capacities in titanium bearing slags and Wall et al. [48] for the activity coefficient of niobium oxide. Recently, a user-friendly software package has been developed, with the purpose of providing an access to the Optical Basicity Databank for technological applications and for the purposes of scientific evaluation [103].

However, the user must take care when using these relations outside their validity domain. For example, it has been shown that the use of the Sosinsky and Sommerville relation to estimate sulphide capacities [104] can lead to errors up to two or three orders of magnitude when applied to MnO and/or FeO rich slags [105].

4. INDUSTRIAL APPLICATIONS

The first application presented hereafter deals with the possibility of dephosphorization of ferro-manganese alloys by slag/metal reaction. The second one illustrates the use of thermodynamic modeling to optimize Ti removal from silico-manganese alloys.

4.1 Dephosphorization of ferromanganese alloys

A majority of the experimental studies on ferromanganese dephosphorization have been performed under oxidizing conditions. In these conditions, the dephosphorization reaction can be expressed as:

$$[P] + 3/2(O^{2-}) + 5/2[O] \rightarrow (PO_4^{3-}) \tag{2}$$

where: [P] and [O] stand respectively for the phosphorus and oxygen activity in the metal,
(PO_4^{3-}) and (O^{2-}) are the PO_4^{3-} and O^{2-} activities in the slag.

The equilibrium condition between slag and metal can be conveniently written in terms of phosphorus partition coefficient $L_P = (\%P)_{slag} / [\%P]_{metal}$ and of phosphate capacity $C'_{PO_4^{3-}}$ that characterizes the slag's ability to trap the phosphates:

$$L_P = C'_{PO_4^{3-}} . f_{\underline{P}} . a_{\underline{O}}^{5/2} . \frac{M_P}{M_{PO_4^{3-}}} \tag{3}$$

where: $f_{\underline{P}}$ is the activity coefficient of phosphorus in the metal, i.e. its activity divided by its concentration expressed in wt%

M_P and $M_{PO_4^{3-}}$ are the molecular weights respectively of phosphorus and phosphate anion.

4.1.1 Effect of slag composition

Experimental studies have been mainly performed with BaO or $BaCO_3$-bearing slags and with C rich alloys for temperatures varying between 1300 and 1400°C [106-108]. They show that these slags have phosphate capacities several orders of magnitude higher than Ca-bearing slags usually used in steel refining [109-113]. With such slags, dephosphorization ratios, defined as $100 \cdot ([\%P]_{final} - [\%P]_{initial})/[\%P]_{initial}$, up to 70% can be obtained [114].

Let us note that these Ba-bearing slags have a sulfide capacity higher than Ca-bearing slags and, therefore, Mn ferro-alloys could be partly desulfurized by these slags during the dephosphorization operation.

4.1.2 Effect of ferro-alloy composition

Contrary to what happens with steels, the presence of carbon enhances ferromanganese dephosphorization (Figure 7) and limits manganese oxidation [106,107,115]. This is due to the fact that an increase of the carbon content increases the phosphorus activity coefficient while decreasing the manganese activity coefficient (Figure 8) and does not decrease the oxygen potential which is imposed by the Mn/MnO equilibrium. Since manganese increases the carbon content at graphite saturation [116-118], this beneficial effect of the carbon content could be used to enhance the dephosphorization of Mn-rich ferro-alloys.

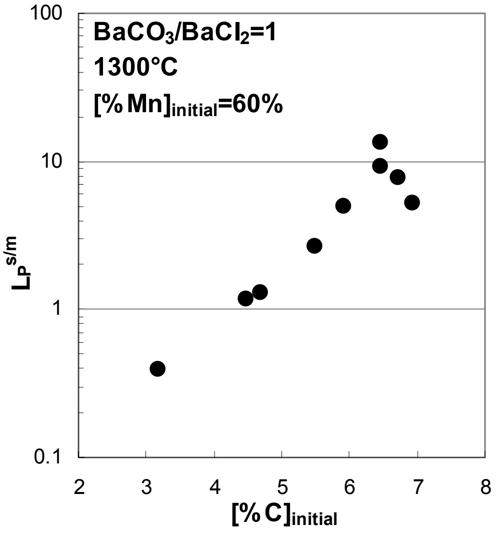

Figure 7. Effect of carbon on P slag/metal partition coefficient [119].

