論 文
Original Paper

Phase Relations and Activities in the Fe-Co-As and Fe-Co-Sb Systems at 1150°C[*]

by Leandro VOISIN[1], Mitsuhisa HINO[2] and Kimio ITAGAKI[3]

Arsenic and antimony activities in the Fe-Co-As and Fe-Co-Sb ternary systems were measured at 1150°C by an isothermal isopiestic method to obtain fundamental information about the behavior of arsenic and antimony in processing intermediate products and cobalt arsenide or antimonide ores. Phase relations between the solid solution and liquid phases in a region of dilute arsenic or antimony in these systems were also determined at 1150°C with a quenching technique. The isoactivity lines of arsenic in the homogeneous liquid phase were almost parallel to the Co-Fe axis of the Fe-Co-As ternary composition diagram, while those of antimony represented a negative gradient due to stronger chemical affinity of antimony to cobalt as compared to iron. The iron and cobalt 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.

KEY WORDS : Phase Relation, Activity, Iron-Cobalt-Arsenic System, Iron-Cobalt-Antimony System, Isopiestic Method

1. Introduction

Thermodynamic data for the Fe-Co-As and Fe-Co-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 cobalt as major components. Such data will also be useful for smelting cobalt arsenide and antimonide ores such as Safflorite (($Fe,Co)As_2$) and Alloclasite (($Fe,Co)(Sb,Bi)S$), which will be important resources of cobalt in the near future, while the present sulfide ores are being depleted.

Although activities in the binary Fe-As system[1] and the binary Fe-Sb and Co-Sb systems[2] were determined by one of the authors, no data have been reported for the ternary Fe-Co-As and Fe-Co-Sb systems. Hence, in the present study, arsenic and antimony activities in these systems were measured by using an isothermal isopiestic method at 1150°C. Phase relations in the range of dilute arsenic and antimony in these systems were also studied at 1150°C to determine tie-lines connecting between the Fe-Co solid solution and liquid phases. The iron and cobalt 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[3]. The Redlich-Kister-Muggianu polynomial formula[4] 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-Co binary system.

A sample of total 1.5 g comprising pure iron, cobalt and arsenic or antimony with more than 99.9 mass % purity was charged with the compositions close to the liquidus line, which was estimated from the constituted binary diagrams, and then vacuum sealed in a quartz tube. The ternary alloy sample, after once heated at 1200°C for 0.5 hr, was held at the experimental temperature of 1150°C for 12 hrs and then quenched in a water vessel. 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. In the present study, the liquidus line was evaluated by searching the appearance or disappearance of the grown primary crystals by slightly altering the composition by 2 atomic % along the path that connects the points in each experimental run.

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The contents of iron, cobalt 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-Co-As system is used as a representative example to explain the experimental apparatus and procedures. The schematic diagram of an isopiestic ampoule adopted in the present experiments is illustrated in **Fig.1**. The pre-melted and homogenized Fe-As and Co-As binary alloys, and three Fe-Co-As ternary alloys with N_{Fe}/N_{Co} mole fraction ratios of 3/1, 1/1 and 1/3 were sealed in vacuum in the quartz isopiestic ampoule of 9 cm length and 2.6 cm ID. Thereafter, the cell was kept at the experimental temperature of 1150°C. It was reported by one of the authors[5] that the equilibration was made in 7days 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 7 days also in the present experiments, and thereafter quenched in a water vessel. The cobalt, iron and arsenic contents of the solidified alloys were determined by Inductively Coupled Plasma Spectrometry (ICP).

As the vapor pressures of iron and cobalt over the alloys are negligibly small compared to that of arsenic, the five alloy samples are saturated with the vapor pressure of arsenic in the ampoule 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 sa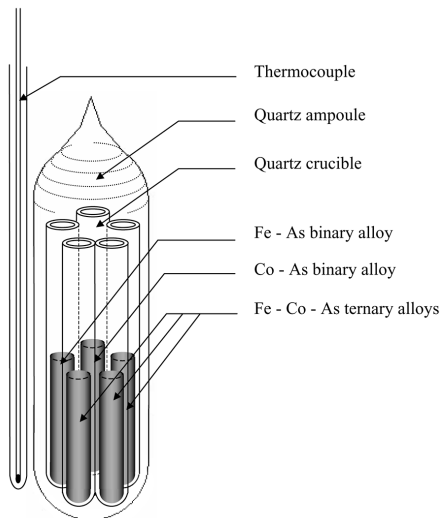mples can be determined. In the present study, the Fe-As and Fe-Sb binary alloys, whose activities were reported by one of the authors[1,2] using a non-isothermal isopiestic method and a transpiration method, respectively, were used as the reference for the Fe-Co-As and Fe-Co-Sb systems, respectively.

