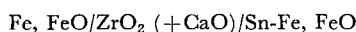# Thermodynamic Study on Sn-Fe Alloys

By

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Thermodynamic properties of molten Sn-Fe alloys were estimated by e.m.f. measurements of the following cell employing solid electrolytes at the temperature range of 900~1250°C

Fe, FeO/ZrO$_2$ (+CaO)/Sn-Fe, FeO

From these experimental results it was found that the activities of components in molten Sn-Fe alloys(hard head)were found to show considerable positive deviation from Raoult's law. Based on the activities of components in molten Sn-Fe alloys and the equilibrium experimental results of Davey and Floyd[1] the equilibrium relations between slag and metal in tin smelting were investigated.

1. Introduction

The complexity of tin smelting is attributed to the fact that a considerable proportion of iron-oxide was reduced together with tin at reduction smelting. So the activities of components in hard head have to be known in order to investigate the equilibrium state of tin smelting. Notwithstanding any experimental results those were not found untill quite recently and only the supposed values were recently presented by Davey[2]. And so we determined[3] the thermodynamic properties of hard head at the temperature range of 900~1250°C by means of e.m.f. measurements employing solid electrolytes. At the same time Yazawa and Koike[4] estimated the activities of components in hard head at the temperature range of 1350~1500°C by means of equilibrium distribution experiments.

In the present paper the outline of our experimental results was described, and based on our experimental results the relations between slag and metal at tin smelting were investigated.

2. Activities of components in hard head (Sn-Fe alloys)

In our investigation the activity of iron in Sn-Fe alloys was determined by e.m.f.

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A: Al_2O_3 crucible
B: ZrO_2-CaO electrolyte
C: wüstite pellet
D: Sn-Fe alloy
E: wüstite powder
F: Fe-wüstite pellet
G: stainless steel plate
H: Fe-wüstite powder
I: Al_2O_3 tube
J: stainless steel wire (oxidized)
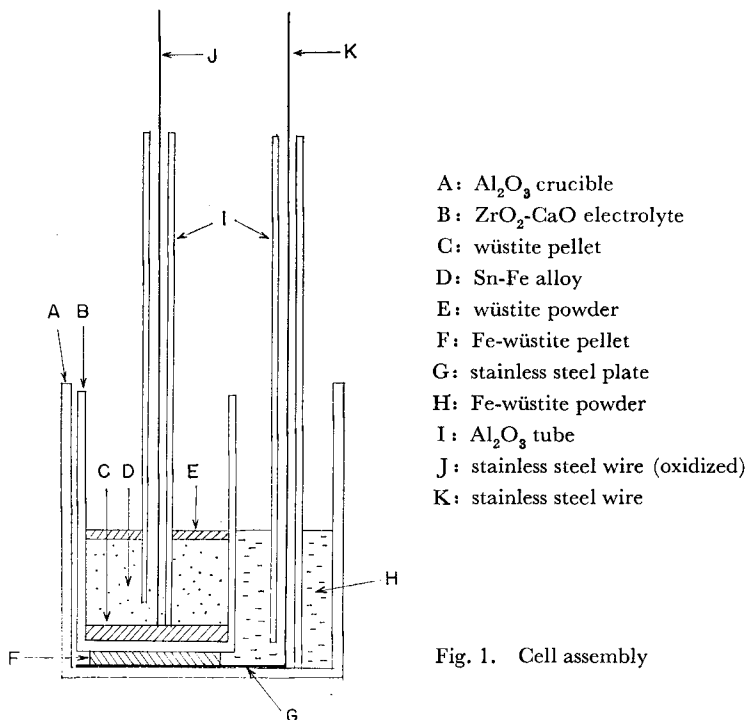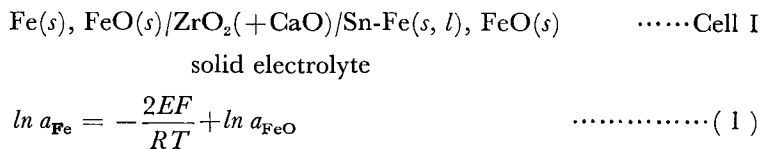K: stainless steel wire

Fig. 1.   Cell assembly

measurements employing solid electrolyte and based on those results the activity of tin was calculated according to the Gibbs-Duhem equation.   The detail of our experimental principle and methods were reported in previous paper[3] and only the outline of those are reported in this paper.

