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SOLUBILITY OF METAL IN LIQUID PHASE EQUILIBRATING WITH MOLTEN METAL

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Synopsis: Complicated phase equilibria in a practical smelting system such as slag-metal or slag-matte is reduced to ternary systems, and the simplified ternary system is derived from the binary data using the regular solution model. In this paper, special interest is focused on the fact that ternary phase separation tendency is observed between a neutral component and strong intermediate compound, although all the constituent binary systems have miscible trend. The experimental results for oxidic dissolution of valuable metal in FeO_x-SiO_2-CaO slag are reasonably explained by taking account of the immiscible trend between MO and xAO·BO in ternary MO-AO-BO system. This type phase separation was observed in the ternary Cu-Pb-As, Sb-Fe-S or Sn-Fe-Si systems, and the metallurgical significance of metal solubility was discussed thermodynamically relating to a practical smelting.

Key words: phase separation, extractive metallurgy, regular solution model, activity, metal loss in slag, FeO_x-SiO_2-CaO, Cu-Pb-As, Cu-Pb-Sb, Sn-Fe-Si, Sb-Fe-S, process design

1. Introduction

Extractive metallurgy usually consists of two essential steps, phase separation followed by chemical reaction. The phase separation step has been provided a qualitative description by mainly practical experience, while excellent quantitative evaluation have been accumulated for various metallurgical reactions on the basis of thermodynamic data when the process is in equilibrium. In this paper, complicated slag-metal or slag-matte equilibria in a practical smelting process are reduced to ternary systems, and the ternary phase equilibria are derived from the data in the constituent binary systems by assuming a regular solution. Special interest is focused on ternary phase separation between a neutral component and strong intermediate compound, and the calculated results are compared with experimental data.

2. Immiscibility evaluation based by the regular solution model with a parameter α

Miscibility or immiscibility may be described by using a suitable thermodynamic model as well as a phase diagram. In this paper, the most simple and well known regular solution model is applied to the evaluation of the thermodynamic properties, and α-function [1], defined as $\alpha_1 = \ln \gamma_1/(1-N_1)^2$, is adopted to indicate the degree of deviation from ideality in a binary system. A negative α value suggests a negative deviation from ideality, and an extremely negative α value means the formation of an intermediate compound. A positive α value, on the contrary, corresponds to positive deviation, and a miscibility gap is observed when the value is more than 2. Most metallurgical processes can be reduced to ternary systems in principle, and a simplified ternary system may be described from the three binary data. By using α function, several ternary miscibility gaps corresponding to typical smelting systems were evaluated from appropriate α values for the constituent binaries with the regular solution model by the authors [2, 3].

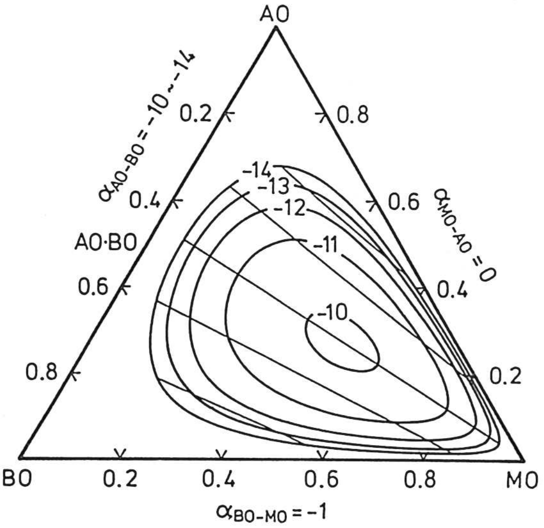

Fig. 1 Effect of the stability of intermediate compound on the region of ternary miscibility gap calculated from binary α values.

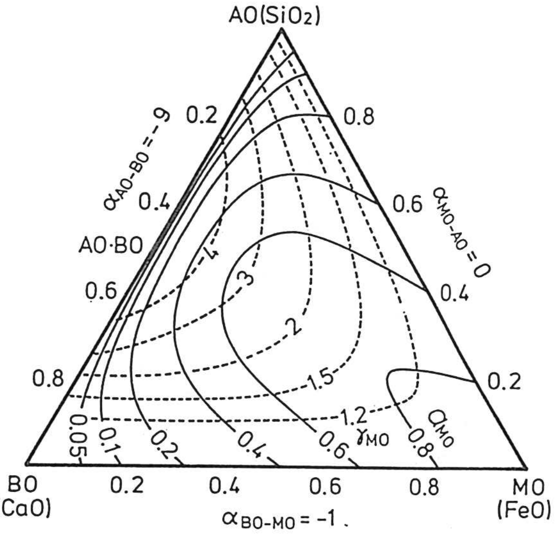

Fig. 2 Isobars of a_{MO} and γ_{MO} derived from α values of -9, 0 and -1 for each binary. No miscibility gap exists in the ternary system.