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-Co-As and Fe-Co-Sb ternary systems at 1150°C are illustrated in **Fig.2** and **Fig.3**, respectively. It is noted in Fig.2 that the liquidus and solidus lines in the Fe-Co-As system are almost parallel to the bottom Co-Fe axis with the solubility limits of $N_{As}=0.19 \sim 0.20$ and $N_{As}=0.05 \sim 0.06$, respectively. The obtained liquidus and solidus compositions in the Fe-As binary system agree well with the reported values[6] within 1 atomic % As. The obtained liquidus composition in the Co-As binary system also agrees well with the reported value[7], while the obtained solidus composition is 2.5 atomic % higher than the reported value[7]. On the other hand, as shown in Fig.3, the liquidus and solidus compositions in the Fe-Co-Sb system slightly increase with increasing iron content. The obtained liquidus and solidus compositions in the Fe-Sb and Co-Sb binary systems agree well with the reported values[8,9].

3・2 Activities of alloying elements

The activities of arsenic and antimony and the isoactivity lines in the Fe-Co-As and Fe-Co-Sb systems at 1150°C are shown in Figs.2 and 3, respectively. Pure liquid arsenic and antimony are the reference of these activities. It is noted in

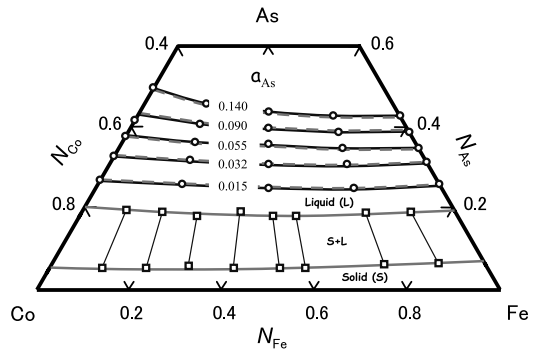Fig. 1 Schematic diagram of isopiestic ampoule.

Fig. 2 Phase relations and isoactivity lines of arsenic in the Fe-Co-As system at 1150°C (---- : isoactivity lines calculated from the polynomial expression).
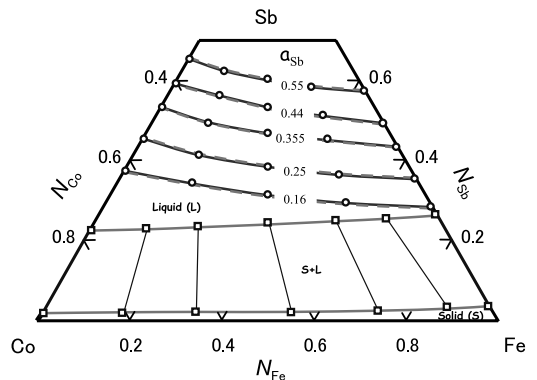

Fig. 3 Phase relations and isoactivity lines of antimony in the Fe-Co-Sb system at 1150°C (---- : isoactivity lines calculated from the polynomial expression).

Fig.2 that the arsenic activity represents a large negative deviation from the Raoultian behavior and that the isoactivity lines are almost parallel to the bottom Fe-Co axis, obeying the additivity rule between the Fe-As and Co-As binaries. These results suggest that arsenic has a very strong chemical affinity to iron and cobalt in the alloy and that the affinity between arsenic and iron is similar to that between arsenic and cobalt, as denoted by large negative heats of formation of Fe_2As and Co_5As_2 compounds[10].

As shown in Fig.3, the antimony activity also represents a negative deviation from the Raoultian behavior 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-Co-Sb system. This behavior may suggest that the chemical affinity of antimony for cobalt is stronger than that for iron.

