

Activity Measurement of the Constituents in Liquid Cu-Al Alloy with Mass-Spectrometry

著者	Oyamada Hiroshi, Nagasaka Tetsuya, Hino Mitsutaka
journal or publication title	Materials Transactions, JIM
volume	39
number	12
page range	1225-1229
year	1998
URL	http://hdl.handle.net/10097/51973

Activity Measurement of the Constituents in Liquid Cu–Al Alloy with Mass-Spectrometry

Hiroshi Oyamada[†], Tetsuya Nagasaka and Mitsutaka Hino

Department of Metallurgy, Graduate School of Engineering, Tohoku University, 02 Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

A mass spectrometer has been used to study activities of the constituents in liquid Cu–Al alloy. According to Belton-Fruehan's treatment, activities and heats of mixing have been able to be determined from a series of measurements of the ratio of the ion current intensities of the solution components. The activities in the Cu–Al system were found to be in excellent agreement with the values recommended by Hultgren *et al.* The activities exhibited negative deviation from ideality and the terms of $RT\ln\gamma_{Al}$ and $RT\ln\gamma_{Cu}$ were almost independent of the temperature within the present experimental range. Partial molar and integral heats of mixing of the liquid Cu–Al system were also estimated.

(Received May 19, 1998; In Final Form August 24, 1998)

Keywords: thermodynamics, activity measurement, mass spectrometry, copper-aluminum system, heat of mixing, Knudsen cell

I. Introduction

A Cu–Al alloy is one of the most widely used practical copper-based alloys for corrosion-resistant materials, die-casting alloys and so on. Therefore, much work^{(1)–(12)} has been done on the thermodynamic properties and the phase diagram of the system for a better control of the processing. Hultgren *et al.*⁽¹³⁾ reviewed available literature data on this alloy system and recommended the most reliable thermodynamic values.

On the other hand, one of the authors⁽¹⁴⁾ has measured the activity of alumina in steelmaking slags by the equilibrium of molten aluminate slag with a liquid Cu–Al alloy in a graphite crucible under a CO–Ar atmosphere at the steelmaking temperature. In this case, the following chemical equilibrium can be established:



$$K_1 = a_{Al}^2 \cdot P_{CO}^3 / a_{Al_2O_3} \cdot a_C^3 \quad (2)$$

where a is the activity of each component, of which the standard state is a pure substance and K_1 means the equilibrium constant of eq. (1). P_{CO}^* equals P_{CO}/P^0 , where P_{CO} and P^0 are the partial pressure of CO (Pa) and the standard atmospheric pressure (101325 Pa), respectively. The equilibrium constant K_1 is known from the available literature value of free energy change of eq. (1). Since the activity of carbon is unity because of the use of graphite crucible as a vessel, eq. (2) can be simply rearranged as

$$a_{Al_2O_3} = a_{Al}^2 \cdot P_{CO}^3 / K_1 = \gamma_{Al}^2 X_{Al}^2 \cdot P_{CO}^3 / K_1 \quad (3)$$

where γ_{Al} and X_{Al} denote the Raoultian activity coefficient and mole fraction of Al in liquid Cu, respec-

tively. According to eq. (3), the activity of alumina in the slag can be determined from the equilibrium Al content in liquid Cu if the activity coefficient of Al in liquid Cu was known. The authors also measured the free energy of formation of spinel ($MgO \cdot Al_2O_3$) and the activities of constituents in spinel solid solution by the same experimental principle⁽¹⁵⁾.

