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AN OVERVIEW OF THE USE OF CALPHAD METHODS IN STEELMAKING

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Abstract

A brief review of the solution models used to describe liquid steels and slags in computational thermodynamics is presented, and their main characteristics are discussed, with emphasis on their application to steelmaking and processing.

Examples of the application of currently available databases and equilibrium calculation software to industrial steelmaking problems are presented, highlighting the vast possibilities that derive from being able to rapidly and accurately determine the equilibrium state of such complex systems. Although presently there are still accuracy limitations both related to data quality and to solution model characteristics, it is concluded that the application of computational thermodynamic to steelmaking is a powerful tool in studies that will lead to better products, lower costs and more efficient processes.

Some of the present limitations of the application of the CALPHAD approach to these processes are mentioned and suggestions for further development are presented.

Keywords: CALPHAD, method, steelmaking

1. Introduction

Steelmaking has been one of the first areas in metallurgy to benefit from the systematic use of thermodynamic information. In view of the complexity both of the iron-base alloys and the non-metallic slags used for refining them, approximate methods for the treatment of thermodynamic problems in steelmaking have been developed for decades. Thus, formalisms for the treatment of dilute solutions were developed and successfully applied to various steelmaking and steel processing problems and, in some case, simple models for the treatment of specific slag systems were also developed and used with success. As competition in the materials arena has increased, so have the requirements on steel properties and consistency. Thus, a more accurate treatment of classical problems as well as tools for investigating the behavior of complex systems has become necessary. Furthermore, the constant pressure for increased efficiency in the use of resources and raw materials, the increasingly stringent environmental requirements and the need to predict the behavior of systems not yet studied has lead to the need of reliable techniques for the performance of accurate thermodynamic calculations in rather complex systems, well beyond the possibilities of simplified methods. This need can be supplied by the use of CALPHAD techniques, if sufficiently accurate models and data are available. This overview is thus centered on a) the discussion of the thermodynamic models currently used for the treatment of steelmaking and processing problems, their potential and limitations and b) the data available and required for the adequate solution of these problems. Furthermore, selected cases of application of CALPHAD techniques to the solution of steelmaking and processing problems are presented and discussed.

2. Solution Models

2.1. *Expressions for the Gibbs free Energy*

As the thermodynamic functions of a phase are related through their definitions, it is the usual practice in the CALPHAD approach to find expressions for the Gibbs free energy of the phases and derive any other property eventually required from their thermodynamic definitions.

The free energy of a pure element *i*, ${}^{o}G^{\Phi,T}_{i}$, is referred to the enthalpy of its stable state φ at 298.15K ($H^{\varphi,298.15K}_{i}$) and denoted as ${}^{o}G^{\Phi,T}_{i}$-H^{SER}_{i}. Values given in the SGTE database [1] are adopted, in general, both for the stable and metastable phases for the pure elements. This choice of reference state is particularly useful in steelmaking as it allows for enthalpy calculations and the performance of heat balances.

For solutions, the molar Gibbs energy can be described as:

$$G^{\Phi,T} - H^{SER} = ({}^{ref}G^{\Phi,T} - H^{SER}) + {}^{id}G_m^{\Phi} + {}^{E}G_m^{\Phi} \tag{1}$$

$$({}^{ref}G^{\Phi,T} - H^{SER}) = \sum_{i=1}^{n} x_i ({}^{0}G_i^{\Phi,T} - H_i^{SER}) \tag{2}$$

$${}^{id}G_m^{\Phi} = R \cdot T \cdot \sum_{i=1}^{n} x_i \ln(x_i) \tag{3}$$

where the first summation in eq. (1) represents the Gibbs energy of the pure components of the solution, ${}^{E}G^{\Phi}$ the excess Gibbs energy in the mixing process and ${}^{id}G^{\Phi}$ the entropy change in the formation of an ideal solution. The main difficulty in describing the thermodynamic properties of solutions is, evidently, in the excess term.

While the simplest formulation is the ideal solution model, in which the excess term vanishes, this seldom constitutes a good description for real steelmaking solutions. Several models have been proposed to describe the excess Gibbs energy. Some of these models, as will be discussed in the next sections, have physical-chemical backgrounds. On purely mathematical basis, the simplest way of expressing the excess Gibbs energy are Redlich-Kister [2] polynomia.

For a binary solution this model can be expressed as:

$$^{E,bin}G_m^{\Phi} = x_1 \cdot x_2 \cdot \sum_{v=0}^{n} L_{1,2}^{\Phi,v} (x_1 - x_2)^v \tag{4}$$

where the $L^v = A^v + B^v T$ are the Redlich-Kister polynomial coefficients of order v and A^v and B^v are the constants determined through the optimization process, for the phase. Extending this model to systems of higher order requires the definition of a manner of weighing the contribution of the binaries as well as the consideration of higher order interactions. The different methods of considering the contributions of the binaries have been reviewed elsewhere [3 - 5]. In all models described here Muggianu's formalism has been adopted [4]. Thus, for the case of a ternary solution, for instance:

$$^{E,bin}G_m^{\Phi} = \sum_{i=1}^{2} \sum_{j=i+1}^{3} x_i \cdot x_j \cdot \sum_{v=0}^{n} L_{i,j}^{\Phi,v} (x_i - x_j)^v \tag{5}$$

$$^{E,ter}G_m^{\Phi} = x_1 \cdot x_2 \cdot x_3 \cdot \sum_{i=1}^{3} ({}^{ter}L_i^{\Phi} \cdot x_i) \tag{6}$$

