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THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIA IN THE TERNARY Cu-Pb-Fe SYSTEM

WŁAŚCIWOŚCI TERMODYNAMICZNE I RÓWNOWAGI FAZOWE W UKŁADZIE TRÓJSKŁADNIKOWYM Cu-Pb-Fe

Using experimental data available in the literature, two binary systems, namely Cu-Pb and Fe-Pb were recalculated. Next, accepting Cu-Fe phase diagram assessment as given by Ansara and Jansson, the ternary Cu-Fe-Pb system was analyzed. Calculated equilibrium lines and thermodynamic functions are compared with existing experimental data. Good agreement was found between the calculated diagram and the experimental results. Having the system optimized, functional dependences of the logarithms of the activity coefficients on temperature and concentrations for Cu, Fe and Pb in the liquid solution are given.

Keywords: Thermodynamic properties, phase equilibria, Cu-Fe-Pb system, phase diagram assessment

Dwa układy podwójne Cu-Pb oraz Fe-Pb zostały powtórnie zoptymalizowane używając danych eksperymentalnych dostępnych w literaturze. Następnie, akceptując optymalizację układu Cu-Fe opublikowaną przez Ansarę i Janssona, poddano analizie trójskładnikowy układ Cu-Pb-Fe. Obliczone linie równowagi faz oraz funkcje termodynamiczne zostały porównane z dostępnymi danymi eksperymentalnymi. Uzyskano dobrą zgodność pomiędzy policzonym układem a danymi eksperymentalnymi. Korzystając z wyników optymalizacji, zostały podane zależności logarytmu współczynnika aktywności w funkcji temperatury oraz Cu, Fe i Pb w funkcji stężenia dla w roztworze ciekłym.

1. Introduction

The slag obtained as a byproduct in direct-to-blister flash smelting process carried out in Polish copper plant Głogów II contains usually 12-16% Cu, which is about one third of the overall amount of copper contained in Polish copper concentrates. This copper can be recovered from the slag in the electric furnace in the presence of a flux. Such a process is characterized by enormous electric energy consumption and, which makes things worse, it has not been possible so far to remove copper from the slag below 0.5 wt. % level. In order to improve this process and to consider intensification of the copper removal, several process parameters namely, composition of the slag, concentration gradients of Cu_2O in the slag and influence of electric current, should be taken into account.

While copper removal process is a dynamic one, it seems advisable to learn about its limits first, i.e. to ask about distribution coefficient of copper between the alloy and the slag under imposed external constraints. When carbon is used in the reduction process carried out in the electric furnace, several reduction reactions are initiated simultaneously and consequently, the product of the copper removal is in fact Cu-Pb-Fe liquid alloy. The slag is multicomponent oxide melt with variable composition. Since equilibrium between the metal and the slag phases can be represented by the reaction:

$$2[Cu]_{alloy} + {}^{1}/_{2}\, O_2 = (Cu_2O)_{slag} \qquad (1)$$

the influence of oxygen potential, temperature, and the alloy and slag compositions must be taken into account. The model of this three-phase equilibrium is schematically shown in Fig. 1. In the real process however, the equilibrium with the gas phase does not exist. Oxygen equilibrium potential corresponds in fact to oxygen potential of the liquid slag.

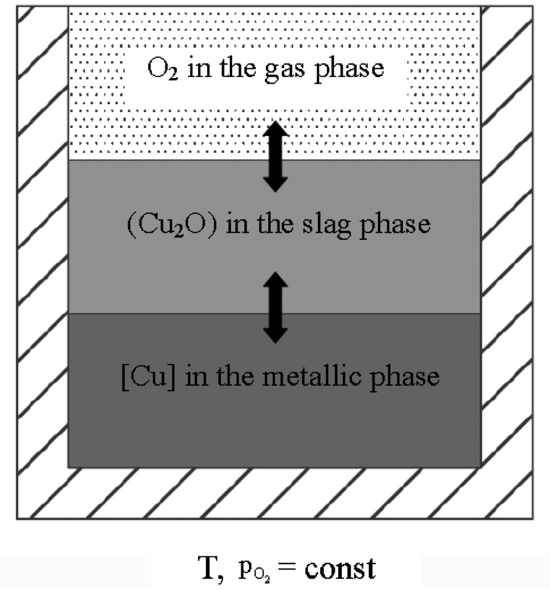

Fig. 1. The model scheme of gas-slag-metallic phase equilibrium

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The dependence of copper content in the slag on oxygen partial pressure and thermodynamic properties of both phases can be derived from eq. (1). It is usually given in the form:

$$X_{CuO_{0.5}} = \left(K_1 a_{Cu} p_{O_2}^{1/4}\right)/\gamma^0_{CuO_{0.5}} \tag{2}$$

from which it is clear that except for equilibrium constant K_1 (which is temperature dependent), copper content in the slag is proportional to oxygen partial pressure in $^1/_4$ power, activity of copper in metallic phase and thermodynamic behavior of Cu_2O in dilute solution in the oxide phase. This dependence was verified experimentally by Toguri and Santander [1] for fayalite slag. Similar correlations were confirmed by Altman and Kellog [2], Altman [3], Taylor and Jeffes [4], See and Rankin [5] and Elliot *et al.* [6]. Thus, to use eq. 2 for Cu solubility prediction under variable external conditions, thermodynamics of both liquid phases must be known and described with reliable thermodynamic models. In this part of our work description of the thermodynamic properties and phase equilibria in the liquid ternary Cu-Pb-Fe system will be given.

The aim of this work is threefold:

- first, the system Cu-Pb will be re-optimized in order to describe temperature and concentration range of the miscibility gap with the highest possible accuracy. This description is crucial for the reliable extension of the miscibility gap upon the ternary system,
- second, the ternary Cu-Pb-Fe system will be calculated and special attention will be given to the temperature evolution of copper-rich homogeneous solution range,
- third, simple analytical expression for activities of solution components will be suggested, which according to Eq. 1 is needed to calculate the copper distribution between metallic and slag phases.

2. Solution Models

The process of thermodynamic modeling is based on optimization of Gibbs free energy of each phase existing in the considered system. As the thermodynamic data concerning liquid solutions are often limited, it is reasonable to use simple models with small number of adjustable parameters, e.g. regular or subregular models. Additionally, in the liquid Cu-Fe-Pb solutions short range order is absent, and consequently liquid alloy can be described by the substitutional model [7]. Solid solutions with limited solubility range can be also described with the substitutional model if the ranges of mutual solubility are known. Thus, corresponding Gibbs free energy function of the liquid, bcc and fcc phases in the ternary Cu–Fe–Pb system can be expressed as:

$$G^\theta = \sum_i x_i^0 G_i^\theta + RT \sum_i x_i \ln x_i + \Delta^{ex} G_m^\varphi + \Delta^{mag} G^\varphi \ (i = Cu, Fe, Pb) \tag{3}$$

where: ${}^0G_i^\varphi$ are Gibbs free energy of the elements given in SGTE - PURE (ver. 4) database [8] providing the reference state for phase description. For metallic systems, the pressure dependence of Gibbs free energy function is usually neglected.

The excess Gibbs free energy of ternary system, $\Delta^{ex}G_m^\varphi$, can be described with the extrapolation method based on binary systems as given by Jacob-Fitzner-Muggianu approach [9, 10]:

$$\Delta^{ex} G_m^\varphi = \Delta^{ex} G_{bin}^\varphi + \Delta^{ex} G_{ter}^\varphi \tag{4}$$

where: $\Delta^{ex}G_{bin}^\varphi$ – excess Gibbs free energy of mixing of the binary system defined by the shortest composition path [11], $\Delta^{ex}G_{ter}^\varphi$ – excess Gibbs free energy of ternary solution;