As it can be realized from eq. (3), the reliability of the measured alumina activity does strongly depend on the accuracy of the activity coefficient of Al in liquid Cu. **Figure 1** reviews the literature values on the activity coefficient of Al in liquid Cu–Al alloy. It is seen from this figure that the agreement among the reported values of the activity coefficient of Al is excellent and no temperature dependence of $RT\ln\gamma_{Al}$ is observed in the high aluminum concentration range. However, there is a considerable disagreement among the observed γ_{Al} in the copper-rich side. Aluminum concentration distributed in liquid copper is only less than a few mass% in the above-mentioned experimental condition of alumina activity measurement in the slag. Therefore, the accuracy of γ_{Al}

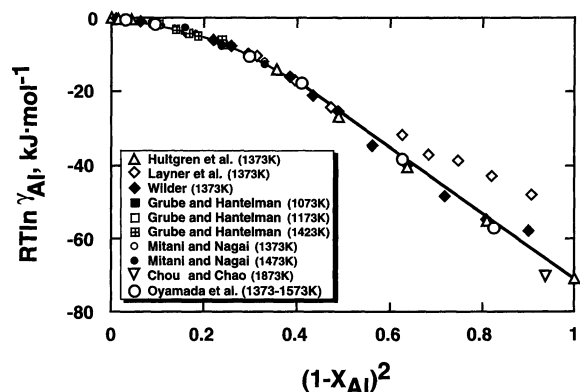


Fig. 1 Activity coefficient of Al in liquid Cu.

[†] Undergraduate Student, Tohoku University, Present address: Paltek Co. Ltd., Yokohama 222-0033, Japan.

in the copper rich side is the most important for the determination of the activity of alumina. For example, the activity coefficient of aluminum in copper at infinite dilution, γ_{Al}^0 , at 1873 K is estimated by assuming $RT \ln \gamma_{\text{Al}}^0 = \text{constant}$ to be 0.01 or 0.034 from the recommended value by Hultgren *et al.*⁽¹³⁾ and the data obtained by Layner *et al.*⁽⁶⁾, respectively. Such a discrepancy of γ_{Al}^0 results in approximately 10 times difference in the activity of alumina in the slag.

Keeping such a background in mind, we have measured the activities of the constituents in the liquid Cu–Al alloy in a wide experimental range of composition and temperature. Mass spectrometry was employed for the activity measurement. The Knudsen cell-mass spectrometer combination technique has made it possible to measure the accurate activities and would be the most suitable method for our purpose.

II. Experimental

The mass spectrometer used in the present work was a magnetic field scanning type Hitachi model RM-6K with a single focusing of 90 deg and a curvature radius of 0.2 m. This equipment consists of a Knudsen cell unit, an ionization chamber, a magnetic field scanning system and a detection unit with the electron multiplier. The atomic or molecular beam of copper and aluminum from the Knudsen cell was directed into the ionization chamber, where the metal vapor species were converted into positive ions by electron impact. The positive ions were then pulsed out of the ion source and accelerated down the flight tube for analysis. The ionization potential and the ion accelerating voltage are generally 20 eV and 12.0 kV, respectively. The masses are separated by scanning the magnetic field for time-of-flight of ion bunches by their mass/charge ratio and were detected by a secondary electron multiplier. The intensity of the scanning magnetic field was in the range of 400 to 15500 Gauss. An analog output circuit was used to detect and display the mass peaks on a monitor or pen-recorder. The system was evacuated by rotary and diffusion pumps to approximately 3×10^{-7} Torr.

The Knudsen cell assembly consisted of a tantalum outer cell with an alumina inner cell which holds the approximately 1 g of the alloy sample. The dimensions of the alumina inner cell were 11 mm in O.D., 9 mm in I.D. and 7 mm in height, with the lid thickness of 0.5 mm and the orifice diameter of mostly 0.3 mm. In some measurements, the orifice diameter of 0.5 mm was also employed. Heating of the Knudsen cell was mainly made by means of electric resistance heating with two sets of tungsten ring heaters. In some of experimental runs above 1523 K, heating of the cell was done by electron bombardment between the tungsten filaments and the cell. The temperature of the Knudsen cell was measured by two sets of Pt-13pct Rh/Pt thermocouples which were respectively placed in two holes drilled at the bottom of the tantalum outer cell with different depth. Calibration of the thermocouple was periodically performed by wire bridge

technique using Au.

