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EXPERIMENTAL DETERMINATION OF PHASE EQUILIBRIA IN THE SYSTEMS As-Ti, As-Zr, As-Cu-Ti AND As-Cu-Zr

DOŚWIADCZALNE WYZNACZANIE RÓWNOWAG FAZOWYCH W UKŁADACH As-Ti, As-Zr, As-Cu-Ti I As-Cu-Zr

The present work analyses the thermodynamic properties of liquid solutions and the phase relations in the systems As-Ti, As-Zr, As-Cu-Ti and As-Cu-Zr. The determination of the compositions of phases existing in equilibrium under controlled arsenic pressure at the temperatures above the melting point of copper was carried out in two independent experiments. The compositions of phases were determined from X-ray microanalyses of quenched samples. On the basis of obtained results and the literature data the thermodynamic description of the system was carried out according to *Calphad* procedure. From the obtained results the activities of components in binary liquid solutions as well as the arsenic activity in ternary liquid phase were calculated. The provisional versions of metal-rich part of binary phase diagrams As-Ti and As-Zr as well as the isothermal sections of As-Cu-Ti and As-Cu-Zr systems were determined.

Keywords: copper, arsenic, refining, activity, equilibrium diagram

Praca analizuje własności termodynamiczne ciekłych roztworów i zależności fazowe w układach As-Ti, As-Zr, As-Cu-Ti i As-Zr-Ti. Przy pomocy dwóch niezależnych eksperymentów określono składy faz pozostających w równowadze pod ustalonym ciśnieniem par arsenu w układzie w temperaturze powyżej punktu topnienia miedzi. Składy faz wyznaczono w schłodzonych próbkach metodą mikroanalizy rentgenowskiej. Na podstawie uzyskanych wyników i danych literaturowych opracowano termodynamiczną charakterystykę rozpatrywanych układów według procedury *Calphad*. Stąd obliczono aktywności składników ciekłych roztworów binarnych oraz aktywności arsenu w trójskładnikowej fazie ciekłej. Opracowano również wstępną wersję fragmentów o dużym stężeniu metalu układów równowag As-Ti i As-Zr oraz przekroje izotermiczne układów As-Cu-Ti i As-Cu-Zr.

1. Introduction

The refining of copper based alloy obtained as a result of reduction of slag from flash smelter consists mainly in removal of iron, lead and arsenic. The procedure of lead and iron bonding in oxygen converter is already well mastered. Arsenic, however, is more difficult in handling due to its high volatility both in metallic and in oxide form as well as high toxicity. The copper smelting works usually report small amounts of arsenic in intermediate products. According to our knowledge the arsenic content in above mentioned copper based alloy may in some cases exceed 1% by weight. Arsenic is a permanent component of copper ores and its removal still remains serious problem. Three main procedures are usually considered. The first one consists in transferring dissolved arsenic into volatile oxide and removal with off-gases, from which the arsenic oxide may be spotted out by dedusting. Another procedure takes advantage of very low activity of arsenic in copper, which allows it to remain in blister copper during oxygen converting. This arsenic may be removed from acidic water solution during electrolytic refining. The last possibility consists in chemical bonding or physical separation of arsenic prior to converting. Present work is linked with the operation of copper refining by means of metallic titanium and zirconium. The results of previous work have revealed that RE metals as cerium or lanthanum effectively remove arsenic from liquid copper and the copper based Cu-Pb-Fe-As alloy. Titanium and zirconium seem to be equally effective, but their cost is lower and detrimental action on physical properties of copper are weaker, than in the case of RE metals. The analysis of possibilities of titanium or zirconium application in bonding arsenic dissolved in liquid copper alloys

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requires the knowledge on activities of components in liquid As-Cu-Ti and As-Cu-Zr liquid solutions as well as the phase equilibria in these systems. The work on thermodynamics of these ternary systems has not been published up to now. The compilations were published only on thermodynamics of binary solutions Cu-Ti and Cu-Zr [1] and on the properties of liquid As-Cu solution [2, 3]. Even approximate optimization of these systems requires additional information for the As-Zr and As-Ti systems. The first aim of the present work is obtaining such information from experiment. Specific properties of arsenic: very high vapour pressure and toxicity strongly restrict the possibilities of precise experiment. The only possibility consists in determination of equilibrium compositions of phases under given pressure (i.e. activity) of arsenic in gaseous phase at elevated temperatures.