The following oxygen concentration cells were constructed as shown in Fig. 1 and from the e.m.f. of these cells the activity of iron in Sn-Fe alloys was estimated according to Eq. (1)

$$Fe(s), FeO(s)/ZrO_2(+CaO)/Sn-Fe(s, l), FeO(s) \qquad \cdots\cdots Cell\ I$$
$$solid\ electrolyte$$

$$ln\ a_{Fe} = -\frac{2EF}{RT} + ln\ a_{FeO} \qquad \cdots\cdots\cdots\cdots\cdots(1)$$

where a_{Fe} and a_{FeO} are respectively activities of iron in Sn-Fe and FeO in wüstite at the right electrode of cell I, E is e.m.f. of cell I, R is gas constant, T is temperature in degree K and F is Faraday constant. a_{FeO} was calculated based on the e.m.f. of cell I (E) and the equilibrium relation of a_{FeO} in wüstite and oxygen partial pressure by Darken and Gurry[5].

The noteworthy point of our experimental procedure is that the connecting wire of right electrode (J) in Fig. 1 was stainless-steel wire with a dense coherent oxide layer which was formed by heating at 700°C for one week in air.

The e.m.f. measurements were carried out at the temperature range of 900～1250°C and in atomosphere of purified argon.   The temperature was alternately increased and decreased and the e.m.f. was measured at each new temperature. The furnace used was of the silicon carbide resistance type and its temperature was controlled automatically in the range of ±1°C.   The first measurement was read after maintaining the cell at a constant temperature for 10～12 hrs. and the latter were kept at constant temperature for 2～3 hrs..

After confirming the reliability of the experiments by a few preliminary experiments, the e.m.f. measurements of cell I were carried out on Sn-Fe alloys of nine different compositions and shown in Fig. 2 where N_{Sn} represents the atomic fraction of tin in Sn-Fe alloys.   From that experimental result it was found that
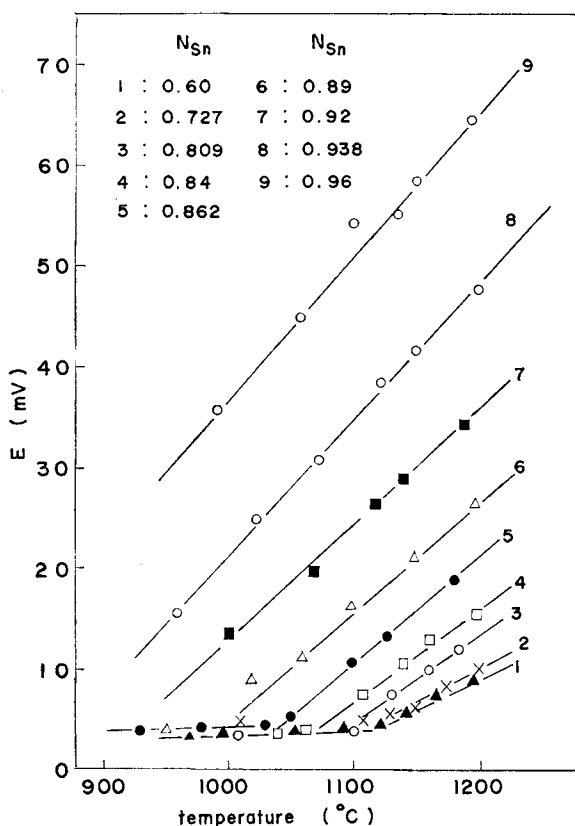