Weighed Cu and Al metals at the aimed composition were charged in the alumina inner cell, and the whole Knudsen cell assembly was positioned 5 to 6 cm below the ionizing region of the mass spectrometer and was adjusted horizontally to maximize the flux of particles into the ion source by maximizing the ion currents. The cell was then heated to above the liquidus temperature and held for 10–15 min at the aimed temperature to allow melting and homogenization of the alloy. Control of the current for tungsten heater and electron bombardment was achieved manually to adjust the temperature of the cell. The ion currents at desired principal mass peaks (27 of Al and 63 of Cu) were monitored on the CRT of a personal computer and recorded on a calibrated chart recorder. The experimental temperature was alternatively decreased and increased between the maximum and the minimum at given alloy compositions. The holding time of 10 min at each temperature was found to be sufficient to obtain constancy of ion current and the measurement was completed within 4 h. It was also confirmed that the ion current ratios were essentially independent of ionizing potential (15–40 eV), individual ion currents, the multiplier gain and the electron bombardment current. Ion current was in the range from 10^{-15} to 10^{-8} A with the relative scattering of $\pm 2\%$. After the measurement, the sample was cooled down to room temperature in the mass spectrometer and was supplied for chemical analysis. Electron microprobe examination detected no significant inhomogeneity in the solidified alloy samples.

III. Results and Discussion

The ion current ratios observed for various compositions of the liquid Cu–Al alloys are presented in **Fig. 2** as a plot of $\ln(I_{\text{Cu}}^+/I_{\text{Al}}^+)$ against the reciprocal of absolute temperature, where I_i^+ denotes the ion current intensity of a mass filter proportional to the partial pressure of the component *i* in the Knudsen cell containing the liquid alloy. At $X_{\text{Cu}} = 0.307$, some additional experiments were conducted using a different orifice diameter, 0.5 mm. As can be seen from **Fig. 2**, no variation in ion current ratio with the orifice diameter was detected. The ion current ratio $\ln(I_{\text{Cu}}^+/I_{\text{Al}}^+)$ decreased with decreasing copper content in the alloy at a constant temperature. The logarithmic ion current ratio at each alloy composition was found to be an almost linear function of $1/T$ in the whole range of the experimental temperatures investigated. Derived temperature functions of ion current are listed in **Table 1**. **Figure 3** represents $\ln(I_{\text{Cu}}^+/I_{\text{Al}}^+)$ at 1473 K calculated from the temperature function in **Table 1** vs. mole fraction of copper in the alloy. The ion current ratio changed smoothly with the varying alloy composition.

Belton and Fruehan⁽¹⁶⁾⁽¹⁷⁾ have introduced a method to determine the activities from the measured ion current ratios of two monoatomic vapors in equilibrium with a binary alloy by substituting the ratio for the activity term in the Gibbs-Duhem relation.

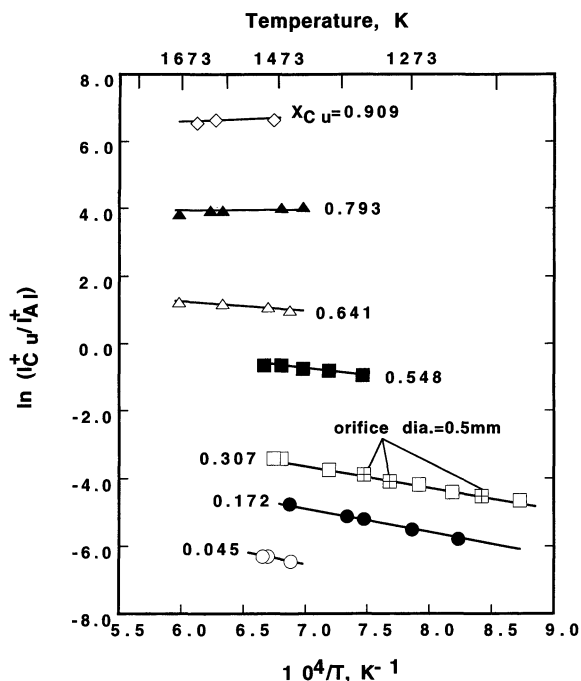


Fig. 2 Ion current ratios as a function of reciprocal temperature in the Cu-Al system. (Orifice diameter was 0.03 mm except for some runs at $X_{Cu}=0.307$)

