A Discussion on Thermodynamics of Pyrometallurgy for Ferroalloys

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Abstracts

To solve the problem about the component activities in multi-component alloys and molten slags, it must rely on the way of melt models. The basic characteristic of SELF-SReM model is introduced in this paper. It intends to give out the systematical value of component activities in the whole homogeneous region of multi-component melt, and then to provide a reliable data base of component activities for the thermodynamic prediction during the processes of technological development. For molten slags, it is considered that the key is to distinguish the curve accuracy of the binaries. The fundamental way for this task is getting through the microscopic bond structure and macroscopic reaction activity; relying upon, on one hand, the measurement by use of high temperature Raman Spectroscopy, on the other hand, the calculation according to MD and QC.

1. Introduction

Ferroalloy is an indispensable raw material for iron and steel production. Usually, the productivity of ferroalloy is about 3% of that of the iron and steel production. The ferroalloy production pursues that how to obtain high quality products with a consumption of the raw materials and energy, which is as low as possible. For this purpose, it is necessary to get a deep understanding on many aspects as the thermodynamics, the kinetics, the heat and mass transferring and the equipment of the ferroalloy smelting processes. Especially, among them a thermodynamic prediction quantitatively is a quite urgent demand in controlling the process and in developing the technology.

The characteristics of this thermodynamic research different from that associating with the iron and steel making processes are two items. The first regards the component activities of the molten alloy and slag. It is indeed, because these are concentrated alloys containing multicomponents. And the associated multicomponent slag is a typical reduction one. In which the component intended to extract is just of quite low content. The second regards the reaction. These are reactions mainly happening among several phases. And they are complex reactions, some of them proceed parallel. and in other case, the products of one reaction may become the agent of the another.

So far, the investigation on the thermodynamics under these complex conditions is quite poor. This situation forced the producer still rely on his experiences to control the production of many kinds of ferroalloy. And the production technology is hindered from further development.

2. Component Activities of Molten Ferroalloy

The problem about component activities of the ferroalloy is one of the central projects in the investigation of thermodynamics. Certainly, it is full possible to apply the principle of thermodynamics for either the developing of the technology or the optimization of the process. Nevertheless, one always faces an embarrassing case, as no suitable data of component activities to carry out the quantitative prediction.

As tradition, running experiment is the sole way to get the data of component activities on several points and curves. To establish a data base covering the whole homogeneous region only depends upon running experiment, however, is a task very difficult to perform. Even for a system which is of multicomponent in high content, to run the task needs a very good financial support in a quite long period. This is frequently not practicable. Meanwhile, making the experiment results to be reliable for the mentioned system is difficult, indispensable errors usually leads to some arguments. Further more, the thermodynamic parameters of some process are still impossible to acquire through measuring. As a practical and reasonable way, the systematic information of component activities covering the entire homogeneous region have to be provided by means of a model, and the prediction of the model on some points and curves should be in a good agreement with relative experimental results.

Concerning dilute alloy as most kinds of steel, the model was matured. That is the familiar approach known as activity interaction coefficients. But this model is no way to use if the system is of multicomponent and concentrated. Therefore, one turned to look for the way from solution models. In thermodynamics, the solution models including regular model, sub-regular model, geometric model and empirical model all base on some kinds of supposition about the micro configuration of the solution to quantitatively predict the variation of the thermodynamic properties following the change of composition.

2.1. Regular Solution Model and Sub-regular Solution Model

The regular solution model was first suggested by Hildbrand[1] in 1927. This concept, as he indicated, is such a solution when combine two kinds of particles to form a solution, the inner energies of 1-1, 1-2, 2-2 are not the same, but the interaction among particles can be neglected and so these particles are in a random distributed state. The phenomenological definition of regular solution is that the excess enthalpy of it, $\Delta H^E \neq 0$, and the excess entropy of it, $\Delta S^E = 0$. Coincide with these characteristics, the following quadratic relation can be proved in statistical thermodynamics.

$$\Delta G^E = AX_1X_2 \qquad (1)$$

here, the parameter A reflects the variation of inner energy when the solution is formed.

Even though only a little kinds of practical solution can be described accurately by means of the regular solution model, so far it still gain attention, because it is so clear and simple in physics. Based on it a lot of new models were developed through the modification of it. The sub-regular solution model[2] is one of them.

In sub-regular solution model, not only the relation between neighboring particles are considered but also the relation among next neighboring particles are taken into account. For the 1-2 binary system, the model gives

$$\Delta G^E = A_1X_1X_2 + A_2X_1^2X_2 + A_3X_1X_2^2 + A_4X_1^2X_2^2 + \cdots \qquad (2)$$

A_1, A_2, A_3, A_4 denote respectively the relation of the pairs of 1-2, 1-1-2, 1-2-2 and 1-1-2-2. Obviously, the description of the properties of an actual metallurgical solution based on sub-regular model is quite better than that based on regular model.