2. Experimental technique

2.1. Experiments for As-Ti and As-Zr systems

The experiment for As-Ti and As-Zr systems was carried out in graphite cell placed in vacuum induction furnace VSG10 (Balzers). Fig. 1. schematically presents the basic part of experimental set, which was placed in the chamber of induction furnace. One of small alundum crucibles contained As-Cu matrix alloy, while another contained pure titanium or zirconium. The experiment consisted in bringing the system to equilibrium, i.e. equal arsenic activities between two liquid phases: As-Cu alloy and As-Ti or As-Zr formed as a result of experiment. This means that during the experiment some amount of liquid appeared in the crucible with Ti or Zr. The equilibrium was executed through the gaseous phase, which was pure arsenic vapour. The As-Cu alloy of known composition was produced from pure elements in vacuum sealed horizontal quartz cell by non-isothermal equilibration (Cu – 1400 K, As – 800 K) [3]. In such thermal conditions the whole amount of arsenic sublimed and bonded with copper. The basic experiment with Ti or Zr was carried out isothermally at the temperatures from the range 1673–1823 K. After cooling the graphite chamber the re-melted part of Ti or Zr was a subject to X-ray microanalysis, from which the arsenic mole fraction in liquid alloy was determined.

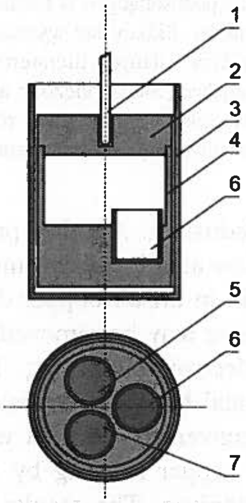

Fig. 1. Schematic diagram of experimental equipment: 1. PtRh18-Pt thermocouple, 2. Graphite lid, 3. Alundum crucible, 4. Graphite cell, 5, 6, 7) Alundum crucibles

2.2. Experiment for As-Cu-Ti system

The experiment for the system As-Cu-Ti was carried out in vacuum-sealed quartz cell, which was schematically shown in Fig. 2. The Cu-Ti alloy of molar proportion 1:1, obtained by melting pure components in induction furnace, was placed in bottom part of the cell. The lumps of arsenic were placed in the upper compartment. During 24 h annealing of the cell arsenic formed various phases with Cu-Ti alloy. Compositions of these phases were identified by means of X-ray microanalysis (EDX, Phillips LX30).

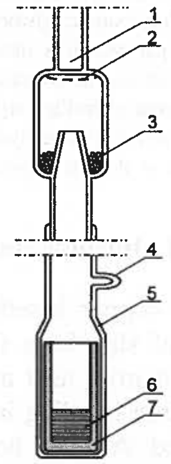

Fig. 2. Schematic diagram of the silica glass cell for phases equilibration in As-Cu-Ti system: 1) Thermocouple well, 2) Condensate of arsenic, 3) Arsenic in position prior to the experiment, 4) Tube for vacuum sealing the cell, 5) Cell of silica glass, 6) Cu-Ti alloy, 7) Crucible of fused Al_2O_3

3. Results

3.1. Experiments on binary As-Ti and As-Zr systems

The obtained results of the experiments are presented in tables 1 and 2. The final composition of As-Cu alloy after equilibration experiment results from the mass balance. This composition determines the activity of arsenic at the temperature of experiment. The composition of liquid As-Ti phase corresponding to the point at liquidus line is obtained from X-ray microanalysis of solidified sample.