If excess properties of binary phases are described with Redlich-Kister [12] polynomials:

$$L_{i,j}^\varphi = \sum_{k=0}^{n} {}^{(k)}L_{i,j}^\varphi (x_i - x_j)^k \tag{5}$$

the extrapolation of excess energy for ternary solution phases can be done with simple formula:

$$\Delta^{ex} G_{bin}^\varphi = \sum_i x_i x_j \cdot {}^{ex}L_{i,j}^\varphi \ (i, j = Cu, Fe, Pb) \tag{6}$$

where: ${}^{ex}L_{ij}^\varphi$ denote excess functions determined from binary systems $i - j$ along shortest composition path. Additionally, Redlich-Kister binary model parameters, ${}^{(k)}L_{i,j}^\varphi$, depend on temperature in the following way:

$${}^{(k)}L_{i,j}^\varphi = A + BT + CT \cdot \ln T + ... \tag{7}$$

The last term in eq. (3), $\Delta^{mag}G^\varphi$, represents magnetic order contribution as given by Hillert and Jarl [13]:

$$\Delta^{mag} G^\varphi = RT \ln(\beta + 1) f(\tau) \tag{8}$$

where $f(\tau)$ is a polynomial expression of normalized temperature, $\tau = T \big/ T_C^\varphi$, and T_C^φ is the Curie temperature for ferromagnetic ordering, and β is a mean atomic magnetic moment in Bohr magneton units.

Both T_C^φ and β can be functions of alloy composition as follows:

$$T_C^\theta = \sum_i x_i^0 T_C^i + x_i x_j \sum_{k=0}^{n} {}^kT_C^{i,j} (x_i - x_j)^k \ (i, j = Cu, Fe, Pb) \tag{9}$$

$$\beta^\theta = \sum_i x_i^0 \beta^i + x_i x_j \sum_{k=0}^{n} {}^k\beta^{i,j} (x_i - x_j)^k \ (i, j = Cu, Fe, Pb) \tag{10}$$

where: ${}^0T_C^i$, ${}^0\beta^i$ are the Curie temperatures and the mean atomic moment of pure elements, respectively. While, ${}^kT_C^{i,j}$ and ${}^k\beta^{i,j}$ are the binary interaction parameters for ferromagnetic ordering.

Finally, the excess Gibbs free energy of ternary solution $\Delta^{ex}G_{ter}^\varphi$ is equal:

$$\Delta^{ex} G_{ter}^\theta = \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} \sum_{k=j+1}^{n} x_i x_j x_k L_{ijk}^\theta \tag{11}$$

where ternary interaction part L_{jki}^θ is expressed by the sum of temperature dependent, (eq.7), ternary interaction parameters:

$$L_{jki}^\theta = x_i^0 L_{ijk}^\theta + x_j{}^1 L_{ijk}^\theta + x_k{}^2 L_{ijk}^\theta \tag{12}$$

3. Binary Systems

3.1. Cu-Pb Binary System

Since the time of the first investigations of this binary system carried out by Heycock and Neville [14], and Friedrich and Waehlert [15], several thermodynamic assessments were completed and the results of calculations for the most part of this system are in good agreement [16-20] with one another.

However, in this system, which is characterized by monotectic reaction, the shape of the miscibility gap is still a subject to controversy. Pelzel [21] used liquid phase chemical analysis while Khairulin and Stankus [22] used γ-ray attenuation technique to determine the two-melt phase boundary of the Cu-Pb system. The results of their investigations disagree with previously published data and show that critical temperature of the miscibility gap may be below the values usually accepted. Also, the extend of this gap seems to be smaller. Additionally, the miscibility data of Khairoulin and Stankus [22] used in the last two assessments of Cu-Pb system by Wang *et al.* [19], and by Vaajamo and Taskinen [46] yielded unwanted discrepancy with the experimental data of enthalpy of mixing in copper rich liquid solutions. Fig. 2 shows the calculated in this work phase diagram, which is compared with the experimental data [14, 15, 21, 23-34] of diagram topology.