2.1. Models for the Metal Phase

2.1.1. Quadratic Formalism

Most steelmaking problems require the description of the thermodynamic behavior of a liquid, iron- rich, phase. This is normally treated as a substitutional solution. Following the CALPHAD approach, this phase would be described through the adjustment of the coefficients of the Redlich-Kister polynomial describing the excess Gibbs energy. On the other hand, following the classical treatment for this type of solution Wagner's formalism for dilute solutions would be used [6]. A large body of data has been accumulated in this form for iron rich solutions (e.g.[7]). Thus, it would be profitable to convert these data to the CALPHAD formalism. Hillert [8] proposed a method to do this, based on Darken's quadratic formalism [9]. In Darken's quadratic formalism, in addition to the temperature independent term L_0 in the Redlich-Kister polynomial (which corresponds to regular solution behavior) a term x_iN_i, depending on the solute *i* concentration was included to improve the description of dilute solutions (rich in solvent *S*). Thus, for a binary solution:

Hillert observed that this is equivalent to a new reference state for the solute *i*, where $G_i = {}^oG_i + N_i$. Thus, for a system with n solutes:

$$G_m = x_S\,{}^0G_S + x_i\,{}^0G_i + {}^{id}G_m + x_S x_i L^0_{iS} + x_i N_i \tag{7}$$

where the solvent is now indicated with the subscript 1, all the $L_{ii} = 0$, $L_{ij} = L_{ji}$, and the values of *L* and *N* can be obtained directly from the activity coefficients and interaction coefficients as derived by Hillert [8].

$$G_m = x_1\,{}^0G_1 + \sum_{i=2}^{n} x_i({}^0G_i + N_i) + {}^{id}G_m + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j L^0_{ij} \tag{8}$$

This approach makes possible the conversion of the existing data that conforms to Wagner's dilute solution formalism to the CALPHAD formalism, but does not change, evidently, the fact that the application of this data is limited to dilute solutions.

The application of this model has the advantage of providing a good description to the properties of dilute solutions. In the CALPHAD approach for thermodynamic assessments, the emphasis is, in general, in the search for simple expressions that can provide a sufficiently accurate description of the solution properties across the whole composition range of the system, without the introduction of an excessive number of adjustable terms. Thus, no special emphasis is given to the adjustment of the Gibbs energy function to the values of properties of dilute solutions when compared to the rest of the composition range. Hence, although a classic CALPHAD description of an iron-based system will provide a better description of the whole system that can be achieved with this conversion from Wagner's formalism, in the case of dilute solutions, in particular liquids, the opposite might be true. Sundman and co-workers [10] have used this approach to convert the data of Sigworth and Elliott [7] to the CALPHAD formalism, in order to describe the liquid steel in the IRSID database.

2.1.2. Compound energy model

Frequently the solid phases in metallic systems can be described in a more simple form using the compound energy formalism or sub-lattice model [11] [12] than using the substitutional solution model. This model and its properties has been extensively described and discussed elsewhere [12] [13] and its formulation will be only briefly discussed here. The main feature of this model is the assumption that instead of complete mixing of the components of a solution, mixing occurs only between constituents in the same sub-lattice. The concept was initially developed for ionic compounds, in which a cationic and an anionic sub-lattice can be identified, and was extended to several other applications, such as the modeling of phases in which both substitutional and interstitial solutes are present. Thus, in the system Fe-Nb-C, for instance, the FCC phase can be modeled as being composed of two sub-lattices, one containing, for instance, Fe and Nb and the other C and vacancies. Thus, the Gibbs energy of the FCC phase would be given as:

$$\begin{gathered} G_m^{FCC} = y_{Fe} y_{Va} \, {}^0G_{Fe}^{FCC} + y_{Nb} y_{Va} \, {}^0G_{Nb}^{FCC} + y_{Fe} y_C \, {}^0G_{FeC}^{FCC} + y_{Nb} y_C \, {}^0G_{NbC}^{FCC} + \\ RT(y_{Fe} \ln y_{Fe} + y_{Nb} \ln y_{Nb}) + RT(y_C \ln y_C + y_{Va} \ln y_{Va}) + {}^E G_m^{FCC} \end{gathered} \tag{9}$$

where the y_i are the site fraction of i in its sub-lattice. As the end-members for this solutions are compounds (hypothetical or not) this has become known as the compound energy formalism.

Modeling the Fe-S system, Fernandez Guillermet and co-workers [14] have demonstrated that, in the case of liquids in which association is expected, this model can also be successfully applied. This is expected, as it has been shown that this treatment, in this case, is mathematically equivalent to the use of an association model. [15].

A further development of this model was proposed by Hillert and co-workers [16] to treat liquid solutions with different tendencies to ionization, in what is commonly referred to as the ionic model. This model can then describe both metallic and non-metallic liquid phases, containing species of various valences, such as slags, for instance. As it description of the metal phase is equivalent to the compound energy model it will be further discussed in the section dedicated to slag models.

2.2. *Models for the Slag Phase*

The complexity of the structure of steelmaking slags has limited the development of good physico-chemical models for this phase. Thus, it is no surprise that most of the difficulties in effectively modeling the thermodynamic of steelmaking systems centers on adequate descriptions of the thermodynamic functions of these phases.

2.2.1. Ban-ya's regular solution model

Ban-ya [17] has proposed modeling silicate-rich liquids as if the species present were the constituent oxides, and then applying Darken's quadratic formalism.