TABLE 1

Results of experimental determination of the points of liquidus line in the As-Ti system

No.	T, K	Matrix alloy As-Cu		Arsenic concentration in As-Ti (analysis)
		Concentration X_{As}	Activity a_{As}	
1	1823	0.232	0.01874	0.135
2	1723	0.221	0.01404	0.024
3	1748	0.224	0.01519	0.057
4	1773	0.246	0.02228	0.107

TABLE 2

Results of experimental determination of the points of liquidus line in the As-Zr system

No.	T, K	Matrix alloy As-Cu		Arsenic concentration in As-Zr (analysis)
		Concentration X_{As}	Activity a_{As}	
1	1773	0.231	0.01756	0.244
2	1773	0.199	0.01016	0.256
3	1748	0.212	0.01234	0.249
4	1723	0.184	0.00721	0.212

3.2. Experiments on ternary As-Cu-Ti system

The non-isothermal experiments on As-Cu-Ti system were carried out under various thermal conditions, i.e. different temperatures of the sample (lower part of the cell) and of arsenic source (upper part) which are presented in table 3. The compositions of obtained phases were determined by means of X-ray microanalysis (EDX, Phillips LX30). The points corresponding to the phases in equilibrium (in two phase area) were marked in Fig. 7.

TABLE 3

Thermal conditions of experiment in the system As-Cu-Ti

Sample nr	Cell temperature, °C	
	Lower part	Upper part
1	1160	400
2	1100	400
3	1130	450
4	1130	365
5	1130	405
6	1130	380

4. Thermodynamic calculations

The parameters of the Gibbs free energy for phases in the system Cu-Ti-Zr system, optimized by Aroyave et al. [1] were utilized in the calculations carried out in the present work together with our own experimental results regarding:

- Compositions of phases in equilibrium,
- Temperature,
- Arsenic activities in the liquid phase.

The above data were used in the optimizing procedure of PARROT module of the system Thermo-Calc [4] regarding the model parameters [5] of Gibbs free energies. The data for pure components were obtained from Dinsdaile work [6]. Because of small amount of realistic thermodynamic data the easiest feasible for such assessment liquid solution model i.e. subregular was proposed. The assessed parameters are presented in Table 4.

TABLE 4

The sub-regular model solution parameters of liquid phase

System	Parameter	Value, J/mol
As-Ti	$^{0}L_{AsTi}$	−57716.2
	$^{1}L_{AsTi}$	−49640.4
As-Zr	$^{0}L_{AsTi}$	−73095.2
	$^{1}L_{AsTi}$	−39747.9

4.1. Results of calculations for the As-Ti system

The results of calculation of components activities at the temperature 1500°C are presented in Fig. 3. The positive deviation from the Raoult's law in the range of high titanium contents may be noticed. Non-asymptotic course of arsenic activity for $X_{As} \rightarrow 1$ is observed in two phase region, where the arsenic activity should be constant. Fig. 4. presents the calculated diagram of phase

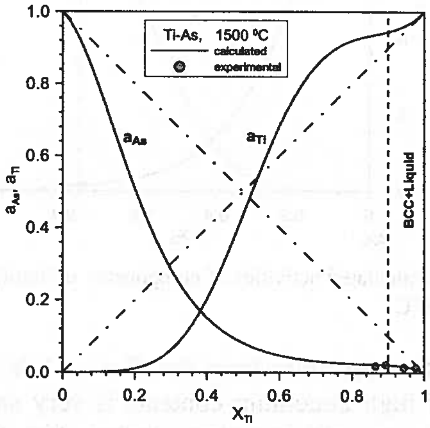

Fig. 3. Calculated activites of components of liquid As-Ti solution at 1500°C

equilibria in As-Ti system, obtained under assumption of equilibrium between liquid solution and solid BCC titanium as well as the invariant type eutectic reaction: L=TiAs+Ti-BCC. The approximate value for temperature of TiAs congruent melting was adopted.