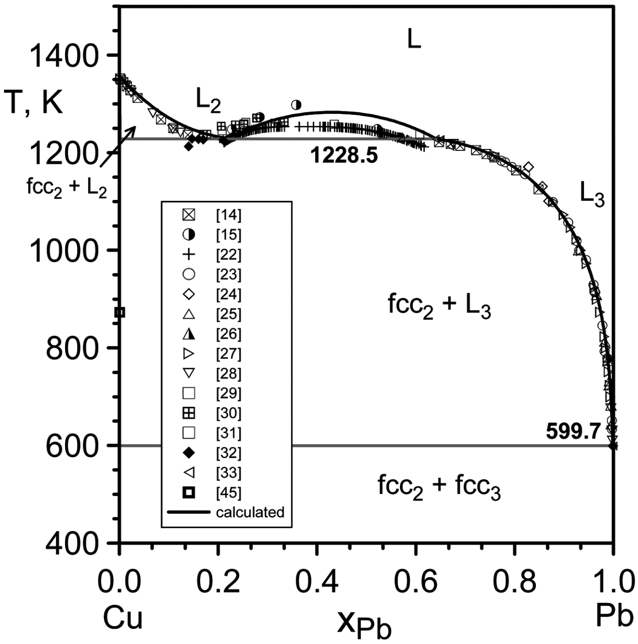

Fig. 2. The phase diagram of Cu-Pb system with superimposed experimental data points. L_2 – copper rich liquid, L_3 – lead rich liquid. fcc_2 and fcc_3 – copper rich and lead rich solid phases

The heat of mixing derived for liquid alloys is compared with the experimental data and is shown in Fig. 3. The SGTE data by Dinsdale [8] were used for pure elements. In the optimization procedure activities of lead in liquid Cu-Pb alloys [35-42] as well as enthalpy of mixing [43, 44] were also taken into account. The enthalpies measured by Deev et al. [37] were not included in this assessment because they differ significantly from more recent and accurate results. Solubility of lead in fcc copper was studied by Raub and Engel [45] at single temperature 873 K. No more data is available for solid phases. Estimated Gibbs energy excess parameters are the compromise between the course of the liquidus on the copper–rich side, heat of mixing concentration dependence and the liquid two-phase boundary below monotectic temperature. The results of calculations demonstrate that our choice of optimized parameters enables satisfactory description of the gathered literature information.

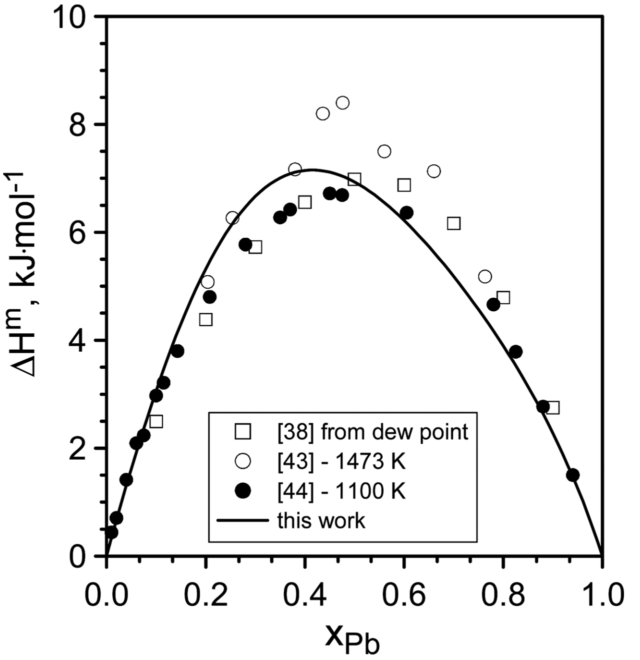

Fig. 3. The enthalpy of mixing of liquid Cu-Pb alloys. The data recalculated from dew point method [38] were enclosed

3.2. Fe-Pb Binary System

This system is characterized by the huge miscibility gap with monotectic temperature at about 1810 K. Limited solubility ranges and lead vapor pressure at elevated temperatures make experiments very difficult. It is thus not surprising that the assessment of the system must be based on very limited information. In this work following data were taken into account:

- solubility of lead in liquid iron [39, 47-49, 53]
- solubility of lead in solid γ-Fe [54]
- solubility of iron in liquid lead [47, 50-52, 54]

The phase diagram of Fe-Pb was already optimized four times, subsequently by Hämäläinen *et al.* [55], Onderka *et al.* [53], David [56] and Vaajamo and Taskinen [54]. Due to very limited set of data calculated phase diagrams are very much similar. In optimization process heat of mixing of liquid solutions predicted from Miedema's model was also taken into account [57]. In the present work, the Pb solubility limit in γ-Fe was optimized using the data of Vaajamo and Taskinen [54].