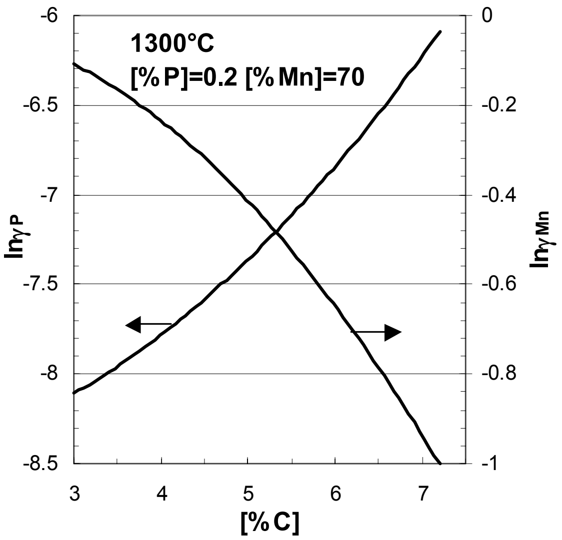

Figure 8. Effect of C on P and Mn activity coefficients [107].

Manganese also has an effect on the phosphorus activity. Schim et al. [115] have shown that the phosphorus activity coefficient decreases with increasing manganese content according to the equation:

$$\log f_P = -0.0029[\%Mn] - \frac{386}{T} + 0.891 \tag{4}$$

This detrimental effect of manganese with respect to dephosphorization remains, of course, of second order, the main effect of this element being its direct impact on the oxidizing conditions.

As with carbon, silicon increases the phosphorus activity coefficient [106,120]. However, many studies show that silicon contents lower than 0.2% are necessary for dephosphorization since higher contents will impose far too reducing conditions [106,108,114,119,120]. The silicon content of ferro-manganese alloys is generally quite large (0.7 to 1.1%) and a desiliconisation operation is therefore necessary prior to dephosphorization. Silicon removal can be performed by gaseous (O_2,CO_2) or solid (FeO_x, Mn_3O_4, $CaCO_3$) oxidizer additions [108].

4.1.3 Effect of temperature

Ahundov et al. [121] studied the effect of temperature on the Mn and P partition coefficient of a Fe-8%Mn-C_{sat} alloy in contact with a BaO-BaF_2 slag. They showed that a low temperature enhances dephosphorization but increases Mn loss in the slag. Therefore, the choice of treatment temperature will be a compromise.

4.1.4 Dephosphorization under reducing conditions

In order to avoid Mn oxidation, experimental studies have been performed on ferro-manganese dephosphorization under reducing conditions. Figure 9 gives the stability domains of the barium and calcium phosphates and phosphides as a function of the oxygen partial pressure and of the phosphorus content of the metal. One can see that, in reducing conditions as in oxidizing conditions, Ba bearing slags potentially lead to much lower final phosphorus contents that Ca bearing slags. The oxygen partial pressure corresponding to the oxidation of the manganese in the Fe-70%Mn-7%C alloy into pure solid MnO is situated well outside the phosphide domain.