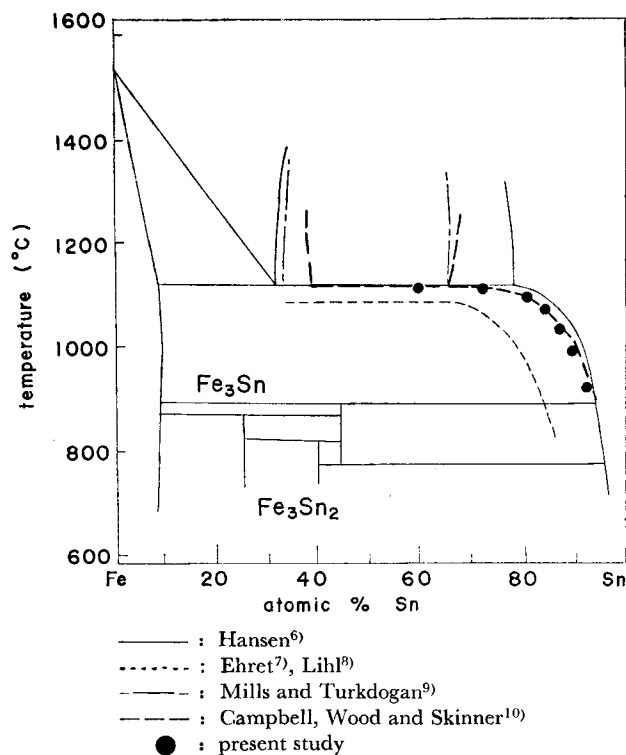Fig. 2.   The electromotive force vs. temperature for the
Sn-Fe system

Fig. 3. Phase diagram of the Sn-Fe system

the e.m.f. can be expressed as a linear function of temperature and the e.m.f.-temperature plots of six alloys in lower tin concentration had refraction points at each peculiar temperature as shown in Fig. 2. These temperatures correspond to those of liquidus line of each composition. Many researchers investigated the equilibrium phase diagram of Sn-Fe alloy as shown Fig. 3, however they are shown to have considerable different point of liquidus line. From Fig. 3 it was found that our results at the temperature range of 900~1130°C were in good agreement with the data of Campbell, Wood and Skinner et al.[10]

Based on the results of e.m.f. measurements in Fig. 2, the oxygen partial pressure of various Sn-Fe alloys in equilibrium with wüstite and the activity of FeO in wüstite in equilibrium with it's oxygen partial pressure were calculated at 1100°C and 1200°C.

Furthermore the activities of iron in Sn-Fe alloys at those temperatures were calculated according to Eq. (1) and shown in Fig. 4 and the activities of tin were calculated according to Gibbs-Duhem equation[11] and shown in this figure. The activities of iron refer to pure solid iron and that of tin refer to pure liquid tin.
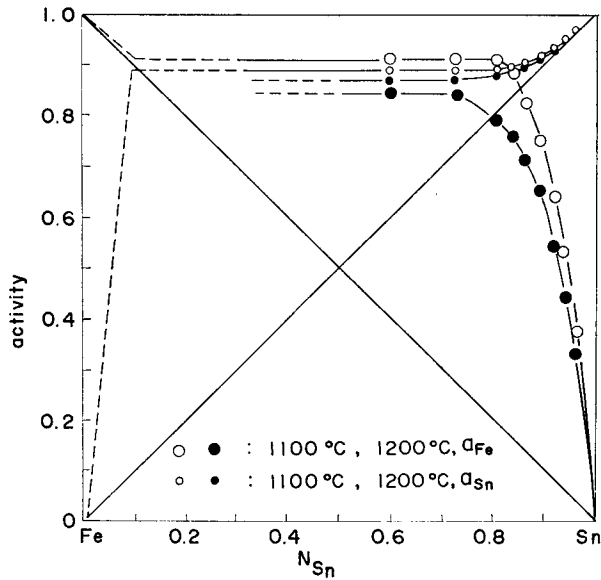
Fig. 4.   Activity-composition curves for Fe and Sn in Sn-Fe
          alloys at 1100 and 1200°C

From the results in Fig. 4 both activities of iron and tin were found to have a positive deviation from Raoult's law and those could be deduced from the fact that the phase diagram has an immisibility gap.   Also this result was found to be in a good agree-
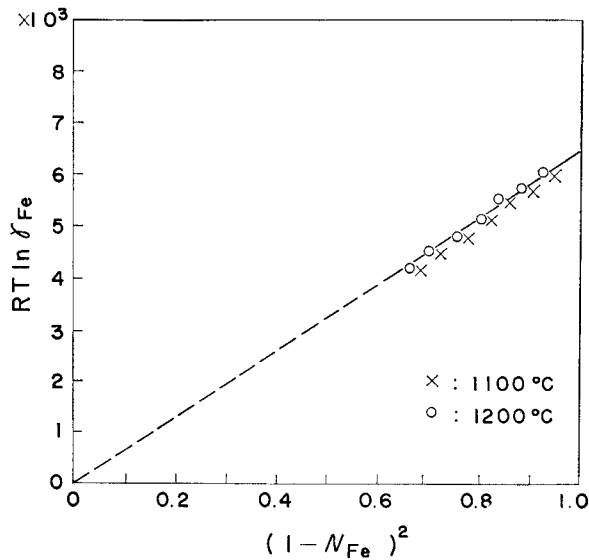

Fig. 5.   The relation of RT ln γ_{Fe} and $(1-N_{Fe})^2$ at
          1100°C and 1200°C

ment with that of Yazawa and Koike[4] taking into account the temperature difference.