The calculated Pb-rich part of the phase diagram is shown in Fig. 4 and compared with the experimental data. There is very good agreement observed between calculated equilibrium lines and experimental data points.

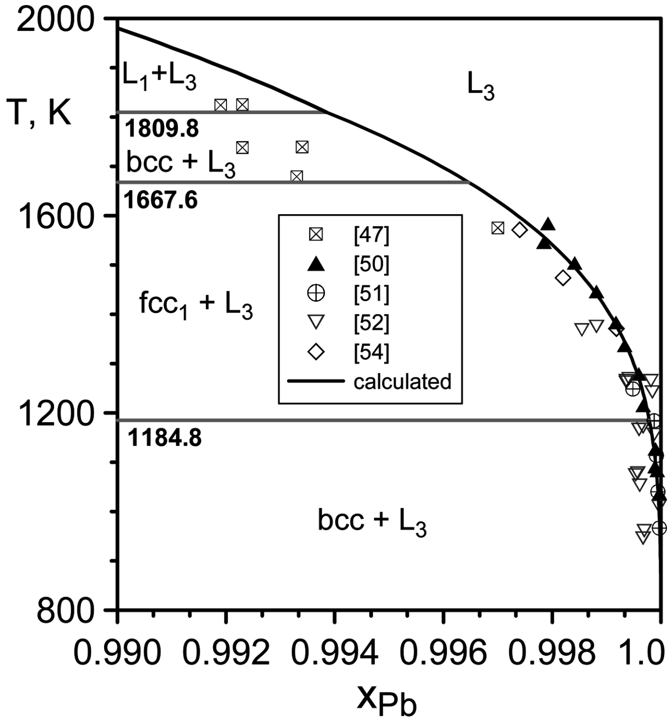

Fig. 4. The Pb-rich part of the Fe-Pb phase diagram with superimposed experimental data points. L_1 – iron rich liquid, L_3 – lead rich liquid. fcc$_1$ – iron rich solid phase

TABLE 1

The assessed thermodynamic model parameters of Cu-Fe-Pb system

Liquid	$^{0}L^{L}_{Cu,Pb}$	+27731-4.620·T
	$^{1}L^{L}_{Cu,Pb}$	+9962-6.766·T
	$^{2}L^{L}_{Cu,Pb}$	+2989 -1.688·T
	$^{3}L^{L}_{Cu,Pb}$	-6988 +5.155·T
	$^{0}L^{L}_{Fe,Pb}$	+110921.9-9.3668·T
	$^{1}L^{L}_{Fe,Pb}$	+29234.6-6.84982·T
	$^{0}L^{L}_{Cu,Fe}$	+36088-2.3297·T
	$^{1}L^{L}_{Cu,Fe}$	+324.5-0.0327·T
	$^{2}L^{L}_{Cu,Fe}$	+10355.4-3.603·T
	$^{0}L^{L}_{Cu,Fe,Pb}$	+260517.9-165.439·T
	$^{1}L^{L}_{Cu,Fe,Pb}$	+92011.5
	$^{2}L^{L}_{Cu,Fe,Pb}$	-116432.4
Bcc	$^{0}L^{Bcc}_{Cu,Fe}$	+39257.9-4.1498·T
	$^{0}L^{Bcc}_{Fe,Pb}$	+80320+36.7·T
	$^{0}L^{Bcc}_{Cu,Pb}$	+1000000
Fcc	$^{0}L^{Fcc}_{Cu,Fe}$	+48232.6-8.6095·T
	$^{1}L^{Fcc}_{Cu,Fe}$	+8861.9-5.2898·T
	$^{0}L^{Bcc}_{Cu,Pb}$	+25101+30.26·T
	$^{0}L^{Bcc}_{Fe,Pb}$	+74850+39.1·T