Recalling that, for a regular solution:

and thus:

Ban-ya proposed the following general equation for the partial molar Gibbs energy of mixing, including the hypothetical change of reference state:

$${}^{E,bin}G^{\Phi} = x_1 \cdot x_2 \cdot L^{\Phi,0}_{1,2} \tag{10}$$

$${}^{E,bin}\overline{G}_1 = {}^{E,bin}\overline{H}_1 = RT\ln\gamma_1 = L^{\Phi,0}_{1,2}(1-x_2)^2 \tag{11}$$

$${}^{E}\overline{G}_i = RT\ln\gamma_i = \sum_j L^0_{i,j}x_j^{\,2} + \sum_j\sum_k (L^0_{i,j} + L^0_{i,k} - L^0_{j,k})x_j x_k + {}^{0,RS}G_i \tag{12}$$

where the constituents (*i*, *j*, *k*) are the oxides making up the slag (SiO_2, Al_2O_3, CaO, *etc*.). In Ban-ya's interpretation, the interaction coefficients L_{ij} reflect the energy of a cell i-O-j in the slag and thus the interaction between cations in the slag. As the model considers the actual oxides as species of the slag, this interpretation is not exactly valid from a physical-chemical point of view. The mixing entropy in this model, for instance, considers only the mixing between oxides and not between these "cells". The optimized values for the L_{ij} as well as for the $^{0,RS}G_i$ can be found in [17] [18].

Although this model has been shown to satisfactorily describe some steelmaking systems [17] [19] it gives a poor description of the behavior of several systems, such as $CaO\text{-}SiO_2\text{-}Al_2O_3$, one of the most important systems for the study of steelmaking slags [20].

2.2.2. The Cell Model

The cell model of slags has been proposed by several authors, in special by Kapoor and Frohberg [21]. Gaye and co-workers at the IRSID [22] have extended these physical-chemical concepts to the application in a multicomponent oxide system and, more recently to mixtures containing sulfur and fluorine [23].

In this model the existence of an anionic vacancy-free sub-lattice occupied by the oxygen ions and a cationic sub-lattice occupied by the cations according to the order of their decreasing electrical charge is assumed. Furthermore, to allow the representation of “cationic entities” such as $(PO)^{3+}$ the presence of cations “bonded” to oxygen atoms has been postulated [23]. This structure is then used to achieve a mathematical description of the system using the quasi-chemical model [21] [24], assuming that cells consisting of a central anion and two cations (or cationic entities) are formed. Thus, the presence of both symmetric cells of the type i-O-i (such as Si-O-Si, representing silica) and asymmetric cells of the type i-O-j (such as Ca-O-Si that represents the interaction of Ca^{+2} with silica) in the slag is assumed. These cells have well defined cell formation and interaction energies.

The model parameters are subjected to several constrains. Thus, the energy for the formation of an asymmetric cell from the symmetric cells (pure oxides in the case of the O anion) is given by:

Cell interaction is considered in two ways. First, the interaction

i-O-i + j-O-j = 2 i-O-j $\Delta E = 2W_{ij}$
e.g. Ca-O-Ca + Si-O-Si= 2 Ca-O-Si $\Delta E = 2W_{Ca\text{-}Si}$

between like cells is considered to be incorporated in their energy of formation. For unlike cells, the interactions between cells is given by parameters $E_{ij\text{-}kl}$ (representing the interaction between i-O-j and k-O-l cells), subjected to the following two constrains:

Thus, for instance:

$$E_{CaCa\text{ - }SiSi} = 2\ E_{CaSi\text{ - }SiSi} \text{ (represented as } E_{CaSi})$$

$$E_{jj\text{ - }ii} = 2\ E_{ij\text{ - }ii} \text{ (represented as } E_{ij})$$

$$E_{ij\text{ - }kk} = E_{ik\text{ - }kk} + E_{jk\text{ - }kk}$$

indicates that:

$$E_{(Ca\text{-}O\text{-}Ca\text{-}Si\text{-}O\text{-}Si)} = 2\ E_{(Ca\text{-}O\text{-}Si\text{- }Si\text{-}O\text{-}Si)}$$

and the interaction energy between a Ca-O-Si and a Mg-O-Mg cell can be calculated as:

$$E_{CaSi\text{ - }MgMg} = E_{CaMg\text{ - }MgMg} + E_{SiMg\text{ - }MgMg}$$

Gaye [22] [23] proposes that the most stable configuration of the system can be determined using the formalism of statistical thermodynamics. A very elegant alternative approach has been put forward by Sundman [10], in which every possible cells is considered a specie in a substitutional solution following the CALPHAD approach. Thus the formation and interaction energies are directly converted into the coefficients for the Redlich-Kister-Muggiannu description of the substitutional solution. In this way, one obtains the Gibbs energies of the end member of the slag as well as the coefficients for the Redlich-Kister polynomial from the coefficients adjusted by Gaye.

2.2.3. The "Ionic" Model

Hillert and co-workers [16] proposed an extension of the two sub-lattice (presently referred to as the compound energy model) in which the valences of the different components does not have to be treated as constant. This is achieved through the introduction of charged vacancies and neutral components. Thus, for a phase with cations C, anions A and neutral species B, a two sub-lattice model may be written as:

Subjected to the following constrains to guarantee electrical neutrality.

Hence, the description of, for instance, the liquid phase in the Fe-O

$$(C_i^{v_i})_P(A_i^{v_i},Va^{-Q},B_i^0)_Q \tag{13}$$

system, can extend from a completely neutral, metallic solution to an ionic

$$P=\sum_i(-v_i y_{A_i})+Qy_{Va} \tag{14}$$

$$Q=\sum_i v_i y_{C_i} \tag{15}$$

oxide melt, using the following model:

Some systems of interest to steelmaking have been well described using this formalism [25] [26] but some limitations exist. First, as the com-

$$(Fe^{+2})_P(O^{-2},Va^{-Q},FeO_{0.5}^0)_Q \tag{16}$$

plexity of the slag systems increase, either new components must be introduced in the sub-lattices, or the contribution of certain elements must be included in a different sub-lattice and additional coefficients must be introduced [27] [26]. This limits the possibility of extension of the presently available assessment to higher order systems, unless a complete reassessment is performed every time. Second, an perhaps more important from the application point of view, a limited number of systems has been assessed using this model, limiting the extent of its application to steelmaking problems, as assessments that describe the liquid as a substitutional phase cannot always be directly combined with those obtained using the ionic model. The mathematical description of the model can be found in [16].