3. Miscibility gap between a neutral component and strong intermediate compound

Much attention is being denoted on the formation of ternary miscibility gap, while all the constituent binaries are miscible. A few ternary miscibility gaps were calculated from the binaries by THERMOCALC[4] with the assumption of the regular solution model to demonstrate the variation of ternary immiscibility.

Fig. 1 is illustrated the miscibility gaps in MO-AO-BO (metal oxide-acidic oxide-basic oxide) ternary system, which were calculated with the conditions of an ideal behavior in the AO-MO binary, slightly negative deviation for the BO-MO, but considerable negative deviation to form a strong intermediate compound AO·BO in the AO-BO system. The stability of AO·BO is suggested by the α-values from -10 to -14, and the region of miscibility gap between MO and AO·BO is greatly affected by the stability of the compound. If α is -9 in the binary AO-BO although the other AO-MO and BO-MO binary systems are kept the same condition, the ternary miscibility gap must disappear. However, the repulsive trend between MO and AO·BO must exist in the single liquid phase, and may be observed on activity and activity coefficient of MO. As an example, the calculated results of isobars of a_{MO} and γ_{MO} in AO-BO-MO system are shown in Fig. 2 with the solid and dashed lines, respectively. Both the isobars represent prominent convexity on the tie line between MO and AO·BO, the dissolution of the neutral component in the melt will become minimum on the tie line.

In Fig. 3, the effect of α value in binary BO-MO for the region of ternary miscibility gap is demonstrated with a fixed value of -12 in AO-BO binary. It is well understood that an island shape miscibility gap is affected not only by stability of the intermediate compound but also by the property of other binaries considerably. Through these discussions, it will be understandable that ternary immiscibility between a neutral component and strong intermediate compound must have great significance for metallurgical processes, especially for the dissolution of neutral valuable metal oxide in slag.

4. Oxidic dissolution of metals in the FeO_x-SiO_2-CaO slag

Valuable metal loss in slag is great concern of a metallurgist, and the optimum slag composition to minimize metal loss has always been pursued by many investigators. The unified thermodynamic interpretation will be given for rather scattered opinions derived from practical experiences.

(1) Iso-activity curves of FeO in the FeO_x-SiO_2-BO systems.

By the above discussions on the ternary immiscibility, the minimum solubility of a neutral valuable metal oxide (MO) seems to be obtained in slag consisting of a strong inter-

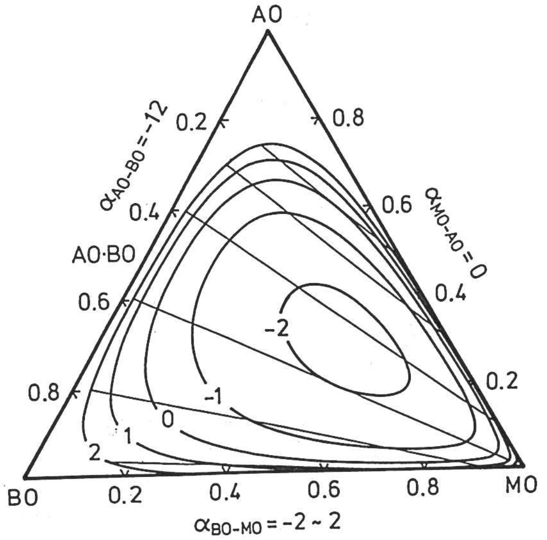

Fig. 3 Effect of α value in binary BO-MO on ternary miscibility gap with fixed stability of an intermediate compound.