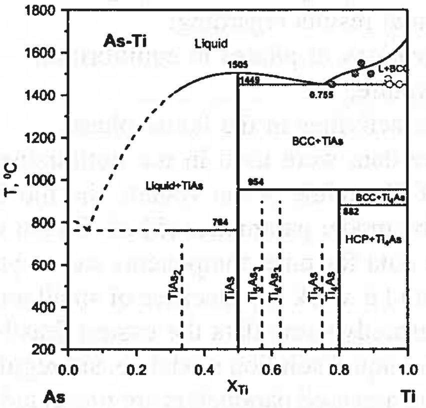

Fig. 4. The calculated diagram of phase equilibria in the system As-Ti. The experimental data from the present work are marked, corresponding to liquidus and eutectic reaction. The dashed lines denote the hypothetical course of liquidus and suggested As-Ti compounds

4.2. The results of calculations for As-Zr system

The results of calculations of components activities in the As-Zr system at 1450° C are presented in Fig. 5.

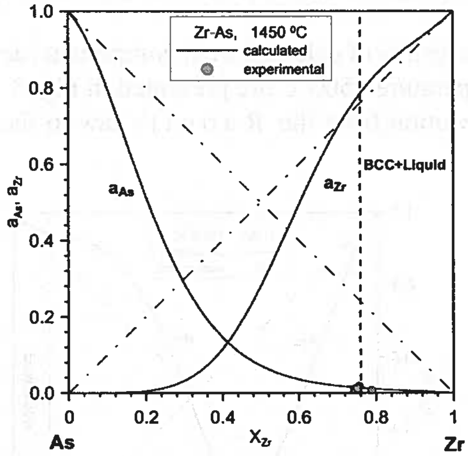

Fig. 5. The calculated activities of components in liquid As-Zr solution at 1450°C

The positive deviation from the Raoult's law in the region of high zirconium contents is very small and it occurs in expected two-phase region. Fig. 6. presents the calculated diagram of phase equilibria in the system As-Ti. Calculations are based on the assumptions of the equilibrium between liquid solution and zirconium-based BCC solid solution as well as invariant eutectic reaction L=Zr_3As_2+Zr-BCC. It follows from thermodynamic analysis possible at this stage of investigations that the equilibrium exists between liquid solution and solid Zr-BCC solution. However, the equilibrium between Zr_3As_2 and Zr-BCC cannot be excluded. Also in case of As-Zr system the approximate value for temperature of congruent melting of Zr_3As_2 was accepted.

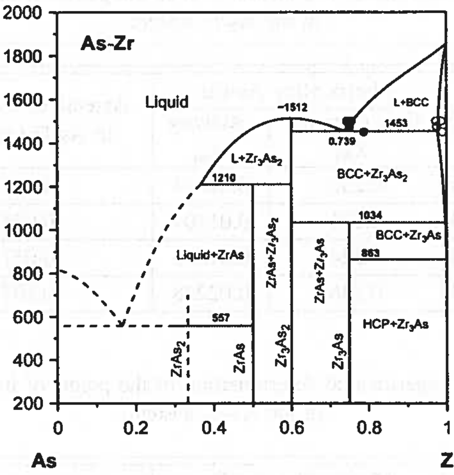

Fig. 6. The calculated diagram of phase equilibria in the system As-Zr. The experimental data from the present work are marked, corresponding to liquidus and solidus. The dashed lines denote the hypothetical course of liquidus and suggested As-Ti compound

The unambiguous solution to this problem requires farther careful studies by means of X-ray diffraction and high-temperature DTA or DSC under controlled pressure of arsenic. However the preparation of samples of required composition appears the crucial point in these studies.

4.3. Results of calculations for the systems As-Cu-Ti and As-Cu-Zr

Fig. 7 presents the isothermal sections of the ternary equilibrium diagram As-Cu-Ti, which was calculated in the present work from thermodynamic description of binary solutions. Because of lack of the coherent data a ternary interaction parameter and the ternary compound phases were not taken into account. The results of the experimental determination of phases composition are also marked in this figure. The isothermal diagrams of phase equilibria in the system As-Cu-Ti for the temperatures 1100°C and 1400°C were presented on Gibbs triangles in Figs. 8 and 9. These figures present also calculated isoactivities of arsenic in ternary liquid solution as well as predicted ranges of three-phase areas BCC+TiAs+Liquid and two-phase area BCC+TiAs. The course of liquidus line was also traced.