The activities of iron and cobalt in the Fe-Co-As and Fe-Co-Sb systems at 1150°C 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 the Gibbs-Duhem integration method which was proposed by Darken[3]. The data of iron and cobalt activities on the solidus line are required for this integration. For the lack of experimental data at 1150°C, they were evaluated in the following way. First, the activity data in the Fe-Co binary system at 1590°C reported by Hultgren et al.[11] were extrapolated to 1150°C by the regular solution model

where $T \log \gamma$ is constant with γ, the Raoultian activity coefficient. Then, the activities of iron and cobalt in the ternary solid solution were estimated by assuming that these decrease linearly with the arsenic or antimony content. This assumption may be a good approximation because arsenic and antimony are very dilute in the solid solution.

The calculated isoactivity lines of iron in the Fe-Co-As and Fe-Co-Sb systems at 1150°C are shown in Fig.4 and Fig.5, while those of cobalt in Fig.6 and Fig.7, respectively. Here, pure solid iron and cobalt are the reference of iron and cobalt 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 5, the isoactivity 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 cobalt and arsenic or antimony. The chemical affinity of iron to arsenic or antimony is considered to be much stronger than that to cobalt because the Fe-As and Fe-Sb systems make compounds while the Fe-Co system a solid solution with a considerably wide solubility range. As shown in Figs.6 and 7, the isoactivity lines of cobalt also represent a considerably steep gradient against the iso mole fraction lines of cobalt. This may be also ascribed to the large difference in the chemical affinity of cobalt 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
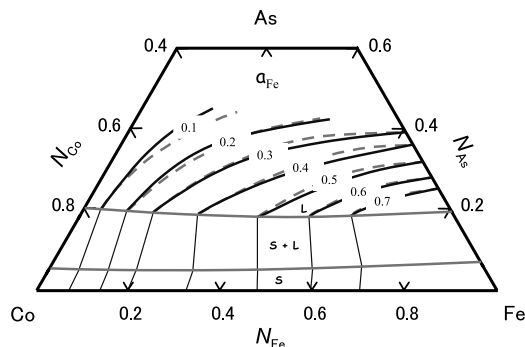

Fig. 4 Isoactivity lines of iron obtained by the Gibbs-Duhem integration method in the Fe-Co-As system at 1150°C (---- : isoactivity lines calculated from the polynomial expression).
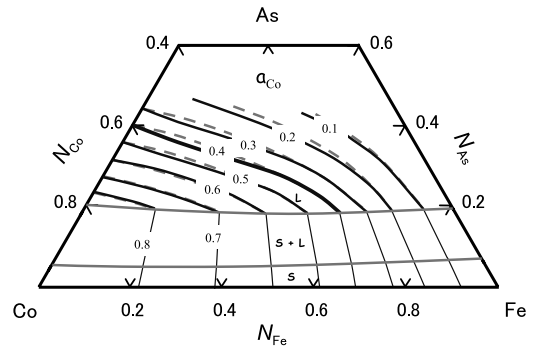

Fig. 6 Isoactivity lines of cobalt obtained by the Gibbs-Duhem integration method in the Fe-Co-As system at 1150°C (---- : isoactivity lines calculated from the polynomial expression).
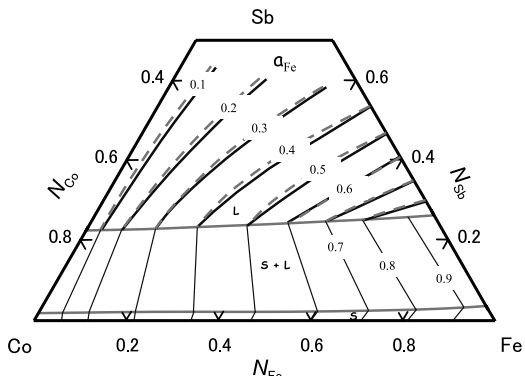

Fig. 5 Isoactivity lines of iron obtained by the Gibbs-Duhem integration method in the Fe-Co-Sb system at 1150°C (---- : isoactivity lines calculated from the polynomial expression).
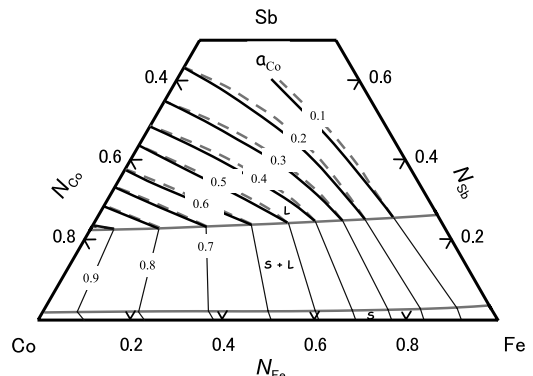