The sub-regular solution model is just a special case of central atom model[3]. According to central atom model, the micro configuration of the solution is some clusters. Every atom is a central atom and at the same time it is the coordinated atom of other central atom. If the bonding energy among a central atom and its coordinated atoms obeys the linearly additive rule, in this case Lupis indicates the central atom model degenerates into sub-regular solution model.

2.2. The Modification of Interaction Parameter Method

In order to calculate the activities of solutes in dilute solution, Wagner proposed the interaction ε–coefficients. This is the first order coefficient. The second order coefficient so called as ρ–coefficients were adopted as a modification of the Wagner's approach by Lupis and Elliot[4]. According to Lupis and Elliot, in a dilute solution with m components, the activity coefficients is

$$\ln\gamma_i = \ln\gamma_i^0 + \sum_{j=2}^{m}\varepsilon_i^j X_j + \sum_{j=2}^{m}\rho_i^j X_j^2 + \sum_{j=2}^{m-1}\sum_{k>j}^{m}\rho_i^{j,k} X_j X_k + R(3) \qquad (3)$$

Where, R(3) is the residual item of the expansion of Taylor Series. For infinite dilute solution, R(3) approaches to zero. Notwithstanding, following the increase of m, R(3) becomes larger and larger, so the error of the calculated result following Wagner-Lupis approach goes up.

The modification suggested by Pelton and Bale[5] is to introduce an additional item representing the activity coefficient of the solvent.

$$\ln\left(\frac{\ln\gamma_i}{\ln\gamma_i^0}\right) = \ln\gamma_S + \sum_{j=2}^{m}\varepsilon_i^j X_j + \sum_{j=2}^{m}\rho_i^j X_j^2 + \sum_{j=2}^{m-1}\sum_{k>j}^{m}\rho_i^{j,k} X_j X_k \qquad (4)$$

$$\ln\gamma_S = -\frac{1}{2}\sum_{j=2}^{m-1}\sum_{k=2}^{m}\varepsilon_{jk} X_j X_k \qquad (5)$$

Essentially, this modification is based on the way of regular solution model. It is a variant of Darken's semi-empirical quadric. And so it cannot provide the data of component activities covering the whole homogeneous region, and is limited to use for iron based alloy.

2.3. Geometric Model

The intention of the so called geometric model is to describe the properties of multicomponent system relying only on the thermodynamic properties of its sub-binary systems. In fact, these model could be either regular one or a sub-regular one. The name of this model comes from that during calculation the geometric relations are adopted[6].

Recently, Chou[7] makes a great progression of geometric model. For the prediction of thermodynamic properties and the phase diagram calculation geometric model is the most widely used method. However, solving the following two problems by use of geometric model is quite difficult. Practically, one used to encounter some homogeneous region, its boundary is composed of parts of the sub-binaries and the lines or curves representing some element's saturation or some compound's separation. The system of C-Fe-Si is an example, as no C-Si binary but SiC carbide. It is difficult to deal with even rely on the new development of Chou. In addition, the geometric model emphasizes to use sub-binaries solely. For a ternary system, the similarity of the binaries are considered by Chou. Nevertheless, the co-functions rising from three components did not be taken into account. For a quaternary homogeneous system, perhaps, the co-function of four components is possibly to be neglected, but the 4 co-functions of three component groups are generally significant. And comparing to binaries, it is more difficult to take the similarity of three components into account.

2.4. Empirical Model

Usually polynomial is adopted by empirical model in description of thermodynamic properties according to the composition. The feature is that this is not a serious model, it is permitted to neglect some of the items in the polynomial.

For a ternary system, introducing an additional empirical item representing the co-function of three elements to the geometric model is one way to improve its prediction result. In order to calculate the component activities of S-Fe-Co-Ni system, the following expression was used by Gokcen[8],

$$\frac{\Delta G^E_{1(1234)}}{RT}=A_{13}X_1X_3(X_1+X_3)+A_{23}X_2X_3(X_2+X_3)$$
$$+A_{14}X_1X_4(X_1+X_4)+X_1X_2X_3(A_{13}+A_{23}+C_2X_2)$$
$$+X_2X_4(A_{42}X_2+A_{24}X_4)X_1X_3X_4(A_{13}+A_{14}+E_4)$$
$$+X_1X_2X_4(A_{14}+A_{42}+D_4X_4) \quad (6)$$

It is obvious that in this expression the descriptions of different sub-systems are not the same. Therefore, the parameters of empirical model is limited for the concerned system. It is not possible to use these parameters for other alloys, even some of the sub-systems are contained in both alloys.