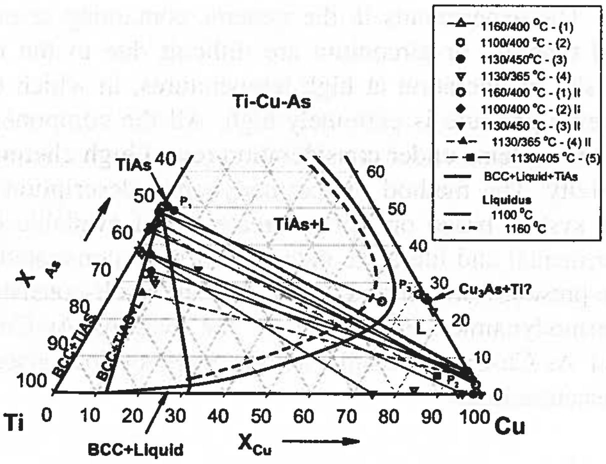

Fig. 7. The equilibrium diagram of As-Cu-Ti system calculated from thermodynamic description of binary systems. The experimental points regarding the phases in equilibrium are marked

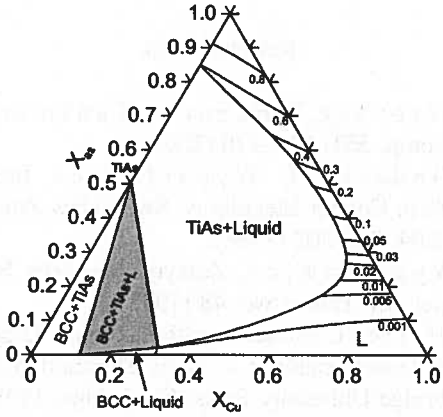

Fig. 8. Isothermal section of the As-Cu-Ti equilibrium diagram for the temperature 1100°C with calculated isoactivities of arsenic

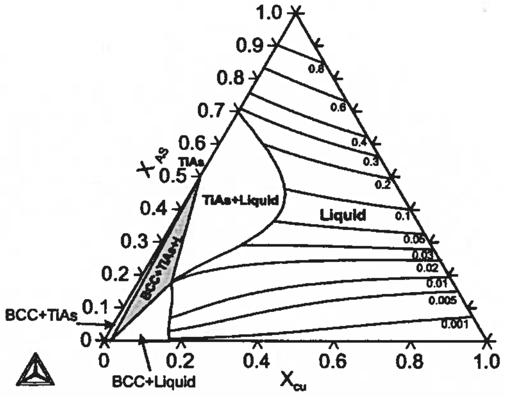

Fig. 9. Isothermal section of the As-Cu-Ti equilibrium diagram for the temperature 1400°C with calculated isoactivities of arsenic

The schematic diagram of phase equilibria in As-Cu-Ti system as well as the corresponding binary systems is presented in Fig. 10, in which the temperature 1100°C, i.e. the temperature for which the calculations of isothermal section were carried out, was marked.

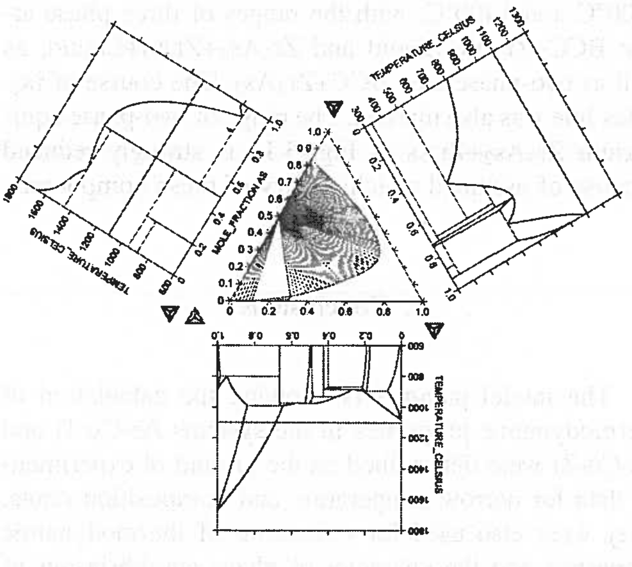

Fig. 10. Schematic diagram of phase equilibria in ternary As-Cu-Ti and binary systems. The line corresponds to temperature 1100°C, for which the isothermal section was calculated in the present work