Fig. 7 Isoactivity lines of cobalt obtained by the Gibbs-Duhem integration method in the Fe-Co-Sb system at 1150°C (---- : isoactivity lines calculated from the polynomial expression).

as a function of the alloy compositions. Hence, the data obtained in the present experiments were regressively analyzed on the basis of the Redlich-Kister-Muggianu polynomial formula[4] for the integral molar excess free energy of mixing in the 1-2-3 ternary systems, G_{123}^{ex}, as given by eq. (1). Then, the partial molar excess free energy of mixing for the component i, $\bar{G}_i^{ex}$, is derived from eq. (2).

$$
\begin{aligned}
G_{123}^{ex} = {} & N_1 N_2 L_{12}^{(0)} + N_1 N_2 L_{12}^{(1)}(N_1 - N_2) \\
& + N_1 N_3 L_{13}^{(0)} + N_1 N_3 L_{13}^{(1)}(N_1 - N_3) \\
& + N_2 N_3 L_{23}^{(0)} + N_2 N_3 L_{23}^{(1)}(N_2 - N_3) \\
& + N_1 N_2 N_3 [\nu_1 L_1 + \nu_2 L_2 + \nu_3 L_3]
\end{aligned} \qquad (1)
$$

$$
\bar{G}_i^{ex} = G_{123}^{ex} + (1 - N_i)\left(\frac{\partial G_{123}^{ex}}{d N_i}\right)_{N_j / N_k} \qquad (2)
$$

where N_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 1-2-3 ternary system and $\nu_i = N_i / (N_1 + N_2 + N_3)$.

The regression analysis was made using the FACT-SAGE software (GTT -Technologies, Aachen, Germany). $L_i^{(0)}$ and $L_i^{(1)}$ 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 from the experimental information obtained for the ternary system. 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 isoactivity 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 isoactivity lines of iron and cobalt in the Fe-Co-As and Fe-Co-Sb systems are close to those determined by using the Gibbs-Duhem integration method. It is considered that the thermodynamic optimization for the Fe-Co-As and Fe-Co-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 Vapor pressures of arsenic and antimony

Vapor 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. Therefore, the vapor pressures of arsenic and antimony in the Fe-Co-As and Fe-Co-Sb systems at 1150°C were evaluated in the present study. As it is known[12] that the predominant gas species of arsenic are As, As_2, As_3 and As_4, while those of antimony Sb, Sb_2 and Sb_4, the total pressures of arsenic and antimony, $p_{As,t}$ and $p_{Sb,t}$, are given by eqs. (3) and (4), respectively.

$$
p_{As,t} = p_{As} + p_{As_2} + p_{As_3} + p_{As_4} \qquad (3)
$$

$$
p_{Sb,t} = p_{Sb} + p_{Sb_2} + p_{Sb_4} \qquad (4)
$$

Table 1 Coefficients of the Redlich-Kister-Muggianu polynomial formula for the excess free energy of mixing (kJ/mol) in the Fe-Co-As and Fe-Co-Sb ternary systems at 1150°C.

	$L^{(0)}$	$L^{(1)}$	
Fe - As	-57.64	19.61	
Co - As	-62.40	4.59	
Fe - Co	32.57	-2.16	
Fe - Sb	-12.31	2.19	
Co - Sb	-5.71	-15.33	
	L_1	L_2	L_3
Fe - Co - As	120.18	-181.74	-143.91
Fe - Co - Sb	99.61	-307.78	68.23

