Phase Relations and Activities in the Fe-Ni-As and Fe-Ni-Sb Systems at 1423 K

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Arsenic and antimony activities in the Fe-Ni-As and Fe-Ni-Sb ternary systems were measured at 1423 K by an isothermal isopiestic method to obtain fundamental information about the behaviour of arsenic and antimony in processing intermediate products, nickel arsenide or antimonide ores. Phase relations between the solid solution and liquid phase in a region of dilute arsenic or antimony in these systems were determined at 1423 K with a quenching technique. The isoactivity lines of arsenic in the homogeneous liquid phase were almost parallel to the Ni-Fe axis of Fe-Ni-As ternary composition diagram, while those of antimony represented a negative gradient due to stronger chemical affinity of antimony to nickel as compared to iron. The iron and nickel activities in these ternary systems were derived from the measured arsenic or antimony activity and the determined phase relations. The Redlich-Kister-Muggianu polynomial formula was successfully applied to express the activities as a function of alloy compositions. Based on the obtained data, the total pressures of arsenic and antimony gas species were evaluated to discuss the possibility to recover or eliminate arsenic and antimony from the alloys by means of volatilization.

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1. Introduction

Thermodynamic data for the Fe-Ni-As and Fe-Ni-Sb systems at high temperature are of importance in a discussion about formation of a speiss phase to recover valuable or detrimental elements in the intermediate products such as sludge, dross, dust and slag produced in nonferrous smelting processes as well as various kinds of ash produced in incinerators, which contain arsenic or antimony along with iron and nickel as major components. Such data will also be useful for smelting nickel arsenide and antimonide ores such as Niccolite (NiAs) and Breithauptite (NiSb), which will be important resources of nickel in the near future, while the present sulfide ores are being depleted.

Although activities in the binary Fe-As and Ni-As systems and the binary Fe-Sb and Ni-Sb systems were determined at 1423 K by one of the authors, no data have been reported for the ternary Fe-Ni-As and Fe-Ni-Sb systems. Hence, in the present study, arsenic and antimony activities in these systems were measured by using an isothermal isopiestic method at 1423 K. Phase relations in the range of dilute arsenic and antimony in these systems were also studied at 1423 K to determine tie-lines connecting between the Fe-Ni solid solution and liquid phases. The iron and nickel activities were calculated from the measured arsenic or antimony activity and the determined phase relations on the basis of the Gibbs-Duhem integration method which was proposed by Darken. The Redlich-Kister-Muggianu polynomial formula was applied to these ternary systems to regressively express integral and partial molar free energies of mixing as a function of mole fractions of the alloying elements.

2. Experimental Method and Procedure

2.1 Determination of two phase region

A quenching method combined with the metallographic and EPMA techniques was adopted to determine the phase equilibrium between solid solution and liquid phases which extend from the Fe-Ni binary system.

A sample of total 1.5 g comprising pure iron, nickel and arsenic or antimony with more than 99.9 mass% purity was charged with the compositions close to the liquidus line, which was anticipated from the constituted binary diagrams, and then vacuum sealed in a quartz tube. The ternary alloy sample, after once heated at 1473 K for 1.8 ks, was held at the experimental temperature of 1423 K for 43.2 ks and then quenched in a water vessel. No reaction was made between the sample and the quartz tube. The solidified sample was examined with an optical microscope to determine the liquidus line. The microstructure of a sample quenched from the homogeneous liquid region showed typical dendrites, while considerably large primary crystals were observed in the alloy sample quenched from the region where the solid and liquid phases coexisted at the experimental temperature. Hence, in the present study, the liquidus line was evaluated by searching the appearance or disappearance of the grown primary crystals by slightly altering the charge composition by 2 atomic % in each experimental run.

The contents of iron, nickel and arsenic or antimony in the primary crystals were determined by electron probe micro analysis (EPMA). The line analysis in the cross section of the crystal revealed that the concentrations of these components were even in the whole cross section. This means that the solid solution was equilibrated with the liquid phase at the experimental temperature. Once the equilibration was confirmed, the line analysis was made for the sample where the primary crystals just appeared in the microstructure. Based on the results obtained for the liquidus line and the compositions of solid solution, an overall evaluation was made to determine the tie lines connecting between the liquid and solid solution phases.