2.2.4. The quasichemical model

In order to take in account the deviation from random mixing that occurs when there is interaction between the components of a mixture, Guggenheim [28] proposed the quasi-chemical model for short – range ordering, that was later modified by Pelton and Blander [29] [30]. In this model the Gibbs energy associated to the formation of nearest neighbor pairs is formulated as:

Then the molar enthalpy and the excess entropy of mixing are assumed to be directly related to the number of (*i-j*) pairs, so that if *X* are the frac-

$$(i\text{-}i)+(j\text{-}j)=2(i\text{-}j) \qquad\qquad \Delta G_m = (\omega - \eta T)$$

tions of species or pairs in the solution and *Z* are the coordination numbers of *i* and *j*:

In contrast to the cell model, the configurational entropy is not assumed as ideal, but can be described using a one dimensional Ising model

$$\Delta H_m - T\Delta S^{E(non-conf)} = (Z_i X_i + Z_j X_j) X_{i-j} \frac{(\omega - \eta T)}{4} \qquad (17)$$

as discussed elsewhere [31]. Pelton has demonstrated that this model can be describe several slag systems requiring a limited number of parameters. The results published by Pelton and co-workers indicate a good adjustment to the experimental data with few parameters. Furthermore, it is claimed that the extension from low to higher order systems in several cases will not require ternary or quaternary parameters [32]. Among the softwares available for equilibrium calculation, presently only F*A*C*T is prepared to handle that model. One particular limitation in this respect is that the parameters adjusted by Pelton and co-workers are not accessible to the user who would like to adjust or improve the description of a given system.

3. Examples of applications to Steelmaking and Processing

3.1. *Oxygen behavior in liquid iron*

Oxygen is probably the most important solute in steelmaking. Not only is oxygen the main refining agent in the steelmaking process but also its subsequent control is of paramount importance to guarantee workability and achieve adequate cleanliness. Thus, the ability to properly describe the behavior of Fe-O solutions is critical. A comparison of the gas-metal equilibrium calculated using different models is presented in Fig. 1. It is apparent that the results calculated using the IRSID model, based on the data of Sigworth and Elliott [7] for liquid steel agree well with those obtained using the values recommended by the Japanese Committee on Steelmaking of JSPS [33], as expected. There is some discrepancy between these values and those calculated using the ionic model [25]. One of the reasons for the discrepancy is the CALPHAD emphasis in finding descriptions that adequately fit the thermodynamic data over the whole system with a minimum number of adjustable coefficients. It is apparent that, in the case of steels and other industrial alloys, descriptions that give a better fit in the composition range of interest (e.g. diluted solutions) might be desirable in order to improve the ability of performing meaningful predictions using the CALPHAD methodology.

3.2. *Non-metallic inclusion engineering*

Non metallic inclusions have a pronounced effect on the properties and the processing ability of steels. While primary inclusions (those formed before the beginning of solidification) can, in principle, be removed, secondary inclusions that precipitate after solidification starts can only be tailored in order to control their effects. Furthermore, even if it is expected that no primary inclusion will find its way into the product, they still must be controlled as their composition and size will influence the ease of their removal as well as processing conditions (since they may cause valve clogging, for instance).

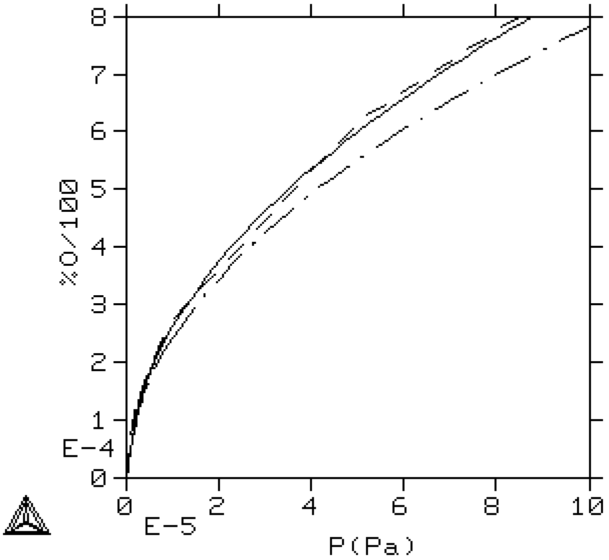

Fig. 1. Calculated oxygen dissolved in iron in equilibrium with oxygen gas. IRSID model (Solid line), ionic model [25] (dash-dot line), values recommended by [33] (dashed line). See text for discussion.

Currently the design of steelmaking processes in order to tailor the non-metallic inclusions to achieve the desired properties has evolved into a well developed science in which computational thermodynamics is finding increasing application [20] as the examples below will demonstrate.

3.2.1. Oxide Metallurgy

As near net-shape continuous casting processes reach maturity, the need for techniques of microstructural control that do not rely heavily on thermomechanical processing increases. One possible route to achieve this goal is through the controlled formation of non-metallic inclusions, as has been first demonstrated in welding (e.g.[34] [35]). One strategy that has been proposed is the production of a fine dispersion of oxides with high solubility for manganese sulfide [36] [37]. According to this concept, these oxides act as nucleii for the sulfides. The subsequent sulfide precipitation produces a depletion in manganese of the surrounding austenite enhancing ferrite nucleation. Thus it is important to know which oxides have higher solubility for sulfides, in order to design the deoxidation process correctly. Fig. 2 presents the calculated MnO-SiO_2 phase diagram as well as the calculated sulfur capacity of the liquid in this system. It is evident that the higher manganese sulfide precipitation observed by [38] [39] correspond to the compositions of calculated high sulfur capacity, indicating the potential of using CALPHAD techniques in the design of more complex oxides.

