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AN EXPERIMENTAL STUDY ON THERMODYNAMICS OF THE Cu-Fe-As AND Cu-Fe-As-RE LIQUID SOLUTIONS

BADANIA TERMODYNAMICZNE CIEKŁYCH, ROZCIEŃCZONYCH ROZTWORÓW Cu-Fe-As I Cu-Fe-As-MISCHMETAL

By the method of the equilibrium vapor saturation there was determined the arsenic activity in the liquid diluted Cu-Fe-As and Cu-Fe-As-Mischmetal alloys a the temperature 1823 K. The measurements were carried out for the following concentrations of components: arsenic from $x_{As} = 0.008$ to $x_{As} = 0.23$; Mischmetal from $x_{Ce} = 0.0059$ to $x_{Ce} = 0.036$; iron from $x_{Fe} = 0.05$ to $x_{Fe} = 0.016$. The Cu-As alloy was accepted as the reference mixture, where the activity coefficient of arsenic was described by the Redlich-Kister equation. The arsenic activity coefficient in the Cu-Fe-As and Cu-Fe-As-Mischmetal alloys were described by the Wagner equation and the interaction parameters in both alloys were determined by the least-squares method. In the Cu-Fe-As alloy $\varepsilon_{As}^{Fe} = -2.7$, and in the Cu-Fe-As-Mischmetal alloy $\varepsilon_{As}^{Fe} = -3.5$ and $\varepsilon_{As}^{Ce} = -25.36$. The calculated ε_{As}^{Ce}, which has a significant negative value means, that lanthanides strongly interact with arsenic and decrease the arsenic activity in cooper alloys.

Metodą równowagowego próżniowego nasycania wyznaczono aktywność arsenu w ciekłych, rozcieńczonych stopach Cu-Fe-As i Cu-Fe-As-Mischmetal w temperaturze 1823 K. Badania wykonano dla zakresu stężeń: arsenu od $x_{As} = 0{,}008$ do $x_{As} = 0{,}023$; Mischmetalu od $x_{Ce} = 0{,}0059$ do $x_{Ce} = 0{,}36$ i żelaza od $x_{Fe} = 0.05$ do $x_{Fe} = 0{,}016$. Jako roztwór wzorcowy stosowano stop Cu-As, w którym współczynnik aktywności arsenu opisany jest równaniem Redlicha-Kistera. Współczynnik aktywności arsenu w stopach Cu-Fe-As i Cu-Fe-As-Mischmetal opisano rówaniem Wagnera. Metodą najmniejszych kwadratów wyznaczono parametry oddziaływania żelaza i Mischmetalu na aktywność arsenu. W stopie Cu-Fe-As $\varepsilon_{As}^{Fe} = -2{,}7$. W stopie Cu-Fe-As-Mischmetal $\varepsilon_{As}^{Fe} = -3{,}5$ i $\varepsilon_{As}^{Ce} = -25{,}36$. Wyznaczony parametr ε_{As}^{Ce} ma dość dużą ujemną wartość ($-25{,}36$), co świadczy o bardzo silnym oddziaływaniu arsenu i lantanowców i o tym, że lantanowce znacznie obniżają aktywność arsenu w stopach miedzi.

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1. Introduction

Descriptions of liquid phases in multicomponent arsenic alloys are so far insufficient, mainly due to the narrow range of composition and temperature accessible for experiments because of the very high arsenic pressure [1]. There is no experimental data on the Cu-Fe-As-RE system (where RE denote the rare earth metals and data on thermodynamics of Cu-Fe-As system are very scare. Wypartowicz [2], basing on the activity coefficients of binary alloys Cu-As, Fe-As and Cu-Fe, yield equations describing the activity coefficients of components as a function of temperature and composition. He also made some experiments by means of isopiestic method at the temperature 1373 K.

The aim of the present work is to estimate the influence of rare earth metals on arsenic in Cu-Fe-As-RE alloys. There is a strong tendency for forming intermetallic compounds between arsenic and rare earth metals. For instance the enthalpy of formation of intermetallic phases of cerium and lanthanum with copper is between -20 and -40 KJ/mole [3], while for phases of cerium and lanthanum with arsenic is between -140 and -155 kJ/mole [4]. Therefore Ce and La should effectively decrease the activity of As.

The present paper shows the results of experimental work on these systems.