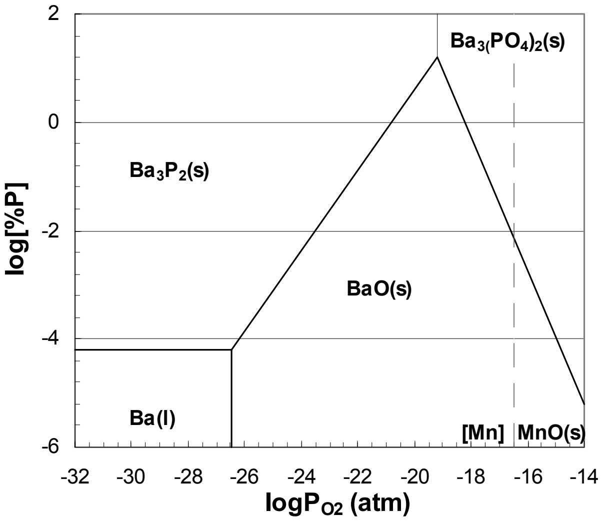

Figure 9. Stability domains of phosphates and phosphides of Ba and equilibrium between Mn oxide and Fe-70%Mn-7%C alloy at 1300°C [107].

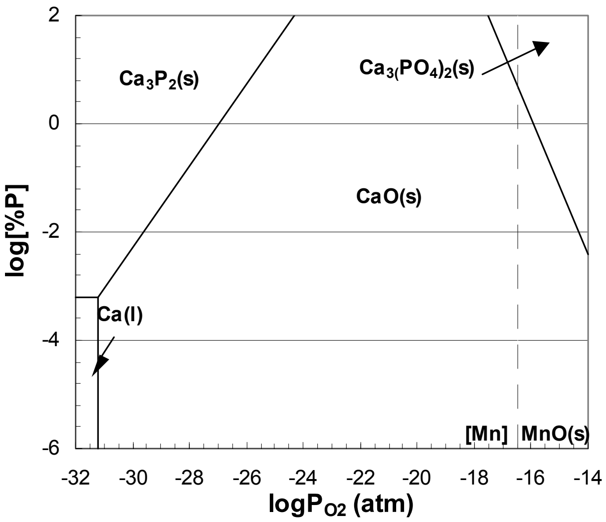

Figure 10. Stability domains of phosphates and phosphides of Ca and equilibrium between Mn oxide and a Fe-70%Mn-7%C alloy at 1300°C [107].

For example, experimental studies on dephosphorization under reducing conditions have been performed with Ca-Si-CaF_2 and CaC_2-CaF_2 slags [113,120,122,123]. Phosphorus is then removed by calcium carbide according to the reaction:

$$3CaC_2 + 2[P] \rightarrow (Ca_3P_2) + 6[C] \qquad (5)$$

Under such reducing conditions, partition coefficients of 500 could be obtained [124], compared to coefficients of less than 100 that can be obtained for dephosphorization under oxidizing conditions [114,116]. In order to be in suitable reducing conditions, aluminum or silicon should be added to the melt. Lee [116] recommends a silicon content larger than 0.6%. The dephosphorization degree decreases noticeably when the carbon content increases or when the manganese content decreases [122,125].

Under such reducing conditions, dephosphorization generates unstable phosphines (PH_3) that are transformed into toxic phosphoric acid in the presence of water [109]. At the present time, no recycling treatment has been developed, either for slag or for gas.

4.2 Titanium behavior description in silico-manganese alloys

Silico-manganese alloys used by the steel industry must meet some strict specifications concerning their maximum contents of tramp elements such as titanium. The aim of the study reported here [126] was to define process conditions in order to obtain, by titanium carbide precipitation and flotation, the lowest possible titanium content for the industrial alloys. To that purpose, a thermodynamic model of alloys had first to be developed and assessed based on laboratory experiments.

4.2.1 Thermodynamic modeling

The thermodynamic properties of the system Mn-Fe-Si-C and all the subsystems have been described by the "Central Atoms" model [127]. This model is based on a physical description of the metallic liquid structure in terms of cells. Each cell is constituted by a central atom surrounded by its nearest neighbors situated on two types of atomic sites distinguished in the structure: the substitutional and the interstitial sites. This model permits, with a small number of parameters, the precise description of the properties of the liquid phase.