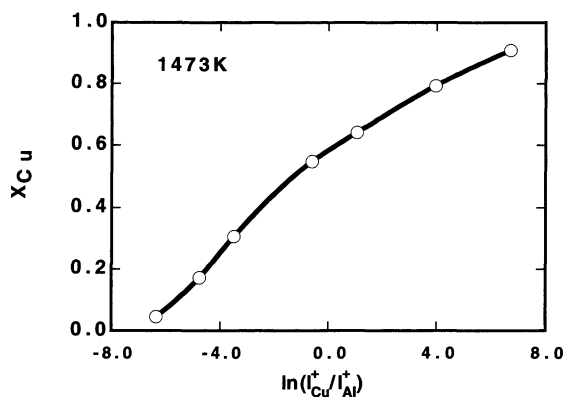


Fig. 3 Variation of ion current ratios with composition for the Cu-Al system at 1473 K.

Table 1 Temperature dependence of ion current ratios at various compositions of the Cu-Al system.

X_{Cu}	$\ln(I_{Cu}^+/I_{Al}^+)$
0.045	$-7460/T - 1.30$
0.172	$-7000/T + 0.02$
0.307	$-6390/T + 0.84$
0.548	$-4485/T + 2.42$
0.641	$-2740/T + 2.92$
0.793	$190/T + 3.83$
0.909	$1430/T + 5.74$

$$\ln \gamma_1 = - \int_{X_1=1}^{X_1=X_1} X_2 d[\ln(I_2^+/I_1^+) - \ln(X_2/X_1)] \quad (4)$$

The values of $\ln(I_2^+/I_1^+) - \ln(X_2/X_1)$ derived from the

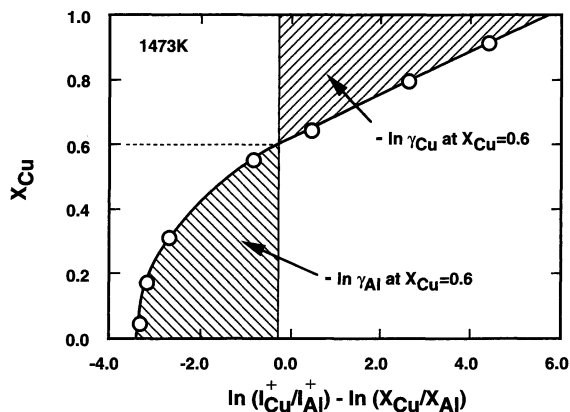


Fig. 4 Integration plot for determination of the activity coefficients of constituents in the Cu-Al system at 1473 K.

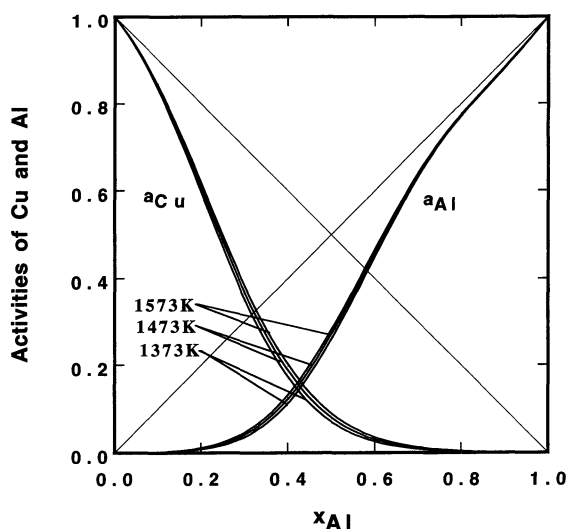


Fig. 5 Activities in the Cu-Al system at 1373, 1473 and 1573 K.