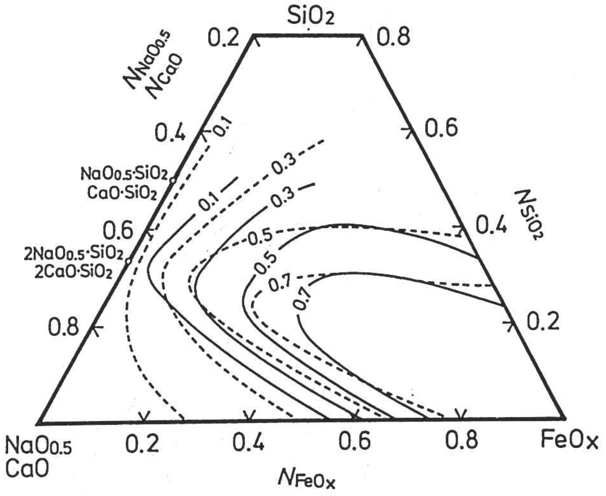

Fig. 4 Iso-activity curves of FeO in the FeO_x-SiO_2-$NaO_{0.5}$ system at 1250°C (solid lines) and the FeO_x-SiO_2-CaO system at 1600°C (dashed lines).

mediate compound in AO-BO binary [2, 5]. As a practical example corresponding to Fig. 2, the iso-activity curves of FeO in the FeO_x-SiO_2-CaO [6] and FeO_x-SiO_2-$NaO_{0.5}$ [7] systems are illustrated in Fig. 4. Although the both slags are a single homogeneous liquid phase, the iso-activity curves show prominent convexity on the tie line between FeO_x and $2BO{\cdot}SiO_2$. It is suggested that the ability of dissolution will become minimum on this line not only for FeO but also for other neutral MO contained in this slag at minor level.

(2) Dissolution of metal oxides in iron oxide slags.

To confirm this prediction for the solubility of minor metal oxide in FeO base slag, FeO_x-SiO_2 (fayalite type A), FeO_x-CaO (ferrite type D), and FeO_x-SiO_2-CaO (ternary B, C) slags were equilibrated with various liquid metal or alloy. The compositions of the employed slag are illustrated in Fig. 5, and slag A, B, C and D are distinguished by the CaO/SiO_2 ratio in mole. The most stable and strongest compound is $2CaO{\cdot}SiO_2$ in the CaO-SiO_2 system. The result obtained from the experiments [8, 9] are summarized in the term of distribution ratio which is plotted against log P_{O_2} in Fig. 6. The distribution ratio L of divalent metal M between slag and metal phases are related to the equilibrium constant K, and corresponding to the oxidic solubility of metal M in slag [5] as shown in eq. (2).

$$M + 1/2O_2 = MO \quad ; K = a_{MO} / a_M P_{O_2}^{1/2} \qquad (1)$$

$$L_M^{s/m} = (\%M)/[\%M] = K(n_T)[\gamma_M] P_{O_2}^{1/2}/[n_T](\gamma_{MO}) \qquad (2)$$

where () and [] denote slag and metal phases, respectively. The logarithmic plot between $L_M{}^{s/m}$ and P_{O_2} for divalent metal will give approximately a straight line with slope of 1/2 as suggested by eq. (2). Only the slope for copper is different because of the monovalent dissolution. On the figure, it is recognized that the solubility of metal oxide in slag decreases gradually from FeO, CaO, SnO, PbO, (NiO), to Cu_2O depending on the value of K for each metal oxide.

It should be noted in Fig. 6 that the solubility of metal oxides in slag is generally lower in ternary slag C, while much higher solubilities are observed in the binary fayalite slag A and ferrite slag D. Referring to the activity or activity coeffi-

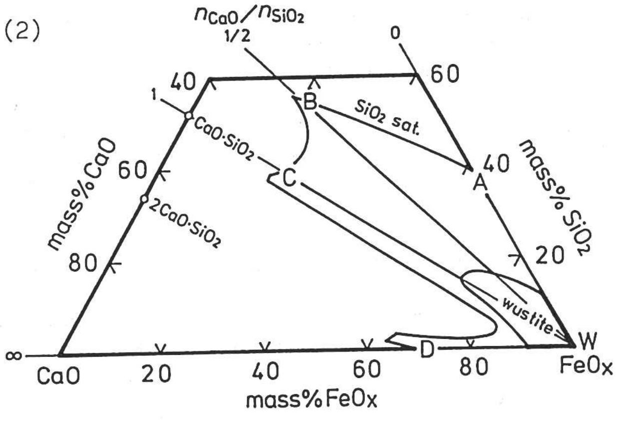

Fig. 5 Liquid region in the FeO_x-SiO_2-CaO system at 1300°C. A: fayalite, D: ferrite binary slag.

cient shown in Figs. 2 and 4, the minimum solubility of metal oxide may be expected in the slag of $CaO/SiO_2 = 2$ if in molten state. The isobars of $CuO_{0.5}$ and SnO estimated from the distribution ratio are illustrated in Fig. 7 [9], in which show similar behavior with those in Figs. 2 and 4.