As an example, Figure 11 shows the satisfactory agreement between Mn activities computed by the model and with the available experimental data on the system Mn-Si-Fe. Another example is provided by Figure 12 that compares experimental carbon and silicon carbide saturation lines and model predictions.

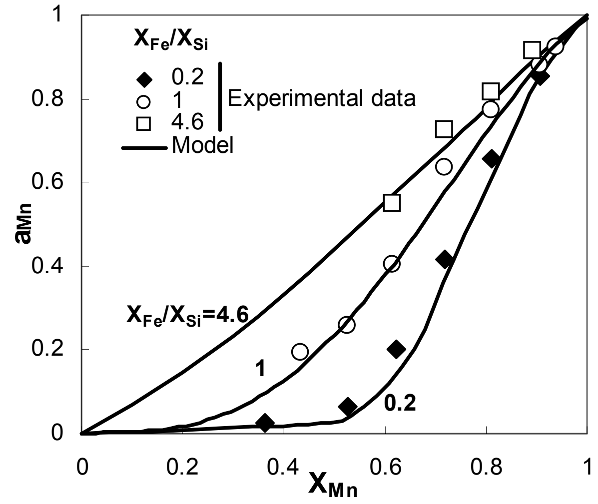

Figure 11. Mn activities in the system Mn-Si-Fe at 1700 K: literature data [128] and modeling.

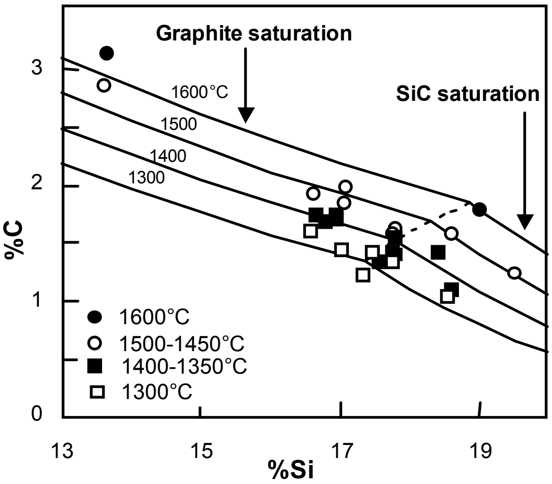

Figure 12. Graphite and SiC saturation in the liquid Mn-Si-Fe-C (10.5<[%Fe]<13.5), comparison between the "Central Atoms" model predictions and the experimental measurements [126].

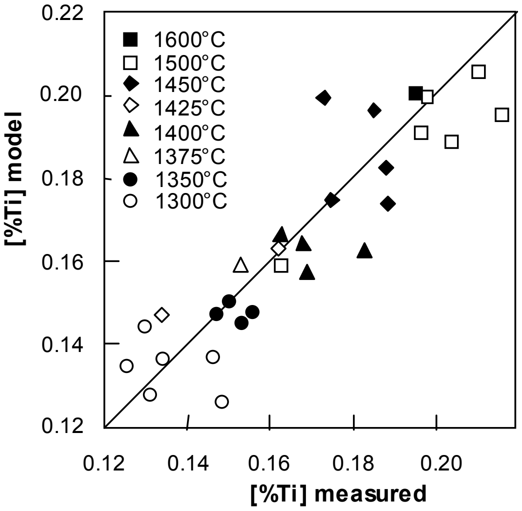

Figure 13. Ti content of the Mn-Si-12%Fe-C alloys at TiC saturation: comparison between the calculated values and the experimental results.

Due to its low content in the alloys, Ti behavior has been modeled with the 1% dilute solution formalism. Figure 13 shows that this modeling gives quite satisfactory estimations of the Ti contents at TiC saturation when compared to the laboratory results obtained on industrial alloys [126].

4.2.2 Industrial application

Analyses of industrial silico-manganese alloys are plotted on Figure 14 along with the different saturation lines (TiC/graphite and TiC/SiC) as predicted by the thermodynamic model.