2.2 Determination of activity

An isothermal isopiestic method was applied to the activity measurement of arsenic and antimony in the ternary systems.
in the present study. The Fe-Ni-As system is used as a representative example to explain the experimental apparatus and procedures. The schematic diagram of an isopiestic cell adopted in the present experiments is illustrated in Fig. 1. The pre-melted and homogenized Fe-As and Ni-As binary alloys, and three Fe-Ni-As ternary alloys with different $N_{Fe}/N_{Ni}$ ratios of 3/1, 1/1 and 1/3 were sealed in vacuum in the quartz isopiestic cell of 0.09 m length and 0.026 m ID. Thereafter, the cell was kept at the experimental temperature of 1423 K. It was reported by one of the authors\(^5\) that the equilibration was made in 605 ks for determination of the arsenic activity in the Cu-Ni-As system, which was done in the same experimental condition as in the present study. Hence, the cell was heated for 605 ks in the present experiments, and thereafter quenched in a water vessel. The nickel, iron and arsenic contents of the solidified alloys were determined by Inductively Coupled Plasma Spectrometry (ICP).

As the vapour pressures of iron and nickel over the alloys are negligibly small compared to that of arsenic, the five alloy samples are saturated with the vapour pressure of arsenic in the cell and the activity of arsenic in each alloy is equal at the equilibrium condition. Thus, if the activity of arsenic in any one of the samples is known as a reference, the arsenic activity of other samples can be determined. In the present study, the Ni-As and Ni-Sb binary alloys, whose activities at 1423 K were reported by one of the authors\(^1\)\(^-\)\(^2\) using a non-isothermal isopiestic method and a transpiration method, respectively, were used as the reference for the Fe-Ni-As and Fe-Ni-Sb systems, respectively.

3. Results and Discussion

3.1 Phase relations between solid solution and liquid phases

Solidus and liquidus lines as well as tie lines connecting between the solid solution and liquid phases in the Fe-Ni-As and Fe-Ni-Sb ternary systems at 1423 K are illustrated in Figs. 2 and 3, respectively. It is noted in Fig. 2 that the liquidus and solidus lines in the Fe-Ni-As system are almost parallel to the bottom Ni-Fe axis with the solubility limits of $N_{As} = 0.17 \sim 0.19$ and $N_{As} = 0.05 \sim 0.06$, respectively. The obtained liquidus and solidus compositions in the Fe-As and Ni-As binary systems agree well with the reported values\(^6\)\(^-\)\(^7\) within 1 atomic % As. On the other hand, as shown in Fig. 3, the liquidus composition in the Fe-Ni-Sb system increases with increasing iron content, while the solidus line represents a concave against the bottom Fe-Ni axis. The obtained liquidus and solidus compositions in the Fe-Sb binary system agree well with the reported values.\(^8\) However, those in the Ni-Sb binary system with the values of $N_{Sb} = 0.17$ and 0.07, respectively, differ considerably from the reported values\(^9\) of $N_{Sb} = 0.21$ and 0.09, respectively.

3.2 Activities of alloying elements

The activities of arsenic and antimony and the isoactivity lines in the Fe-Ni-As and Fe-Ni-Sb systems at 1423 K are shown in Figs. 2 and 3, respectively. Pure liquid arsenic and antimony are the reference of these activities. It is noted in Fig. 2 that the arsenic activity represents a large negative
deviation from the Raoultian behaviour and that the isoactivity lines are almost parallel to the bottom Fe-Ni axis, obeying the additivity rule between the Fe-As and Ni-As binaries. These results suggest that arsenic has a very strong chemical affinity to iron and nickel in the alloy and that the affinity between arsenic and iron is similar to that between arsenic and nickel, as denoted by large negative heats of formation of Fe$_2$As and Ni$_5$As$_2$ compounds.\textsuperscript{10}

As shown in Fig. 3, the antimony activity also represents a negative deviation from the Raoultian behaviour but the deviation is not so significant when compared with that of the arsenic activity. The isoactivity lines have a negative gradient against the iron content. This indicates that the antimony activity at a specified antimony composition increases with increasing iron content in the Fe-Ni-Sb system. This behaviour may suggest that the chemical affinity of antimony for nickel is stronger than that for iron.

The activities of iron and nickel in the Fe-Ni-As and Fe-Ni-Sb systems at 1423 K were derived from the measured arsenic and antimony activities and the determined phase relations between the solid solution and liquid phases in the ranges of dilute arsenic and antimony by using the Gibbs-Duhem integration method which was proposed by Darken.\textsuperscript{3} The data of iron and nickel activities on the solidus line are required for this integration. For lack of the experimental data at 1423 K, they were evaluated in the following way. First, the activity data in the Fe-Ni binary system at 1873 K reported by Hultgren \textit{et al.}\textsuperscript{11} were extrapolated to 1423 K by using the regular solution model where $\log \gamma_1$ is constant with $y_1$, the Raoultian activity coefficient. Then, the activities of iron and nickel in the ternary solid solution were estimated by assuming that these decrease linearly with the arsenic or antimony content. This assumption may be acceptable because arsenic and antimony are very dilute in the solid solution.