2.5. SELF-SReM Model

SELF-SReM[9] model is a sub-regular melt model developed by SELF. For a quaternary homogeneous region, as that in C-Mn-Fe-Si alloy, SELF-SReM4 model can be shown as follows.

$$\Delta G_1^E=\sum_{j=2}^{j^*}\sum_{k=0}^{k^*}\sum_{n=0}^{n^*}A_{jkn}Y^jZ^kT^n \quad (7)$$

$$\Delta G_2^E=\sum_{j=2}^{j^*}\frac{A_{j00}}{j-1}+\sum_{j=2}^{j^*}\sum_{k=0}^{k^*}\sum_{n=0}^{n^*}A_{jkn}Y^jZ^kT^n[1+\frac{j-k}{Y(1-j)}] \quad (8)$$

$$\Delta G_3^E=\sum_{j=2}^{j^*}\sum_{k=0}^{k^*}\frac{A_{jk0}}{j-1}$$
$$+\sum_{j=2}^{j^*}\sum_{k=0}^{k^*}\sum_{n=0}^{n^*}A_{jkn}Y^jZ^kT^n[1+\frac{j-k}{Y(1-j)}+\frac{k-n}{YZ(1-j)}] \quad (9)$$

$$\Delta G_4^E=\sum_{j=2}^{j^*}\sum_{k=0}^{k^*}\sum_{n=0}^{n^*}\frac{A_{jkn}}{j-1}+\sum_{j=2}^{j^*}\sum_{k=0}^{k^*}\sum_{n=0}^{n^*}A_{jkn}Y^jZ^kT^n[\frac{j-k}{Y(1-j)}]$$
$$+\sum_{j=2}^{j^*}\sum_{k=0}^{k^*}\sum_{n=0}^{n^*}A_{jkn}Y^jZ^kT^n[\frac{k-n}{YZ(1-j)}+\frac{n}{YZW(1-j)}] \quad (10)$$

$$\Delta G^E=\sum_{j=2}^{j^*}\frac{A_{j00}}{j-1}Y+\sum_{j=2}^{j^*}\sum_{k=1}^{k^*}\frac{A_{jk0}}{j-1}YZ+\sum_{j=2}^{j^*}\sum_{k=0}^{k^*}\sum_{n=0}^{n^*}\frac{A_{jkn}}{j-1}YZT$$
$$+\sum_{j=2}^{j^*}\sum_{k=0}^{k^*}\sum_{n=0}^{n^*}\frac{A_{jkn}}{1-j}Y^jZ^kT^n \quad (11)$$

The subscripts 1, 2, 3, 4 denotes respectively the component: C, Mn, Fe, Si. ΔG_i^E is the partial mole excess free energy of the component i. And ΔG^E is the integral mole excess free energy of the quaternary system itself. The parameters A_{jkn} included in the model should be evaluated according to the known "boundary conditions". The sum of j*+ k*+ n* is the order of the model, and usually take j*, k*, n* as an integral smaller than 4. The mole fraction of component "i" is shown by X_i. Y, Z, T compose another kind of the composition, as

$$Y=1-X_1 \quad (12)$$
$$Z=1-X_2/Y \quad (13)$$
$$W=1-X_3/YZ \quad (14)$$

SELF-SReM model belongs to the category of sub-regular solution model. This is obvious, if one compare Eq.(7)~(11) with Eq.(2). Differing from empirical model SELF-SReM model is a serious model. If (j*+k*+n*)=m is given, the set of A_{jkn} parameters is confirmed. The evaluation of A_{jkn} parameters is carried out following Gibbs-Duhem Eq. And so various known "boundary conditions" make their co-restriction to the value of these parameters through Gibbs-Duhem Eq.

If take $\xi^{(m)}$ to express the interaction coefficient of m order, and provide (j*+ k*+n*)=m, then A_{jkn} parameters correspond to $\xi^{(m)}/RT$. Thus, it is easy to understand that SELF-SReM model unifies the activity calculation in both dilute solution and concentrated solution. Not only the interaction coefficients for iron based alloy but also the "interaction coefficients" for the solution, in which Mn or Si or Cr is the solvent are proposed. Further more, these A_{jkn} parameters similar to Wagner-Lupis type interaction coefficients, they all are widely usable. For example, In both the homogeneous region of C-Cr-Fe-Ni alloy and C-Cr-Fe-P alloy, the A_{jkn} parameters associating with C-Cr-Fe sub-ternary are very the same.

SELF-SReM model gets some points differing from geometric model too. SELF-SReM model intends to provide a reliable activity database for the thermodynamic prediction of engineering projects. It is emphasized in SELF-SReM model to collect reliable boundary conditions, the more the better. Even these conditions are some scattered information, through the model they become an integral knowledge.