each temperature function of the ion current presented in Table 1 are plotted against the composition in Fig. 4. The graphical integration of areas under and above the curve in Fig. 4 yields $\ln \gamma_{Al}$ and $\ln \gamma_{Cu}$, respectively, according to eq.(4). For example, the shaded areas in Fig. 4 correspond to the values of $-\ln \gamma_{Al}$ and $-\ln \gamma_{Cu}$ at $X_{Cu}=0.6$, respectively. The activities of the constituents in the liquid Cu-Al system were evaluated at 1373, 1473 and 1573 K in such a manner and are presented as a function of composition in Fig. 5. The activities exhibits large negative deviation from ideality over the entire composition range and this deviation becomes slightly smaller at a higher temperature.

The activity coefficients of aluminum determined in the present work are compared with the literature data as the plot of $RT \ln \gamma_{Al}$ against $(1-X_{Al})^2$ in Fig. 1. As it was mentioned earlier, the accuracy of γ_{Al} in the dilute concentration range of aluminum is the most important for our another experiment on the determination of the alumina activity in the slag. The values of the activity coefficient of aluminum determined in the present work are in excellent agreement with recommended values by Hultgren

et al.⁽¹³⁾ over the entire composition range of the liquid Cu–Al system. Chou and Chao⁽⁷⁾ determined γ_{Al} at $X_{\text{Al}}=0.031$ and 1873 K by the equilibrium of liquid copper with the alumina-saturated slag. Their results are in good agreement with ours. Grube and Hantelman⁽¹⁾ and Wilder⁽²⁾ determined the activity of aluminum in liquid copper by EMF measurements, and Layner *et al.*⁽⁶⁾ observed it by vapor pressure measurements. The results of the present work also agree well with the values observed by them in a high aluminum concentration range. However, much higher values are reported by Layner *et al.* in a low concentration range of aluminum. The term of $RT \ln \gamma_{\text{Al}}$ in the present work was calculated at 1373, 1473 and 1573 K as plotted in Fig. 1. It can be seen from this figure that the values of $RT \ln \gamma_{\text{Al}}$ at a constant alloy composition slightly depend on the temperature. However, with the experimental error taken into account, they would be approximated by a single smooth curve, indicating that the term of $RT \ln \gamma_{\text{Al}}$ is almost independent of the temperature within the experimental range of the present work. The activity coefficient of Al can be reasonably estimated by assuming $RT \ln \gamma_{\text{Al}} = \text{constant}$ at given composition as shown in Fig. 1. The value of $RT \ln \gamma_{\text{Cu}}$ was also confirmed as being almost independent of temperature at a constant alloy composition. **Table 2** gives the comparison of the activity coefficient of aluminum at infinite dilution in liquid copper with the literature values. Perakis *et al.*⁽⁵⁾ measured the activities in liquid Cu–Al alloy by mass spectrometry. Their results of γ_{Al}^0 are also listed in Table 2. The values of γ_{Al}^0 determined in the present work are approximately two times larger than those of Perakis *et al.* at the same temperature.

Belton and Fruehan⁽¹⁶⁾⁽¹⁷⁾ also derived the relation between ion current ratio and the partial molar heat of mixing of the component as follows,

$$\Delta \bar{H}_1 = -R \int_{X_1=1}^{X_1=X_1} X_2 d[\ln(I_2^+/I_1^+)/d(1/T)] \quad (5)$$

where, $\Delta \bar{H}_1$ and R are the partial molar heat of mixing of the component 1 and a gas constant, respectively. The partial molar heats of mixing of the components in the Cu–Al system were determined through eq. (5) by graphical integration of the slopes of ion current against $1/T$ which are given in Table 1. **Figure 6** represents the plot

Table 2 Comparison of the activity coefficient of aluminum at infinite dilution in liquid copper.