(3) Special behavior of lead solubility in calcium ferrite slag.

An important exception was found in Figs. 6 and 7 for the extremely low solubility of lead in ferrite slag D. On the basis of the results, the authors [10] recommended to use ferrite slag in the lead smelting, but no reasonable explanation has been given. The model calculation is carried out in MO-AO-BO ternary to explain such special behavior of γ_{PbO} with the assumptions of substantially negative deviation for the $PbO-SiO_2$ and repulsive trend in the PbO-CaO system. The derived a_{MO} and γ_{MO} are illustrated in Fig. 8 with solid and dashed lines, and the trend of γ_{MO} may describe those of γ_{PbO}.

(4) Effect of slag amount on oxidic dissolution loss of metals.

Through above discussions, ternary optimum conditions to maximize γ_{MO} or minimize (%M) will be predicted, if the thermodynamic data in binaries are available. The total metal loss in slag is evaluated by $(M_t) = (\%MO) \times (\text{amount of slag})$, and the slag which has optimum ratio of BO:AO to minimize (%MO) tends to minimize the removability of iron oxide into slag, and hence to maximize the amount of slag. Since there are inversely proportional relation between (%MO) and (γ_{MO}), and also slag amount and FeO content in the slag respectively, the equation, $(M_t) = c/(\gamma_{MO})(N_{FeO})$ is obtained, where c is a given coefficient. If the behavior of FeO and MO are similar as the most simple assumption, the equation becomes $(M_t) = c/a_{MO}$. Thus, a_{MO} curves in Figs. 2 and 8 correspond to the isobar of (M_t).

5. Example of island shape ternary miscibility gap and their process implications

(1) Lead-speiss equilibria in the Cu-Pb-As and Cu-Pb-Sb systems.

Although there are many examples for an island shape miscibility gap in a ternary

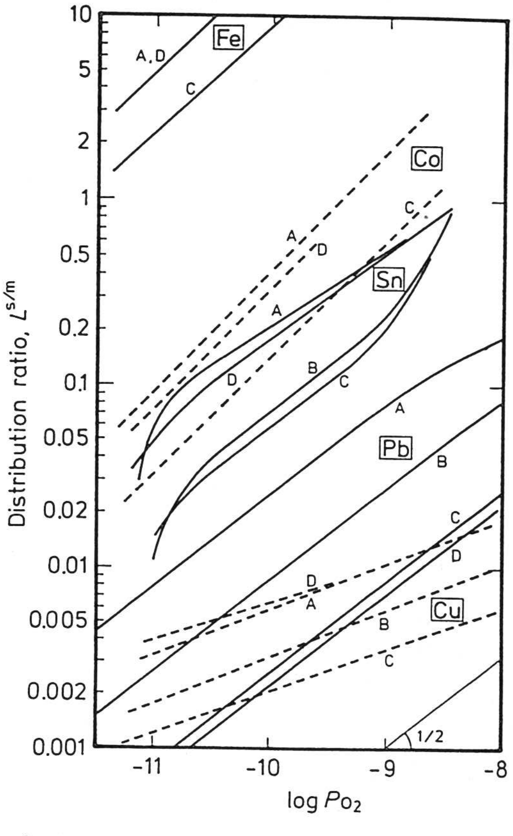

Fig. 6 Distribution ratio of metals between FeO_x-SiO_2-CaO slag and liquid metal in relation with oxygen potential at 1300°C.