The calculated isoactivity lines of iron in the Fe-Ni-As and Fe-Ni-Sb systems at 1423 K are shown in Figs. 4 and 5, while those of nickel in Figs. 6 and 7, respectively. Here, pure iron and nickel are the reference of iron and nickel activities. The isoactivity lines illustrated with dashed lines in these figures were obtained on the basis of a polynomial expression as described in the following section. As shown in Figs. 4 and

![Fig. 4 Isoactivity lines of iron obtained by the Gibbs-Duhem integration method in the Fe-Ni-As system at 1423 K (---- isoactivity lines calculated from the polynomial expression).](image-url)

![Fig. 5 Isoactivity lines of iron obtained by the Gibbs-Duhem integration method in the Fe-Ni-Sb system at 1423 K (---- isoactivity lines calculated from the polynomial expression).](image-url)

![Fig. 6 Isoactivity lines of nickel obtained by the Gibbs-Duhem integration method in the Fe-Ni-As system at 1423 K (---- isoactivity lines calculated from the polynomial expression).](image-url)

![Fig. 7 Isoactivity lines of nickel obtained by the Gibbs-Duhem integration method in the Fe-Ni-Sb system at 1423 K (---- isoactivity lines calculated from the polynomial expression).](image-url)
5, the isactivity lines of iron represent a considerably steep gradient against the iso mole fraction lines of iron in its higher composition range. This may be ascribed to the difference in the chemical affinity of iron between nickel and arsenic or antimony. The chemical affinity to arsenic or antimony is considered to be much stronger than that with nickel because the Fe-As and Fe-Sb systems make compounds while the Fe-Ni system a solid solution with a considerably wide solubility range. As shown in Figs. 6 and 7, the isactivity lines of nickel also represent a considerably steep gradient against the iso mole fraction lines of nickel. This may be also ascribed to the large difference in the chemical affinity of nickel between iron and arsenic or antimony.

3.3 Polynomial expression

It will be very helpful in use of the thermodynamic data on the multi component systems if they are properly expressed as a function of the alloy compositions. Hence, the data obtained in the present experiments were regressed analytically on the basis of the Redlich-Kister-Muggianu polynomial formula for the integral molar excess free energy of mixing in the 1-2-3 ternary systems, as given by eq. (1). Then, the partial molar excess free energy of mixing for the component $i$ is derived from eq. (2).

$$G_{123}^{ex} = x_1x_2L_{12}^{(0)} + x_1x_3L_{13}^{(0)}(x_1 - x_2)$$
$$+ x_1x_2L_{12}^{(1)} + x_1x_3L_{13}^{(1)}(x_1 - x_3)$$
$$+ x_2x_3L_{23}^{(0)} + x_2x_3L_{23}^{(1)}(x_2 - x_3)$$
$$+ x_1x_2x_3[v_1L_1 + v_2L_2 + v_3L_3]$$

$$G_{i}^{ex} = G_{123}^{ex} + (1 - x_i) \left( \frac{\partial G_{123}^{ex}}{\partial x_i} \right)_{x_j/x_k}$$

where $x_i$ is the composition of component $i$ in mole fraction, $L_{ij}^{(n)}$ is the $(n + 1)$th Redlich-Kister coefficient of the binary subsystem $i-j$, $L_1$, $L_2$, and $L_3$ are coefficients of the $i-j-k$ ternary system and $v_i = x_i/(x_i + x_j + x_k)$.

The regression analysis was made using a FACT-SAGE software (GTT-Technologies, Aachen, Germany). $L^{(0)}$ and $L^{(1)}$ were firstly determined, basing on the experimental data for each binary, then, the ternary parameters of $L_1$, $L_2$ and $L_3$ were evaluated. The determined values of the parameters in eq. (1) are listed in Table 1. As shown with the dashed lines in Figs. 2 and 3, the calculation can very well reproduce the experimentally determined isactivity lines of arsenic and antimony, respectively. Furthermore, as shown with the dashed lines in Figs. 4 and 5, and Figs. 6 and 7, respectively, the calculated isactivity lines of iron and nickel in the Fe-Ni-As and Fe-Ni-Sb systems are very close to those determined by using the Gibbs-Duhem integration method. Hence, it is considered that the thermodynamic optimization for the Fe-Ni-As and Fe-Ni-Sb ternary systems will be possible by using the Redlich-Kister-Muggianu polynomial formula if the data on the activities and the phase relations at other temperatures are provided.