This figure clearly shows the potential benefit of a flotation treatment consisting, of a soft gas stirring, in floating out the TiC particles. Even at 1600°C, TiC flotation is far from being complete and it would be possible to obtain, by a flotation treatment at 1300°C, much lower titanium contents. For instance, for a 20% Si alloy produced at 1600°C, a titanium content of 0.16% could be reached whereas an even lower content of 0.11% could be obtained for a 16% Si alloy. This flotation treatment would be more beneficial for low Si, graphite saturated alloys than for high Si, SiC saturated alloys. For these high Si alloys, a flotation treatment will cause a Si loss that could be commercially detrimental.

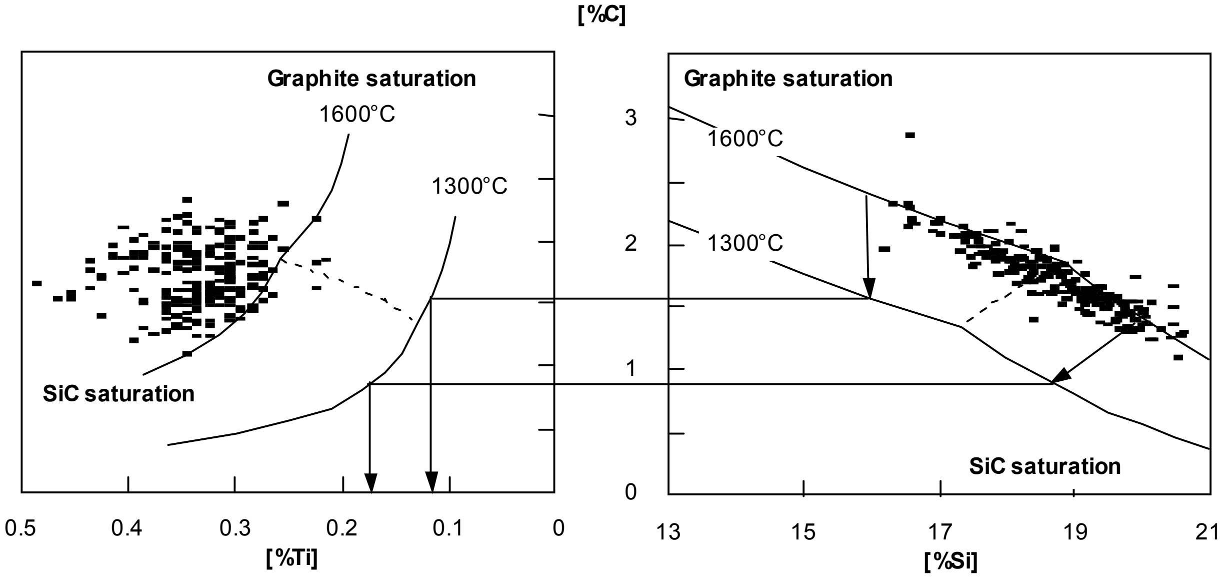

Figure 14. Equilibrium titanium contents of TiC saturated Mn-Si-12%-Fe-C alloys, effect of a flotation treatment at 1300°C on two alloys with different silicon contents smelted at 1600°C.

5. CONCLUSIONS

In the last decades, both thermodynamic modeling of slags and complex equilibrium calculation software have made decisive progress. For example, it is now possible to describe quite accurately, by using this software, the equilibrium state of most of the chemical systems of interest to the steelmaker.

As far as the ferro-alloys industry is concerned, thermodynamic modeling could also be used in numerous interesting situations, as has been illustrated in this paper with the example of Ti-removal from a manganese alloy. But, unfortunately, important gaps remain in the knowledge of the thermodynamic properties of important elements for this industry such as Nb or V. Prior to any attempt to model the behavior of such elements, the literature review in this paper shows that what is missing the most to fill this gap is experimental results.

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