The accuracy of the prediction by means of SELF-SReM model is determined mainly by the reliability of the used boundary conditions. First of all is those of sub-binaries. In fact, the evaluation of A_{jkn} parameters is carried out step by step, from binary to ternary and then to quaternary itself. Regarding to sub-ternaries and the quaternary itself, the component solubility lines or curves as well as the compound separating lines or curves are selected for the evaluation of A_{jkn} parameters, because these lines or curves are easier to measure and more reliable.

3. The Component Activities in Molten Slag

For an entire thermodynamic prediction the component activities of molten slag are indispensable also due to that slag almost takes part in every pyrometallurgy process. The problem is that either the experimental measurement or the theoretical analysis concerning slag is much more difficult than that for alloy. Regarding even the component activities in binary slag, one used to encounter several contradictory reports. On the other hand, in an actual alloy the concentrated component is usually no more than 4~5, but in a molten slag generally the main component could be more than 7~8.

The contrariety appearing in the investigation on component activity of molten slag can be caused by various reasons. The following is one of them. The components of alloy are elements, not only on microscopic scale but also on macroscopic scale. The components of slag are various compounds[10]. Notwithstanding, compound is just an apparent state. The microscopic configuration of molten slag has not been discovered in detail so far. In recent years, the widely accepted view point declares that the unit of microscopic configuration of molten slag is i-O-j bonds, i and j denote cations and O denotes oxygen anion. The cell model[11] (Gaye model) and the modified quasi-chemical model[12] (MQ model or Pelton model) all are attributed to the statistical thermodynamic model based on the assumption of i-O-j bonds. The applications of these two models for

steelmaking processes have shown some achievements. But for ferroalloy field the results are frequently not so well. This may be resulted from that the characteristic bonding energies of different i-O-j bonds are evaluated mainly from macroscopic thermodynamic properties of concentrated components, but not from that of dilute components. As the slag associating with ferroalloy production is a typical multiple reduction slag, the components to be extracted are just of dilute content.

On the other hand, according to these models, the used thermodynamic properties for evaluation are mainly of binary systems. But even in the system of $CaO\text{-}SiO_2$, for the component activity 5~7 curves with obvious contradictory were reported. Therefore, the first thing for the establishing a model or a data base is to distinguish which is the correct curve in a binary slag.

The concept of component activity and that of chemical potential of element either in a system or in a surroundings are equivalent. As it is indicated by the density function theory, the microscopic bonds get their chemical potentials also, $\mu = \frac{\partial E}{\partial \rho}$. This parameter means that the energy variation for loss or gain a charge when the bond takes part either in a reaction or mixes with the others to form a solution. Essentially, the component activity in macroscopic is just a reflection of the relevant chemical potential in microscopic. So in order to distinguish which is the correct and provide a correct concept it is necessary to link up the microscopic configuration and the macroscopic properties. SELF is just running this research for binary and ternary molten slags. The purpose of this project is to establish SELF-BoSS model. On one hand, by means of high temperature Raman spectroscopy to measure the information of bonds directly from a molten slag. On the other hand, based on molecular dynamics and quantum chemistry to calculate the bonding configuration and the mixing energy.

4. The Description of Reaction Equilibrium among Multiple Phases

The equilibrium among multiple phases emerges in a lot of cases. As the combustion of fuels in rocket it has been investigated thoroughly. However, the investigation of this kind specially for ferroalloy smelting process is in shortage. The reactions happening in sub-merged arc furnaces are very complex. The analysis of this kind reaction should be run as the following way. At first, divide the relative "space" into elementary volumes. And then carry out the equilibrium research among multiple phases in every elementary volumes, one by one. Finally establish the integral image in the "space".

The principle of equilibrium among multiple phases is to make the integral free energy (G) of the system to be its minimum.

$$\sum n_i^{liq}\mu_i^{liq} + \sum n_j^{sol}\mu_j^{sol} + \sum n_k^{gas}\mu_k^{gas} \qquad (15)$$

The superscript "liq" denotes liquid, "sol" denotes solid, "gas" denotes gas. n express mole fraction, μ is the chemical potential, P is partial pressure. And this process aiming at evaluating the minimum should be run under some restrictions, as

1). the phase rule
2). the parallel reactions and the reactions in series
3). the possible chemical reactions
4). the possible phase transformation

and so on. Thus. this is a mathematics question of evaluating the limit under restrictions.

5. Conclusions

The ferroalloy smelting processes so far are still run relying mainly on the experiences of the producers. For the modernization of this industry, the thermodynamic research is an indispensable task. Mainly there are two projects. One is to establish the component activity database for the ferroalloy and the associating molten slags. The another is to run the equilibrium research among multiple phases.

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