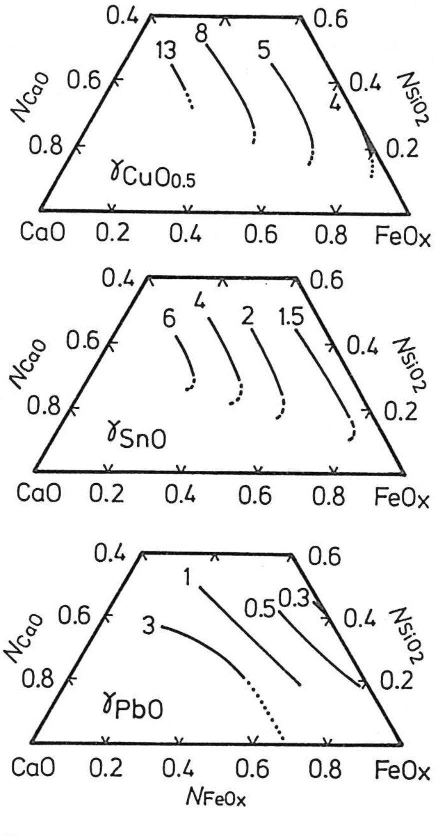

Fig. 7 Isobars of activity coefficients of $CuO_{0.5}$(top), SnO(middle) and PbO(bottom) in FeO_x-SiO_2-CaO slag at 1300°C.

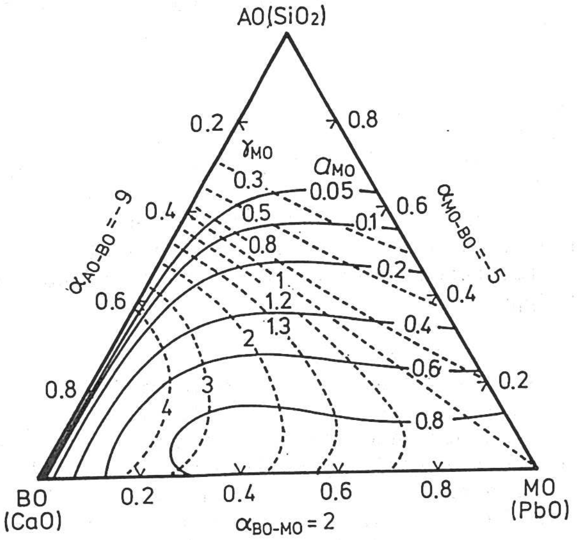

Fig. 8 Isobars of a_{MO} (solid lines) and γ_{MO} (dashed lines) in AO-BO-MO slag. Binary α values are assumed that MO has similar property to PbO.

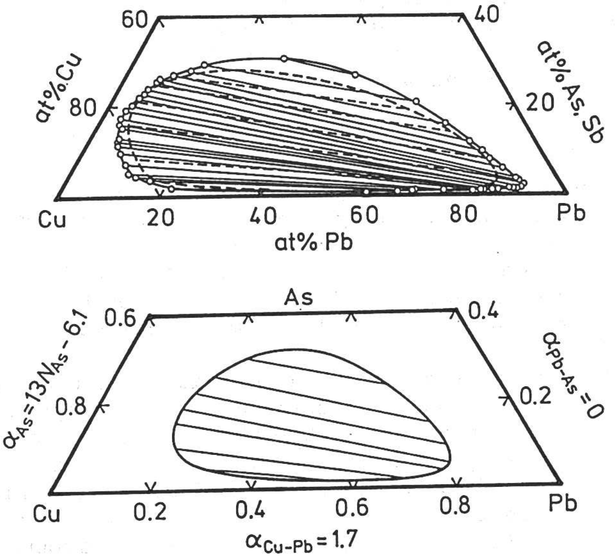

Fig. 9 Top: the experimental results of micibility gaps for the Cu-Pb-As (solid line) and Cu-Pb-Sb (dashed line) systems at 1200°C. Bottom: the miscibility gap derived from α values in the each binary.

system, just a few examples determined by the present authors' group will be discussed in this paper. The phase separations in the Cu-Pb-As and Cu-Pb-Sb systems shown in Fig. 9 were determined to establish lead-speiss equilibria [11]. Phase separation takes place between neutral lead and strong compound of copper arsenide or antimonide at 1200°C, resulting two phase equilibria of molten lead and speiss system, while all the binary solutions are homogeneous. These ternary miscibility gaps have great significance in lead metallurgy, especially in the stage of lead bullion refining.

To demonstrate the availability of thermodynamic derivation of ternary miscibility gap from binary data, α function for each binary are assumed as shown in the bottom figure in Fig. 9. A sub-regular solution is adopted in the Cu-As binary as the two parameter model because of the unsymmetrical thermodynamic property, while a regular solution is employed for the other two binaries. The obtained miscibility gap in the bottom figure is agreeable in general trend with those experimental ones, and more good agreement will be expected by adjustment of a sub-regular model equation.