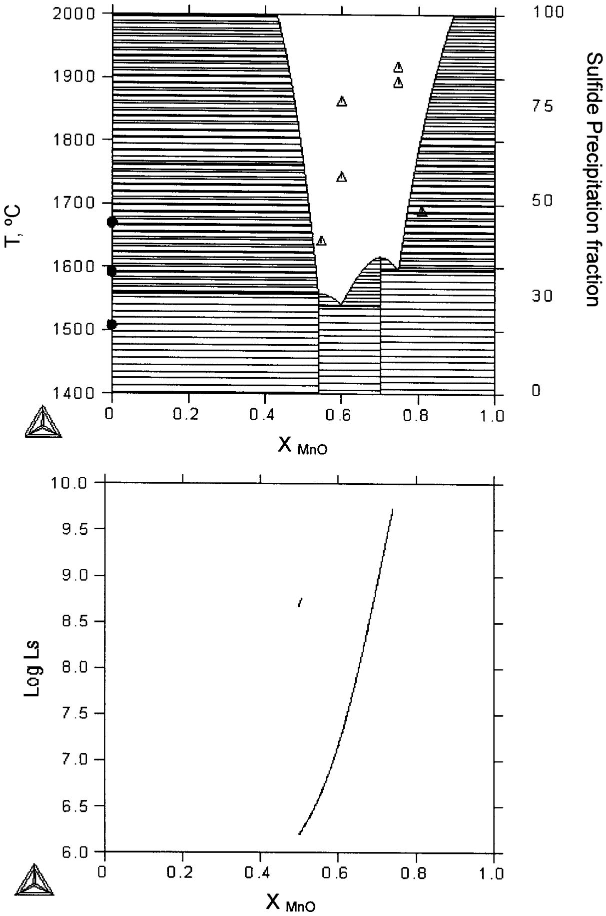

Fig. 2. Calculated SiO_2-MnO phase diagram and sulfide capacity in the liquid, compared with the measured MnS precipitation ratio reported by [38] [39]. See text for discussion.

3.2.2. Inclusions in Wires

The prevention of the formation of hard alumina inclusions is important in several cases. During the continuous casting of steel, for instance, alumina inclusions can cause valve clogging and prevent the successful casting of clean steel. One of the remedies in this case is the addition of calcium in order to form molten calcium aluminates instead of alumina as deoxidation products. The use of computational thermodynamics to define the correct calcium addition has been demonstrated elsewhere (e.g. [20]). In the case of long products, alumina can also be a significant problem, either causing the rupture of the wire during working (e.g. tire cord steel [40] [41]) or reducing the fatigue life of the parts (e.g. springs [42]) produced from this wire. In the case of valve spring steel (AISI 9254) Oshiro and co-workers [42] have presented results of the adjusted steel composition for the prevention of the occurrence of hard, high melting inclusions. Evidently, aluminum cannot be used as a deoxidant in this case. The strategy proposed in [43] and [41] can be applied to design the ladle processing of this steel. Thus, the composition required to prevent the formation of high melting inclusions in the CaO-SiO_2-Al_2O_3-MnO system at temperatures close to the start of solidification for this steel can be calculated using, for instance, the IRSID- cell model, as shown in Fig. 3. Then, the slag composition required to control the steel composition to this level of aluminum and oxygen can be calculated using the same models, at the temperature of ladle furnace treatment. Alumina is present in the ladle slag mostly from contamination from previous heats. This way, the maximum alumina content acceptable in the slag for a given basicity can be calculated, and the slag adjusted to guarantee the correct steel composition. In this case the results show that the ladle slag basicity should not deviate too much from $CaO/SiO_2=1$ for reasonable Al_2O_3 contents, in agreement with the reports of [43] [40]. The use of the CALPHAD approach in this case can significantly reduce the number of experimental heats required to reach a satisfactory wire quality.

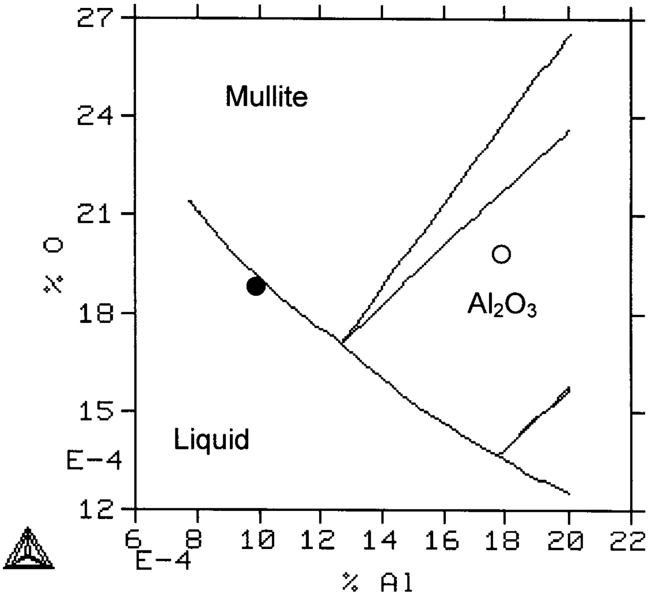

Fig. 3. Calculated non-metallic phases in equilibrium with steel containing 0.5%C, 1.5%Si, 0.7%Cr, 0.7%Mn at 1520°C. Experimental points are from Oshiro and co-workers [42] (○ - regular steel, Si-Mn deoxidized, ● - improved ladle slag deoxidation for better fatigue resistance). See text for discussion.