Based on these experimental results the relation of $\Delta \bar{F}_{Fe}^{ex}(=RT\ ln\ \gamma_{Fe})$ and N_{Sn}^2 was estimated and shown in Fig. 5 where γ_{Fe} is the activity coefficient of iron and $\Delta \bar{F}_{Fe}^{ex}$ is the partial molal excess free energy of iron. From this figure it was found that the relation was represented as nearly one linear function regardless of temperature and this relation shows that this molten Sn-Fe alloy is nearly regular solution. Based on the result in Fig. 5 the following Eq. (2) could be obtained at the composition range of homoginious liquid alloys

$$RT\ ln\ \gamma_{Fe} = 6700\ (1-N_{Fe})^2 \qquad \cdots\cdots\cdots\cdots\cdots(2)$$

In regard to this relation Davey[2] obtained various equations for calculation of γ_{Fe}' based on equilibrium phase diagram and according to the assumptions of Henry's law, regular solution, sub-regular solution and the statistical model of Lumsden[12] and those calculated values (γ^0) from those equations were shown in Fig. 6 as a function of N_{Sn}^2. In this figure γ_{Fe}' refer to supercooled pure iron at 1401°K and represented in a scale of logarithm.

In order to compare our calculated value with those results the activity-
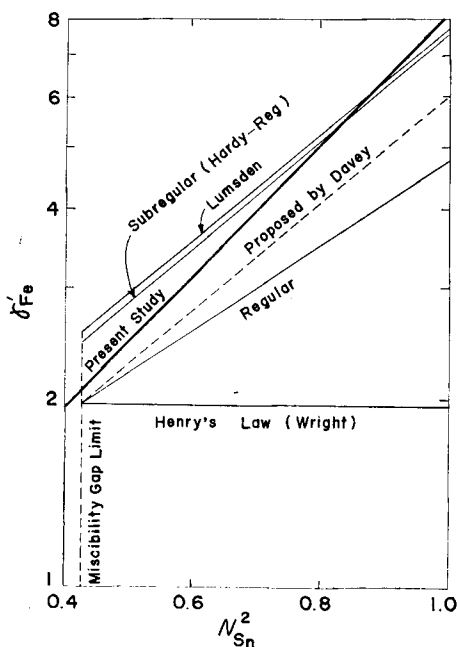

Fig. 6. Activity-coefficient (refer to liquid pure Fe) of Fe in Sn-Fe alloys at 1401°K (quoted from the figure of Davey)

coefficients of iron should be represented as those which refer to supercooled pure iron at 1401°K and the following Eq. (3) was obtained.

$$\log \gamma'_{Fe} = 1.04 \ N^2_{Sn} - 0.135 \quad \cdots\cdots\cdots\cdots (3)$$

The thick real line in Fig. 6 represents the values calculated according to Eq. (3), and from this figure the proposed values by Davey was found to be nearly in agreement with our results.

Then the reliability of the results of our experiments would be investigated. As described above a few preliminary experiments comfirmed that the e.m.f. of oxygen concentrated cell could be measured by using the type of cell in Fig. 1. Also as shown in Fig. 2 the linear plot of e.m.f. against temperature was obtained in spite of the fact that the temperature change was alternately increased and decreased. This linear relation indicates that the same e.m.f. can be obtained when a particular temperature was attained from higher or lower temperatures and e.m.f. remains unchanged for nearly 20 hrs. and this may be regarded as evidence for cell reversibility and the effect of irreversible phenomena such as varying composition or contamination of melts could be considered as negligible.