Authors	Ref.	γ_{Al}^0
Wilder	2	0.0055 (1373 K)
Layner <i>et al.</i>	6	0.010 (1373 K)
Perakis <i>et al.</i>	5	0.0012 (1373 K) 0.0019 (1473 K)
Hultgren <i>et al.</i>	13	0.002 (1373 K)
Present work		0.0020 (1373 K) 0.0032 (1473 K) 0.0045 (1573 K)

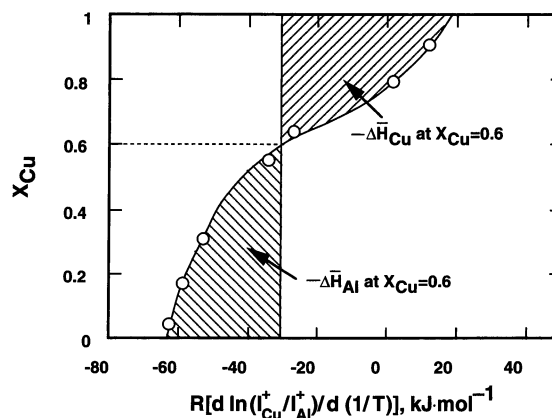


Fig. 6 Integration plot for determination of the partial molar heat of mixing in the Cu–Al system.

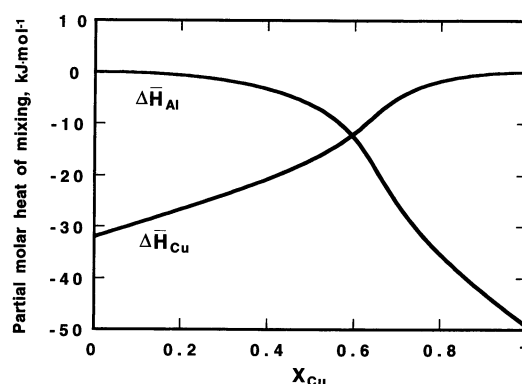


Fig. 7 Partial molar heat of mixing in the Cu–Al system.

of $R[d \ln(I_{\text{Cu}}^+/I_{\text{Al}}^+)/d(1/T)]$ against copper concentration in the alloy. Integration of the smooth curve drawn through the data in Fig. 6 yields the values presented graphically in **Fig. 7**. The partial molar heats of mixing of aluminum and copper exhibited negative over the whole composition range of the Cu–Al system. Integral heat of mixing of the Cu–Al system, ΔH_{mix} , is also evaluated by eq. (6) and is plotted in **Fig. 8** together with the available literature data^{(8)–(11)(13)}.

$$\Delta H_{\text{mix}} = \Delta \bar{H}_{\text{Al}} X_{\text{Al}} + \Delta \bar{H}_{\text{Cu}} X_{\text{Cu}} \quad (6)$$

The integral heat of mixing of Cu–Al alloy evaluated in the present work is the exothermic in the whole composition range and the maximum value of approximately -12.2 kJ/mol is observed at around $X_{\text{Cu}}=0.6$. The maximum exothermic value has also been observed at this composition by other investigators. The heats of mixing directly observed by Itagaki and Yazawa⁽¹⁰⁾ and recommended by Hultgren *et al.*⁽¹³⁾ are slightly less negative than that of the present work, but such a difference might be acceptable. On the other hand, Kawakami⁽⁸⁾, Sandakov *et al.*⁽⁹⁾ and Stolz *et al.*⁽¹¹⁾ reported more exothermic values of heat of mixing than the present result. The difference in the maximum exothermic value by mixing is approximately 5 to 9 kJ/mol at $X_{\text{Cu}}=0.6$.