Using the equilibrium constants[12] for the reactions to make the gaseous species from pure liquid arsenic and antimony at 1150°C 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 Fe-Co-As and Fe-Co-Sb systems at 1150°C were calculated and the results are shown in Fig.8 with solid and dashed lines, respectively. As shown in Fig.8, $p_{As,t}$ at a considerably high content of arsenic around $N_{As} = 0.4$ is an order of 0.1 atm, while less than 10^{-3} atm in a region near the liquidus line. It is suggested by Kellogg[13] that vaporization of an alloying element in a gas stream will be rapid when the vapor pressure exceeds 0.1 atm, while low when the pressure is less than 10^{-3} atm. According to this criterion, the elimination of arsenic by means of volatilization will be difficult for the Fe-Co-As alloys having the compositions near the liquidus line. Hence, use of vacuum will be required for these alloys to enhance the volatilization. On the other hand, $p_{Sb,t}$ is still low at less than 10^{-2} atm even in a high region of the antimony content around N_{Sb} of 0.5 and the elimination of antimony by means of volatilization will be more difficult when compared with arsenic.

4. Conclusions

In order to obtain fundamental data that are required in the discussion of arsenic and antimony behaviors in processing intermediate products, cobalt arsenide or antimonide ores, the arsenic and antimony activities in the Fe-Co-As and Fe-Co-Sb systems were measured at 1150°C by the isopiestic method. Phase relations between solid solution and liquid phases extended from the Fe-Co binary system were also determined for the same ternary systems at 1150°C by the quenching method combined with the metallographic and EPMA techniques.

The arsenic activities in the Fe-Co-As ternary system agree with the additivity rule between the Fe-As and Co-As binaries, while the antimony activities in the Fe-Co-Sb ternary system exhibit negative deviation from the additivity rule in the homogeneous liquid phase. The determined activities were regressively 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.
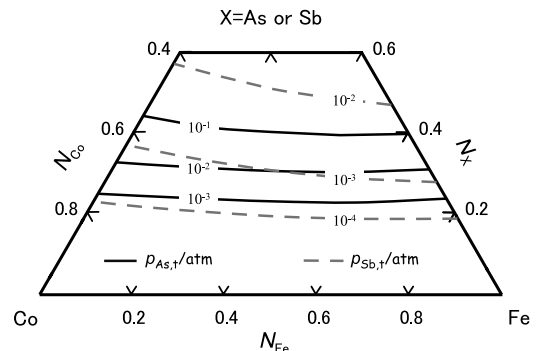

Fig. 8 Iso total pressure lines of arsenic (—) and antimony (----) in the liquid Fe-Co-As and Fe-Co-Sb systems at 1150°C ($p_{As,t}$/atm$= p_{As}$ $+ p_{As_2} + p_{As_3} + p_{As_4}$, $p_{Sb,t}$/atm$= p_{Sb} + p_{Sb_2} + p_{Sb_4}$).

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Fe-Co-As および Fe-Co-Sb 合金の 1150°C における相関係と成分活量

Leandro VOISIN[1]　　日　野　光　久[2]　　板　垣　乙　未　生[3]

　製錬中間産物やコバルトの砒化鉱石，アンチモン化鉱石の処理工程におけるヒ素やアンチモンの挙動解明の基礎的情報を得るため，Fe-Co-As および Fe-Co-Sb3 元系合金中の成分活量を等温等圧法によって 1150°C で測定した．また，ヒ素およびアンチモンの希薄組成域における固溶体と融体の相関係を急冷法によって1150°Cで決定した．その結果，Fe-Co-As 系の均一融体組成域におけるヒ素の等活量線が3元組成図の Co-Fe 組成軸にほぼ平行となること，しかし Fe-Co-Sb 系のアンチモンの等活量線は，コバルトに対するアンチモンの化学親和力が鉄に対する親和力に比べて大きいため，Co-Fe 組成軸に対して負の勾配を呈することなどが分かった．

　また，ヒ素およびアンチモンの活量データおよび相関係データに基づいて合金中の鉄およびコバルトの活量を導出し，Redlich-Kister-Muggianu の多項式を用いることによってヒ素，アンチモン，鉄およびコバルトの活量を成分組成の関数として良く表示できることが分かった．さらに，ヒ素およびアンチモンのガス種が呈する分圧の総和を算出し，合金中のヒ素およびアンチモンの揮発除去の可能性について検討した．

1. 東北大学研究生
2. 工博　東北大学元助教授　多元物質科学研究所
3. 普通会員　工博　東北大学教授　多元物質科学研究所
キーワード：相関係，活量，ヒ素，アンチモン，鉄－コバルト－ヒ素合金，鉄－コバルト－アンチモン合金，等圧法