In a case of consideration of the experimental error the possibility of following substitutional reaction (4) must be examined.

$$FeO(s) + Sn(l) = SnO(l) + Fe(l) \quad \cdots\cdots\cdots\cdots (4)$$
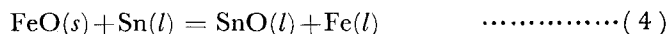
The standard formation free energy of this reaction was calculated based on those of $FeO(s)$[13] and $SnO(l)$[14] and activities of both components in Sn-Fe alloys and it was found to be negligible in our experimental consitions.

3. Investigation on the reaction of fire tin smelting

The equilibrium relation between slag and metal in fire tin smelting were investigated based on our experimental results.*
Let us consider the following reaction (5), where (M) and (S) represent the phases of metal and slag.
If K is the equilibrium constant of the reaction (5),

$$K = \frac{a_{Sn}}{a_{Fe}} \times \frac{a_{FeO}}{a_{SnO}} = \frac{\gamma_{Fe}}{\gamma_{Fe}} \cdot \frac{N_{Sn}}{N_{Fe}} \times \frac{\gamma_{FeO}}{\gamma_{SnO}} \cdot \frac{N_{FeO}}{N_{SnO}} \quad \cdots\cdots\cdots\cdots (6)$$

where a_{Sn}, a_{Fe}, a_{FeO}, a_{SnO}, N_{Sn}, N_{Fe}, N_{SnO}, N_{FeO}, γ_{Sn}, γ_{Fe}, γ_{FeO} and γ_{SnO} are the activities, atomic or mole fractions and activity coefficients of tin and iron in

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* according to the calculating method of Davey and Floyd

metal phase and FeO and SnO in slag phase. Also if W_{Fe}, W_{Sn}, W_{Fe} and W_{Sn} are the weight % of iron and tin in slag and metal phases,

$$K = \frac{r_{Sn}}{r_{Fe}} \times \frac{W_{Sn}}{W_{Fe}} \times \frac{r_{FeO}}{r_{SnO}} \times \frac{W_{Fe}}{W_{Sn}} \qquad \cdots\cdots\cdots\cdots\cdots(7)$$

and according to the definition of W_{Sn}/W_{Fe} $W_{Fe}/W_{Sn}=k$ and assumption of $r_{FeO}/r_{SnO}=1$ that means the same behavior of SnO and FeO in molten slag, Eq. (8) is obtained.

$$K = k\frac{r_{Sn}}{r_{Fe}} \qquad \cdots\cdots\cdots\cdots\cdots(8)$$

From our experimental results it was found that the relations between the activity coefficients and compositions were represented by the following equations

$$\log r_{Fe} = \alpha N_{Fe}^2, \quad \log r_{Fe} = \alpha N_{Sn}^2$$

where α is constant. Substituting these in Eq. (8),

$$\log k = \log K + \alpha(1-2N_{Fe}) \qquad \cdots\cdots\cdots\cdots\cdots(9)$$

Since the value of α is able to be estimated at any temperature based on our experimental results, the equilibrium constant of reaction (5) is able to be calculated providing k is determined.

Davey and Floyd carried out the equilibrium experiments between slag and metal and those results were represented in Fig. 7.

In their experiments, the metallic tin and the slag consist of 25% FeO, 35% SiO_2, 20% CaO, 10% Al_2O_3, 5% B_2O_3 and 5% CaF_2 were molten in a crucible and after those attained to equilibrium state at 1150°C those were quenched. The compositions of each phase of metal and slag were determined by chemical analysis and based on these values the value of k was estimated.

In such experiments iron had to transfer from slag to metal and tin had to transfer from metal to slag. If equilibrium failed to be established one would expect to obtain the larger k than correct value. The data of such experiments represented by (high ○) in Fig. 7 and while (low ×) indicated the values of k which were estimated based on equilibrium experiments approached from the other side, by reacting together a slag higher in tin and a metal higher in iron.