2. Experimental technique

The analyzed alloys show a gread difference between the vapor pressures of elements at the temperature 1823 K. The arsenic pressure is many times higher then the atmospheric pressure, while pressures of other elements are below 100 Pa [5, 6]. Therefore the activity measurements of As were carried out by the use of the method of equilibrium vapor saturation, described in details in references 7 and 8. The studied mixtures (Cu-Fe-As and Cu-Fe-As-RE) and the reference mixture (Cu-As) were placed inside a closed crucible (Fig. 1) and saturated with vapor until equilibrium was reached. The activity of As in all mixtures was the same and if the activity of As in the reference mixture was known it was possible to calculate the activity of As in studied alloys:

$$\gamma_{As(Cu-Fe-As)} = \frac{x_{As(Cu-As)} \cdot \gamma_{As(Cu-As)}}{x_{As(Cu-Fe-As)}}, \tag{1}$$

where: $x_{As(Cu-As)}$ and $x_{As(Cu-Fe-As)}$ denote the equilibrium mole fraction, while $\gamma_{As(Cu-Cu)}$ and $\gamma_{As(Cu-Fe-As)}$ are the corresponding activity coefficients of As.

Alloys were prepared from: copper pellets, oxygen free (99.99 mass per cent), arsenic (99.999 mass per cent), iron (99.98), and RE in the form of Mischmetal (99.6 mass per cent, average composition: Ce:Nd:Pr:La:others = 50:18:6:22:4 (by weight)). Alfa Aesar (Johnson Matthey Comp.) delivered all materials. Because of the very high arsenic pressure Cu-As alloys were synthesized in two-compartment silica ampoules sealed

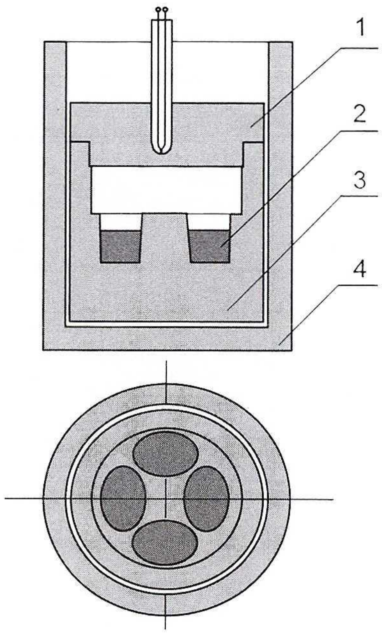

Fig. 1. The cell for the gas saturation method: 1) graphite cup, 2) alloy sample, 3) graphite cup, 4) alundum crucible.

under vacuum. In barrel-shaped crucibles (Fig. 1), there were placed the following alloys: Cu-As, Cu-Fe, Cu-Fe-RE and pure copper. The equilibrium compositions of alloys were determined by the method of atomic absorption. The equilibration time was three hours at the temperature 1823 K, and the argon pressure was 50 kPa.

3. Results

The vapor saturation method was used for determining the influence of RE (mainly Ce) on the activity of As in Cu-Fe-As-RE alloy at the temperature 1823 K.

The experimental activity of As was calculated from equation (1). The activity coefficients γ_{As} in the reference mixture Cu-As were earlier calculated [9] and there were obtained the following parameters in Redlich-Kister equation:

$$L^{0,liquid}_{As,Cu} = -45857.442 - 7.0593 \cdot T$$

$$L^{1,liquid}_{As,Cu} = 8941.7091 + 18.2381 \cdot T \qquad (2)$$

$$L^{2,liquid}_{As,Cu} = -789.0528 + 8.0076 \cdot T$$

The results are presented in Table 1 and 2.

TABLE 1

The experimental values of $\ln\gamma_{As}$ in Cu-Fe-As and equilibrium compositions of the tested and reference mixtures

$x_{As(Cu-As)}$	$\ln\gamma_{As(Cu-As)}$	$x_{As(Cu-Fe-As)}$	$x_{Fe(Cu-Fe-As)}$	$\ln\gamma_{As(Cu-Fe-As)}$
0,0075	−4,493	0,0162	0,530	−5,250
0,0052	−4,516	0,0110	0,411	−5,255
0,0078	−4,490	0,0130	0,160	−5,000
0,0078	−4,490	0,0144	0,136	−5,102
0,0047	−5,526	0,0139	0,109	−5,615
0,0053	−4,516	0,0078	0,077	−4,896
0,0027	−4,541	0,0082	0,066	−5,623
0,0053	−4,514	0,0130	0,120	−5,409