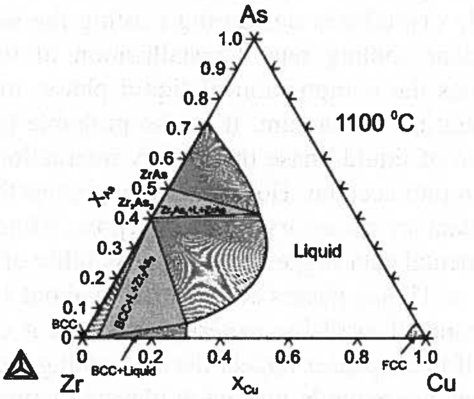

Fig. 11. Provisional version of the isothermal section of As-Cu-Zr equilibrium diagram at 1100°C, calculated in the present work

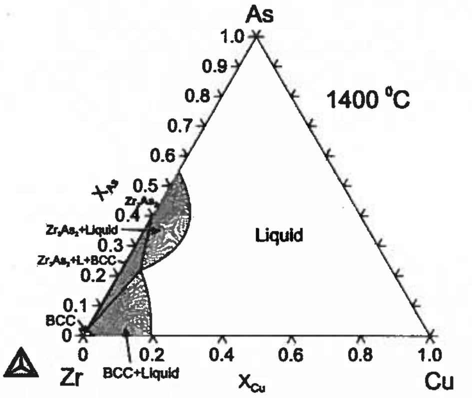

Fig. 12. Provisional version of the isothermal section of As-Cu-Zr equilibrium diagram at 1400°C, calculated in the present work

Figs. 11 and 12 present the predicted image of phase equilibria in the system As-Cu-Zr at the temperatures

1100°C and 1400°C, with the ranges of three phase areas: BCC+Zr_3As+Liquid and Zr_3As_2+ZrAs+Liquid, as well as two-phase area BCC+Zr_3As_2. The course of liquidus line was also marked. The range of two-phase equilibrium Zr_3As_2+ZrAs in Fig. 3.11 is strongly reduced because of assumed stoichiometry of these compounds.

5. Conclusions

The model parameters allowing the calculation of thermodynamic properties in the systems As-Cu-Ti and As-Cu-Zr were determined on the ground of experimental data for narrow temperature and composition range. They were also used for estimation of thermodynamic properties and the character of phase equilibria out of this range.

In Fig. 7, which compares the experimental data with the phase diagram calculated on the ground of data for binary systems, the presence of phase denoted P3 of the composition Cu_3As may be observed. This phase probably crystallizes out during cooling the samples at insufficient cooling rate. Crystallization of this phase influences the composition of liquid phase, mainly the concentration of titanium. It is also probable that in description of liquid phase the ternary interactions should be taken into account. However, more precise thermodynamic data are necessary for this purpose. Moreover, the experimental data suggest also the possibility of presence Ti_5As_3 or Ti_4As_3 phases at temperature about 1000°. On the ground of available experimental data it cannot be stated, if these phases appear during cooling the samples or if they are actually present at elevated temperatures.

The experiments in the systems containing arsenic and titanium or zirconium are difficult due to the necessity of operation at high temperatures, in which the arsenic pressure is extremely high. All the components of the systems under consideration reveal high chemical activity. The method of thermodynamic description of the system based on critical treatment of available experimental and literature data, which is demonstrated in the present work, allows for evaluation of self-consistent thermodynamic descriptions of the systems As-Cu-Ti and As-Cu-Zr, especially in the range of low arsenic concentrations.

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