3.3. Silicon-aluminum equilibrium in Al-killed steels

Silicon is frequently undesirable in flat products for forming operations. These steels are, in general, deoxidized with aluminum. When deoxidation is performed together with ladle metallurgy operations in which slag-metal equilibrium is favored, one problem to be considered is silicon reversion form the silica in the slag. As silica is present in the ladle slag due either to converter slag carry over or incomplete converter slag removal from ladle, it is important to know the silicon distribution between metal and slags in the system MgO-CaO-$Si0_2$-Al_20_3. Figure 4 presents results of calculations performed using the IRSID- cell model for CaO saturated slags containing up to 5% $Si0_2$, compared with experimental results obtained at 1580°C in a ladle furnace [44]. The calculated values are a good indication of the actual ($Si0_2$)/Si equilibrium under these conditions.

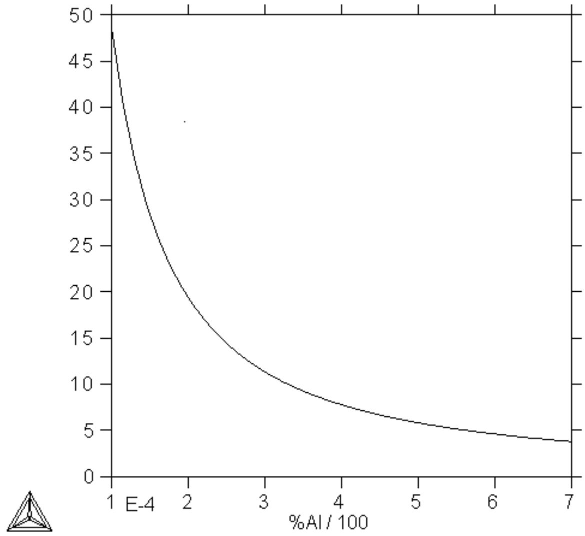

Fig. 4. The ratio % SiO_2%Si for lime saturated slags in the CaO- Al_2O_3- SiO_2 system in equilibrium with steel, as a function of aluminum content of steel. Slags with % SiO_2< 5%. Experimental points from [44]

3.4. Slag-Refractory Interaction

3.4.1. MgO solubility in converter slag

The saturation of steelmaking converter slags in MgO is important to avoid refractory dissolution and thus extend the lining life. The addition of MgO must be controlled, however, as it contributes to the increase of process costs and reduces the defosforization power of the slag, when compared to CaO [45] [46]. As converter slags are complex systems, several attempts at developing statistical correlations between slag composition, temperature and MgO solubility have been performed [47] [48] with different degrees of success. In general, the application of these formulas is limited to the range of compositions and temperatures used in the statistical treatment. An alternative approach is the use of computational thermodynamics to calculate, for a given slag composition and tap temperature if the slag is saturated in MgO or not, what is the fraction of undissolved MgO and what would be the liquidus temperature of the slag. These calculations can be performed either as part of a predictive model, i.e., together with the static model calculations before the heat, or as an adaptive calculation, performed as soon as the actual slag analysis after the heat is available. One significant improvement in this respect is the introduction of the TQ Interface [49] that enables the coupling of the most usual equilibrium calculation softwares (such as Thermocalc and Solgasmix) with codes developed in other languages such as FORTRAN. This development makes it possible for the process control softwares in the steel plant to include precise equilibrium calculations and take actions based on these results. As an example, Fig. 5 presents the results of the evaluation of MgO saturation in slags obtained during three days of operation of a commercial melt shop. Presently, this melt shop is developing a control model to adjust dolomitic lime and lime additions in order to reach MgO saturation at minimum cost, using this type of calculations.

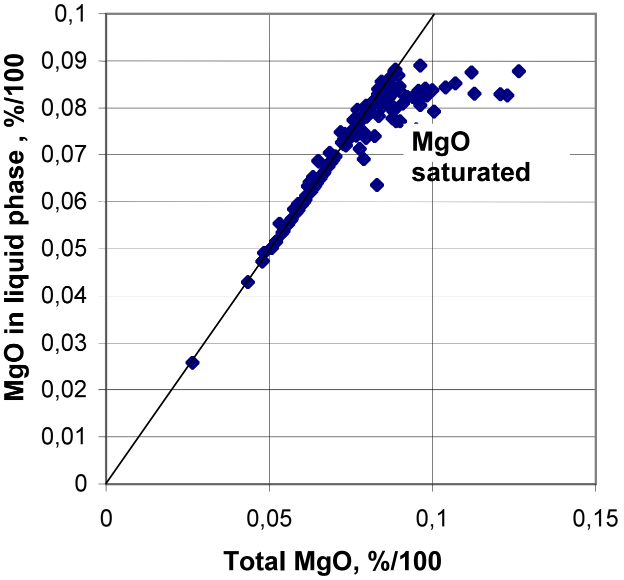

Fig. 5. MgO content in liquid phase as a function of MgO content of steelmaking converter slags. The region to the right of the line indicates saturation in MgO. Slag compositions on the line are not saturated in MgO. Slag compositions to the left of the line are saturated in another phase (e.g. calcium silicate). See text for discussion.