When $\log k$ is plotted agzinst $(1-2\ N_{Fe})$, the straight line would be expected based on experimental results and the slope of straight line indicates the value of α and the intercept of ordinate indicates $\log K$. The mean value of $\log K$ in respect to each experimental points in Fig. 7 are calculated by using the value of $\alpha = 0.78$
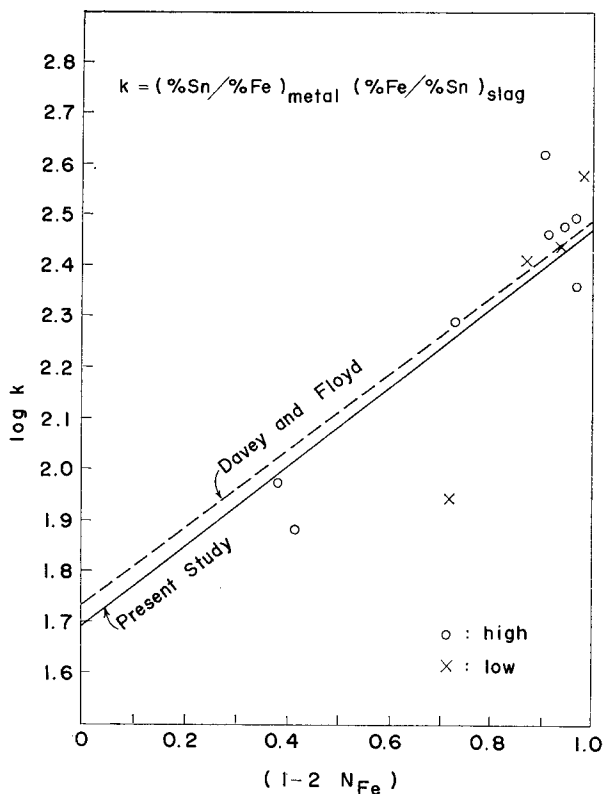
Fig. 7.   Plots of log k against $(1-2N_{Fe})$

which were estimated from our experimental results at 1150°C.   The straight line in Fig. 7 indicates the equation of log $k = 1.69 + 0.78$ $(1-2\ N_{Fe})$ which is determined based on the activities of components in hard head and this line was found to be in good agreement with the experimental results of Davey and Floyd. Also from the value of log $K = 1.69$ the standard free energy of the reaction (5) at 1160°C was calculated as follows

$$\Delta F^0 = -11,000 \text{ cal.}$$

While the value was calculated from the reliable standard formation free energy of SnO[13] and FeO[14] and it was $-9,000$ cal and was nearly in agreement with the former.

4.   Conclusion

The e.m.f. measurements of the following cell were carried out at the temperature range of 900~1250°C

$$\text{Fe, FeO}/\text{ZrO}_2 \; (+\text{CaO})/\text{Sn-Fe, FeO}$$

and from these experimental results it was found that the activities of components in molten Sn-Fe alloys hare considerable positive deviation from Raoult's law and the properties of that alloy solution were nearly regular solution in the composition range of homogeneous liquid phase. The activities of components were found to be in good agreement with the experimental results of Yazawa and Koike and nearly in agreement with the proposed value of Davey.

Based on these results the relations between slag and metal were investigated and its result was in good agreement with that of Davey and Floyd.

Acknowledgement

References

1) T.R.A. Davey and J.M. Floyd: Proc. Aust. Inst. Min. Met., **219**, 1 (1966)

2) T.R.A. Davey: Trans. Inst. Min. Met., C278 (1967)

3) Z. Kozuka, Y. Shidahara, E. Sugimoto, N. Watanabe and J. Moriyama: J. Min. Met. inst. of Japan, **84**, 1657 (1968) (in Japanese)

4) A. Yazawa and K. Koike: J. Min. Met. inst. of Japan, **85**, 39 (1969) (in Japanese)

5) L.S. Darken and R.W. Gurry: J. Amer. Chem. Soc., **67**, 1398 (1945)

6) M. Hansen: "Constitution of Binary Alloys", McGraw-Hill

7) W. Ehret: J. Amer. Chem. Soc., **65**, 1226 (1943)

8) F. Lihl: Monatsh, **86**, 1031 (1955)

9) K.C. Mills and E.T. Turkdogan: Trans. AIME, **230**, 1202 (1964)

10) A.N. Campbell, J.H. Wood and G.B. Skinner: J. Amer. Chem. Soc., **71**, 1729 (1949)

11) L.S. Darken and R.W. Gurry: "Physical Chemistry of Metals", MaGraw Hill, 265 (1953)

12) J. Lumsden: "Thermodynamics of Alloys", London Institute of Metals 384 (1952)

13) Z. Kozuka, O.P. Siahaan and J. Moriyama: Trans. J. inst. of Metals, **9**, 200 (1968)

14) Z. Kozuka, N. Sato, H. Asao and J. Moriyama: in press (Memorirs of Fac. Eng. Kyoto Univ.)