3.4 Vapour pressures of arsenic and antimony

Vapour pressures of volatile elements in alloys are of importance as the fundamental data for recovering or eliminating the valuable or detrimental components by means of volatilization. Hence, the vapour pressures of arsenic and antimony in the Fe-Ni-As and Fe-Ni-Sb systems at 1423 K were evaluated in the present study. It is known that the predominant gas species of arsenic are As$_2$, As$_4$, As$_8$, As$_{13}$ and As$_{31}$, while those of antimony Sb$_2$, Sb$_3$ and Sb$_{13}$. Hence, the total pressures of arsenic and antimony, $p_{As}$ and $p_{Sb}$, are given by eqs. (3) and (4), respectively.

$$p_{As} = p_{As_2} + p_{As_4} + p_{As_8} + p_{As_{13}}$$ (3)
$$p_{Sb} = p_{Sb_2} + p_{Sb_3} + p_{Sb_{13}}$$ (4)

By using the equilibrium constants for the reactions to make the gaseous species from pure liquid arsenic and antimony at 1423 K and combining the activity values of arsenic and antimony as derived by eqs. (1) and (2), the iso total pressure lines of arsenic and antimony in the liquid Fe-Ni-As and Fe-Ni-Sb systems at 1423 K were calculated and the results are shown in Fig. 8 with solid and dashed lines, respectively. As shown in Fig. 8, $p_{As}$ at a considerably high content of arsenic around $N_{As} = 0.4$ is an order of $10^{4}$ Pa, while about $10$ Pa in a region near the solidus line. It is suggested by Kellogg that vaporization of an alloying

<table>
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<tr>
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<th>$L^{(0)}$</th>
<th>$L^{(1)}$</th>
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<tr>
<td>Fe-As</td>
<td>-57.64</td>
<td>19.61</td>
</tr>
<tr>
<td>Ni-As</td>
<td>-172.21</td>
<td>22.56</td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>12.43</td>
<td>1.06</td>
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<tr>
<td>Fe-Sb</td>
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<td>2.19</td>
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<td>Ni-Sb</td>
<td>-47.21</td>
<td>9.97</td>
</tr>
<tr>
<td>Fe-Ni-As</td>
<td>2.11</td>
<td>-59.33</td>
</tr>
<tr>
<td>Fe-Ni-Sb</td>
<td>-40.61</td>
<td>-142.31</td>
</tr>
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Table 1 Coefficients of the Redlich-Kister-Muggianu polynomial formula for the excess free energy of mixing (kJ/mol) in the Fe-Ni-As and Fe-Ni-Sb ternary systems at 1423 K.
element in a gas stream will be rapid when the vapor pressure exceeds $10^4 \text{ Pa}$, while slow when the pressure is less than $10^3 \text{ Pa}$. According to this criterion, the elimination of arsenic by means of volatilization will be difficult for the Fe-Ni-As alloys having the compositions near the solidus line. Hence, use of vacuum will be required for these alloys to enhance the volatilization. On the other hand, $P_{\text{As}}$ is still low at about $10^3 \text{ Pa}$ even in a high region of the antimony content around $N_{\text{Sb}}$ of 0.6 and the elimination of antimony by means of volatilization will be difficult when compared with arsenic.

4. Conclusions

In order to obtain fundamental data that are required in the discussion of arsenic and antimony behaviours in processing intermediate products, nickel arsenide or antimonide ores, arsenic and antimony activities in the Fe-Ni-As and Fe-Ni-Sb systems were measured at 1423 K by an isopiestic method. Phase relations between solid solution and liquid phases extending from the Fe-Ni binary system were also determined for the same ternary systems at 1423 K by a quenching method combined with the metallographic and EPMA techniques.

The arsenic activities in the Fe-Ni-As ternary system agree with the additivity rule between the Fe-As and Ni-As binaries, while the antimony activities in the Fe-Ni-Sb ternary system exhibit negative deviation from the additivity rule in the homogeneous liquid phase. The determined activities were regresively expressed in the Redlich-Kister-Muggianu polynomial formula.

On the basis of obtained activity data, the total pressures of arsenic and antimony species were evaluated and the possibility of recovering or eliminating arsenic and antimony in the alloys by means of volatilization was discussed.

REFERENCES