3.4.2. Ladle Furnace slag

Ladle furnace slags has to fulfill several requirements. Not only a high sulfur capacity and low activity of the deoxidation products is required, but interactions with the ladle refractories must be minimized. The ability to describe the desulfurizing capacity of slags using the IRSID model is discussed in another section and in other publications [20]. Two aspects of slag interaction with ladle refractories must be considered: a) saturation in the constituent oxides of the slag line refractories (dolomite or magnesite) is desired, to minimize chemical attack; b) furthermore, it might be desirable to avoid the presence of liquid slag on the bottom of the ladle after pouring, in special when the ladle bottom refractories are not basic. Lee and co-workers [50] have developed a proprietary slag model and one of its applications has been the calculation of ladle slag behavior on cooling. Similar calculations using the IRSID model give the equilibrium constitution of a ladle slag as a function of temperature (Fig. 6.). The fractions of MgO and CaO present at the refining temperature as well as the liquid fraction to be expected as the slag cools in the bottom of the ladle after the heat is cast can be determined. This information allow the slag composition to be adjusted to optimize both refining conditions and compatibility with the refractories.

3.5. Ladle Desulfurization

One of the most important ladle metallurgy operations is sulfur removal. In this case adequate control of the oxygen potential and desulfurizing power of the slag are essential.

The selection of slags for desulfurization is frequently based on a trial and error method, using available data from the literature, not always complete. Furthermore, the ability to deoxidize and the possibility of sulfur reversion are factors that must also be considered when selecting a slag. A thermodynamic model can be useful in this stage, to guide the slag selection process as well as the analysis of trial results. Fig. 7. presents partition ratios reported by Turkdogan [44] for slags saturated in lime. Turkdogan's slag analysis reach 30% SiO_2, which is not compatible with lime saturation in accordance with the applicable phase diagram [51]. When using the IRSID model, calculated partition ratios in agreement with Turkdogan's results could be reached using 40% Al_2O_3 in the slag - the alumina saturation limit in the CaO-Al_2O_3 system - as demonstrated in Fig. 7.

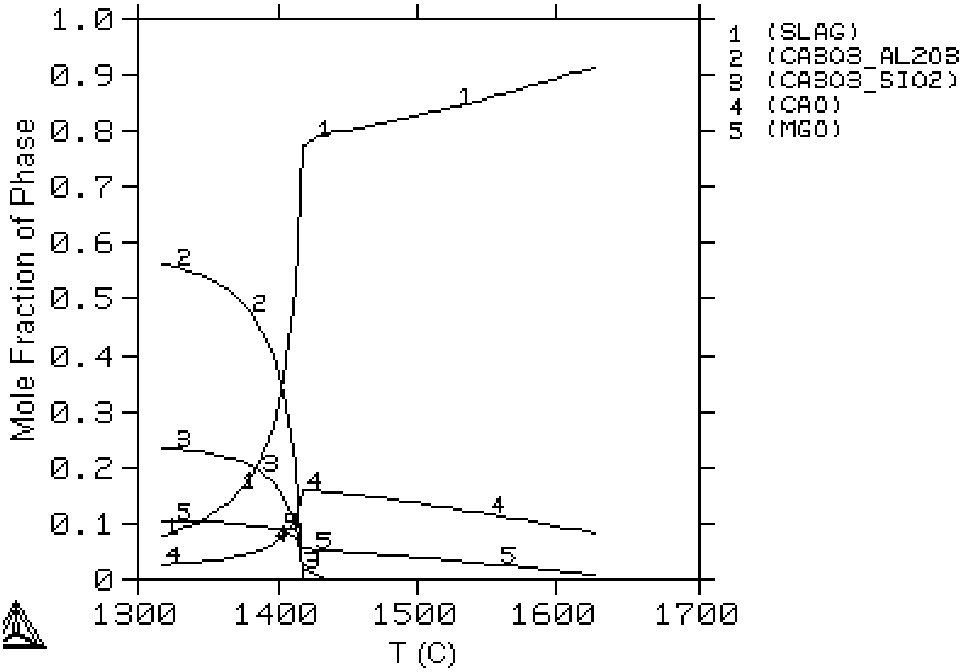

Fig. 6. Calculated evolution of mole fraction of phases present upon equilibrium cooling of a ladle slag containing 60% CaO, 7% MgO, 6%SiO_2, 25%Al_2O_3 and 1.5% FeO. See text for discussion.

3.6. Solute Redistribution during Solidification

Segregation is one of the most relevant sources of heterogeneity and defects in steel products produced either by static or continuous casting. The last decades have seen considerable progress in the modeling of the thermal phenomena associated with solidification and some attempts at describing segregation (e.g. [52] [53] [54] [54]). These models, rely mostly on simple empirical relations to describe solute redistribution, however. Only recently have more complex thermal models started to be coupled with CALPHAD

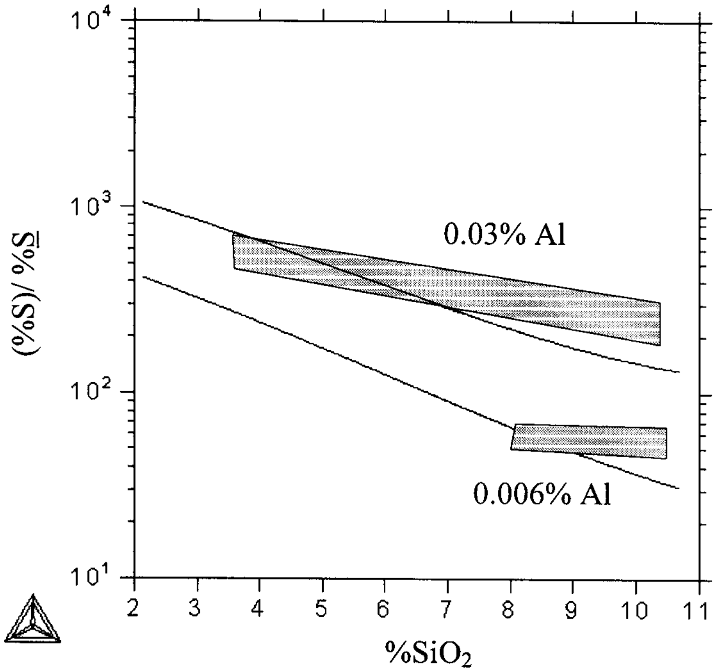

Fig. 7. *Calculated (%S)/%S for CaO- Al_2O_3- SiO_2 slags with 40%Al_2O_3, as a function of silica content in slag. Steel contains 0.03 or 0.006%Al a 1600°C. Experimental data from [44].*