TABLE 2

The experimental values of $\ln\gamma_{As}$ in Cu-Fe-As and equilibrium compositions of the tested and reference mixture

$x_{As(Cu-As)}$	$\ln\gamma_{As(Cu-As)}$	$x_{As(Cu-Fe-As-Ce)}$	$x_{Fe(Cu-Fe-As-Ce)}$	$x_{Ce(Cu-Fe-As-Ce)}$	$\ln\gamma_{As(Cu-Fe-As-Ce)}$
0,0053	−4,516	0,0107	0,1623	0,0068	−5,160
0,0139	−4,427	0,0229	0,1503	0,0110	−4,923
0,0127	−4,438	0,0172	0,1095	0,0059	−4,739
0,0080	−4,487	0,0141	0,1347	0,0059	−5,044
0,0042	−4,526	0,0081	0,0989	0,0074	−5,178
0,0053	−4,516	0,0100	0,1623	0,0069	−5,160
0,0028	−4,540	0,0083	0,0497	0,0375	−5,623
0,0053	−4,515	0,0131	0,0500	0,0361	−5,409

As the properties of lanthanides are very similar, it was accepted to assume the concentration of RE as the concentration of cerium. The influence of Ce on the activity of As was calculated by the means of the Wagner equation:

$$\ln\gamma_{As(Cu-Fe-As)} = \ln\gamma^0 + \varepsilon_{As}^{As} x_{As} + \varepsilon_{As}^{Fe} x_{Fe} \tag{3}$$

$$\ln\gamma_{As(Cu-Fe-As-Ce)} = \ln\gamma^0 + \varepsilon_{As}^{As} x_{As} + \varepsilon_{As}^{Fe} x_{Fe} + \varepsilon_{As}^{Ce} x_{Ce}. \tag{4}$$

In equation (3) values of γ_{As}^0 and ε_{As}^{As} were accepted from the binary alloy, but the value of ε_{As}^{Fe} was calculated from the experimental results by means of the least-squares method.

In equation (4) values of γ^0_{As} and ε^{As}_{As} were accepted from the binary alloy, while the values of ε^{Fe}_{As} and ε^{Ce}_{As} were calculated on the basis of the experimental values of the studied micture. The activity coefficient of As in Cu-Fe-As and Cu-Fe-As-Ce alloys, calculated on the basis of presented experimental data are described by eqauations:

$$\ln\gamma_{As(Cu-Fe-As)} = -4.57 + 15.33x_{As} - 2.7x_{Fe} \quad (5)$$

$$\ln\gamma_{As(Cu-Fe-As)} = -4.57 + 15.33x_{As} - 3.54x_{Fe} - 25.36x_{Ce}. \quad (6)$$

4. Conclusions

In the present work by the means of the equilibrium vapor saturation the interaction coefficient ε^{Fe}_{As} was determined in the alloys Cu-Fe-As and Cu-Fe-As-Ce and the interaction parameter ε^{Ce}_{As} in the alloy Cu-Fe-As-Ce at the temperature 1823 K. The value $\varepsilon^{Ce}_{As} = -25.36$ means, that rare earth elements introduced in the form of misch-metal highly decrease the activity of arsenic in the studied alloy. Values of ε^{Fe}_{As} calculated by two methods do not differ much (-2.7 and -3.54), what speaks for consistency of the results.

REFERENCES

[1] J. Wypartowicz, Arch. Met. **37**, 15 (1992).

[2] J. Wypartowicz, Interpretation of Thermodynamic Properties of Liquid Solutions in Cu-Pb-Fe-As System, Scientific reports of Silesian Techmical University, ser. Metallurgy, 48, Gliwice 1995 (in Polish).

[3] P. Subramanian, D. Laughlin, Bull. Allay Phase Diagrams **9**, 322 (1988).

[4] K. Gshneider, F. Calderwood, Bull. Alloy Phase Diagrams **7**, 274 (1986).

[5] J. Wypartowicz, Arch. Met. **9**, 15 (1992).

[6] O. Kubaschewski, C. Alcock, Metallurgical Thermochemistry. Pergamon Press Oxford (1979).

[7] T. Pomianek, J. Golonka, J. Met. Technol. **6**, 433 (1979).

[8] T. Pomianek, J. Midure, J. Chem Thermodynamics, **22**, 946 (1990)

[9] B. Onderka, T. Pomianek, J. Romanowska, G. Wnuk, J. Wypartowicz, 10th International IUPAC Conference on High Temperature Materials Chemistry, Jülich, Germany, April 2000.

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