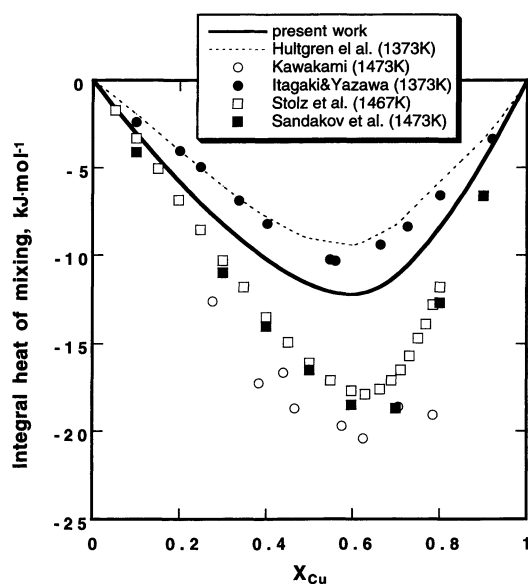


Fig. 8 Integral heat of mixing in the Cu–Al system.

IV. Conclusions

The activities of Cu and Al in liquid Cu–Al alloy have been determined by mass spectrometry in the temperature range from 1146 to 1673 K. The following conclusions can be obtained.

(1) The activities exhibit negative deviation from ideality and this deviation becomes slightly smaller at higher temperature.

(2) The activities observed in the present work are in good agreement with those recommended by Hultgren *et al.*

(3) Partial molar heats of mixing of Al and Cu, and

the integral heat of mixing of Cu–Al alloy are determined. The integral heat of mixing shows the maximum exothermic value of approximately -12.2 kJ/mol at around $X_{Al}=0.6$.

Acknowledgment

The authors are grateful to Dr. Mitsuhiro Hino, Associate Professor, Research Institute of Advanced Materials and Processing, Tohoku University, for useful suggestions to modify mass-spectrometer.

REFERENCES

- (1) G. Grube and F. Hantelman: *Z. Electrochem.*, **48** (1942), 399.
- (2) T. C. Wilder: *Trans. Met. Soc. AIME*, **233** (1965), 1202.
- (3) H. Mitani and H. Nagai: *J. Jpn. Metal Soc.*, **33** (1969), 344.
- (4) G. I. Batalin, E. A. Beloborodova and V. N. Vasil'ev: *Ukr. Khim. Zh.*, **38** (1972), 920.
- (5) J. Perakis, C. Chatillon and A. Pattoret: *Compt. Rend. Acad. Sci. Paris, Ser. C*, **276** (1973), 1513.
- (6) D. I. Layner, L. M. Ostrovskaya and O. S. Serebryannikova: *Izv. Akad. Nauk SSSR. Met.*, **15** (1976), 15.
- (7) Y.-H. Chou and P.-N. Chao: *J. China Metal Soc.*, **18** (1969), 137.
- (8) M. Kawakami: *Sci. Rept. Tohoku Univ.*, **19** (1930), 521.
- (9) V. M. Sandakov, Y. O. Esin, P. V. Geld and V. D. Shantarin: *Russ. J. Phys. Chem.*, **45** (1971), 1150.
- (10) K. Itagaki and A. Yazawa: *Trans. JIM*, **16** (1975), 679.
- (11) U. K. Stolz, I. Arpshofen, F. Sommer and B. Predel: *J. Phase Equilibria*, **14** (1993), 473.
- (12) J. L. Murray: *Int. Met. Rev.*, **30** (1985), 211.
- (13) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelly: *Selected Value of the Thermodynamic Properties of Binary Alloys*, ASM, Metal Park, U.S.A., (1973), 151.
- (14) M. Hino, S. Kinoshita, Y. Ehara, H. Itoh and S. Ban-ya: *Proc. of 5th Int. Conf. on Molten Slags, Fluxes and Salts*, Sydney, Australia, The Iron and Steel Society, Warrendale, PA, (1997), 53.
- (15) K. Fujii, T. Nagasaka and M. Hino: to be published in *J. Am. Ceram. Soc.*
- (16) G. R. Belton and R. J. Fruehan: *J. Phys. Chem.*, **71** (1967), 1403.
- (17) G. R. Belton and R. J. Fruehan: *Metall. Trans.*, **1** (1970), 781.