type thermodynamic descriptions of the liquid and solid phases in order to make possible the accurate calculation of solute redistribution (e.g. [55] [56] [57]). When more than one solute segregates, presuming additive effects is not always a reasonable option and the use of computational thermodynamics is required. Fig. 8 presents the expected solute redistribution for an experimental steel composition in unidirectional solidification assuming a) that carbon redistributes under equilibrium and b) all other solutes follow Scheil's model, i.e. perfect homogenization in the liquid and no diffusion in the solid. In this case, the liquid was modeled as a substitutional solution while the solid phases (both FCC and BCC) where considered to be substitutional solutions, except for carbon, that was modeled as dissolving interstitially. The solid phases are then treated as having two sub-lattices: BCC-Fe is modeled as (Fe,Mn,B,P,Ti)1(C)3 and FCC-Fe as (Fe,Mn,B,P,Ti)1(C)1 and the data of [10] and [58] is adopted. Interestingly, when the solute redistribution is calculated in all relevant binaries, a much lower degree of segregation is observed, that could not account for the results observed in practice (see also [59]). Unfortunately, the precipitation of secondary inclusions as well as carbides and nitrides could not be satisfactorily included in this simulation due to the lack of accurate assessed data compatible with the databases used, albeit there are examples in the literature of satisfactory performance of similar calculations [60]. It is particularly interesting to observe that most reliable assessments of the Fe-Mn-S system have been made using either the sub-lattice or the ionic liquid description [61] [14] [62]. Thus, coupling this information with the Gibbs energy description used for the other elements in the liquid (normally simple substitutional solution models), has to be performed with care, when at all possible. Evidently, a solution for this limitation is of paramount importance for the more extensive and successful application of the CALPHAD method to steelmaking problems [63].

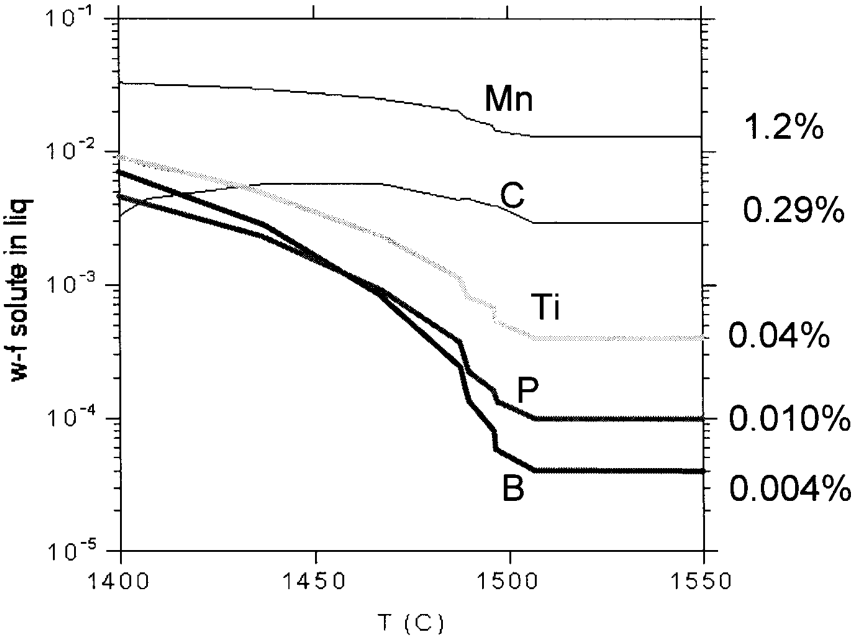

Fig. 8. Calculated solute redistribution for an experimental steel composition in unidirectional solidification assuming a) that carbon redistributes under equilibrium and b) all other solutes follow Scheil's model. See text for discussion.

4. Conclusions

Modern steelmaking and steel processing are industrial fields where thermodynamic calculations are extremely important for process and product development and control. Presently, the classical methods of calculation can be replaced by the use of the CALPHAD approach of computational thermodynamics with great advantage in several areas as hopefully was demonstrated in this overview. Perhaps one of the greatest advantages of this is the renewed interest in the application of thermodynamics to the most complex areas of steelmaking and processing, as the use of computational techniques makes this less cumbersome and hopefully more accurate. However, several challenges remain if the application of the CALPHAD is to gain complete acceptance in this area. Some of the more important are:

a) Current thermodynamic equilibrium software cannot handle different species in different phases. This can make slag metal equilibrium computations cumbersome. Either this is taken care with an interface or a user-written code or the software must evolve to allow the use of the most convenient species in each of the relevant phases.

b) Data in some important slag systems is still missing. There is still controversy over the melting point of CaO, for instance, and no database has a good description of fluorine containing slags.

c) A large number of the applications in steelmaking presently require good knowledge of the behavior of dilute solutions. Steel systems will benefit from better descriptions in the dilute range, even if, at the present state, this would somehow sacrifice the across-the-range description of the system as recommended in the classical CALPHAD approach. In the future, descriptions that are accurate enough both in the dilute and overall range will hopefully be achieved.

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