(2) Sn-Fe-Si system and ferro-silicon process for hard-head

Phase equilibria in the Sn-Fe-Si system were determined by Koike and Tozawa [12] at 1350°C and the revised figure is shown in Fig. 10. A binary Sn-Fe alloy forms so-called hard-head and represents a rather narrow miscibility gap. However, the silicon addition isolates nearly pure tin from the binary alloy because of the ferro-silicon formation. The hard-head is an intermediate product in the tin smelting and the recovery of tin from it is rather troublesome, but this ternary phase separation between neutral tin and strong Fe-Si compound is sometimes applied to the ferro-silicon process for treatment of hard-head. The condition of minimum loss of tin in a ferro-silicon phase is clearly observed in Fig. 10.

(3) Sb-Fe-S system and iron precipitation process of stibnite.

Phase equilibria in the Sb-Fe-S system were established at 1200°C in the authors' laboratory[13], and illustrated in Fig. 11. The extended ternary miscibility gap is observed between neutral Sb and strong intermediate compound FeS, and expands to the miscibility gap in the binary $Sb-Sb_2S_3$. Iron precipitation process of stibnite is reasonably understood from this metal-matte equilibria; that is, by the addition of suitable amount of scrap iron to molten Sb_2S_3, antimony metal is obtained through the reaction: $Sb_2S_3 + 3Fe = 2Sb + 3FeS$. The condition for obtaining maximum antimony recovery and minimum antimony loss in slag (FeS matte) is observed and also must be predicted thermodynamically based upon the binary data.

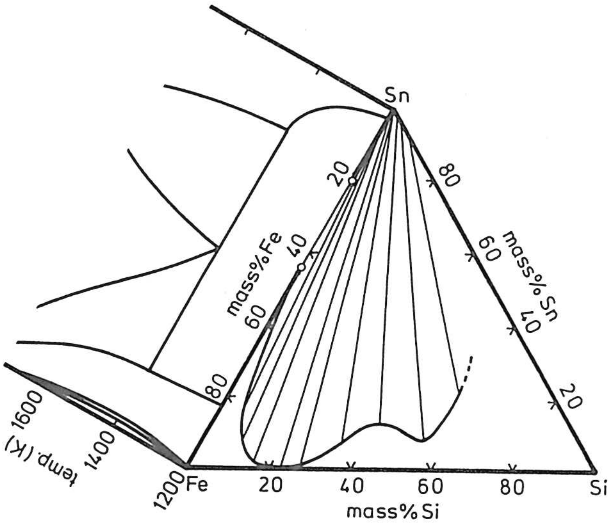

Fig. 10 Phase relation for the Fe-Sn binary and Fe-Sn-Si ternary systems at 1300°C.

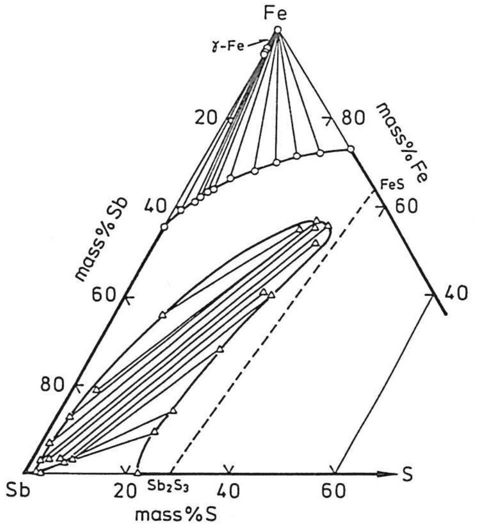

Fig. 11 Phase relations in the Fe-Sb-S system at 1200°C.

6. Summary

Most smelting processes may be reduced to ternary system, and ternary phase equilibria including activity or activity coefficient were estimated from the binary thermodynamic data by the simple regular solution model, and compared with the experimental results. The oxidic dissolution of metal in slag is reasonably explained by immiscible trend between MO and xAO·BO in ternary MO-AO-BO. The behavior of activity coefficient of $CuO_{0.5}$, SnO and PbO in FeO_x-SiO_2-CaO slag were also successfully derived with α values for the three binaries. The metal loss in slag could be calculated by means of the FeO content and activity coefficient of minor metal oxide, then, illustrated on the ternary diagram. Moreover, the ternary miscibility gaps established experimentally in the Cu-Pb-As, Cu-Pb-Si and Sb-Fe-S systems were explained based upon the similar principle of phase separation, and relating practical processes were clarified thermodynamically. These thermodynamic assessments will be available for a process design in the extractive metallurgy.

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