3.3. Cu-Fe Phase Diagram

No intermediate phases are reported in the critical evaluation of Cu-Fe system given in Massalski [58]. One of the earliest assessments of this system was provided by Kubaschewski et al. [59], in 1977. Later, in 1980, the Cu-Fe system was reassessed twice by Hasebe and Nishizawa [60] and Lindqvist and Uhrenius [61]. The assessment of Hasebe and Nishizawa [60] paid attention to the retrograde solidus curve and the effect of magnetic transition on the copper solubility. On the basis of their own experimental results Lindqvist and Uhrenius [61] recalculated the Cu-Fe system using a subregular thermodynamic model similar to the description presented by Kubaschewski *et al.* [59]. The next assessment was reported by Chen and Jin [62] in 1995. A new reassessment of Cu-Fe system covering all existing experimental data was made by Ansara and Jansson [63]. In 2003 a new reassessment of this system was published by Turchanin *et al.* [64] who used the solid solubility limits of bcc- and fcc-solutions determined from the melt quenching. However, the parameters of mixing for the liquid phase are different from those reported by Ansara and Jansson [63] and suggested temperature dependence is physically unlikely. The values calculated in the work of Ansara and Jansson [63] and data of Turchanin *et al.* [64] for the enthalpy of mixing at 1873 K are similar to each other and both are within the uncertainty range of available experimental data. In the present work the assessment of Ansara and Jansson [63] was chosen for the phase diagram description.

All Gibbs free energy model parameters used in the present work are gathered in Table I.

4. Ternary Cu-Fe-Pb System

This ternary system is not well known. Similarly to Fe-Pb system, limited composition range of liquid solutions, high temperature and high lead vapor pressure at elevated temperatures make experimental work very difficult and reliable data are still missing. There are only a few reports related to the course of the liquidus surface. Moser *et al.* [65] determined 25 points of the liquidus surface in the range of Pb and Fe concentration up to 10 atomic pct. Part of isotherms for this liquidus surface was also given by Zajączkowski *et al.* [66], and Wypartowicz [39]. Activity of lead in these ternary alloys was measured by Onderka *et al.* [67] and Pomianek and Golonka [68]. Thermodynamic properties of liquid ternary solutions were calculated from information on respective binary systems by Wypartowicz *et al.* [69].

Calculated part for copper-rich compositions of plane projection of the liquidus surface together with isotherms is shown in Fig. 5. Next two Figures 6 and 7 show lead activity (pure liquid lead as a reference) calculated for x_{Fe}/x_{Pb} = 1:3 and 2:1 ratio, respectively, compared with Pb activity [67] measured in Cu-Pb-Fe liquid solution at 1723 K. Two isophlets calculated for x_{Pb} = 0.06 and x_{Fe} = 0.05 are shown in Figures 8 and 9, respectively. All results of calculations show very good agreement with available experimental data. Necessary parameters used in our calculations are also gathered in Table I.

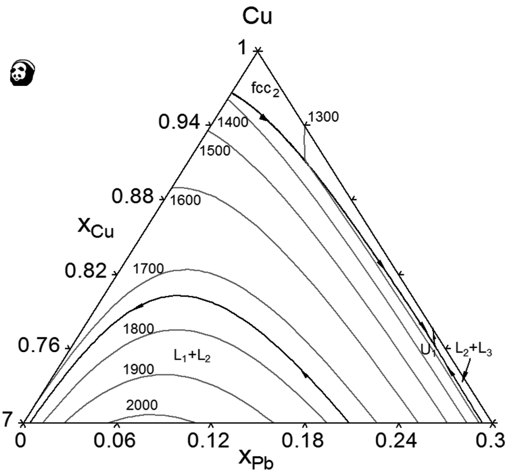

Fig. 5. The calculated copper-rich liquidus projection of Cu-Fe-Pb system. The liquidus isotherms in range 1300-2000 K were attached. L_1 – iron rich liquid, L_2 – copper rich liquid, L_3 – lead rich liquid. fcc_2 – copper rich solid phase. Reaction U_1: $L_2+fcc_1 = L_3+fcc_2$

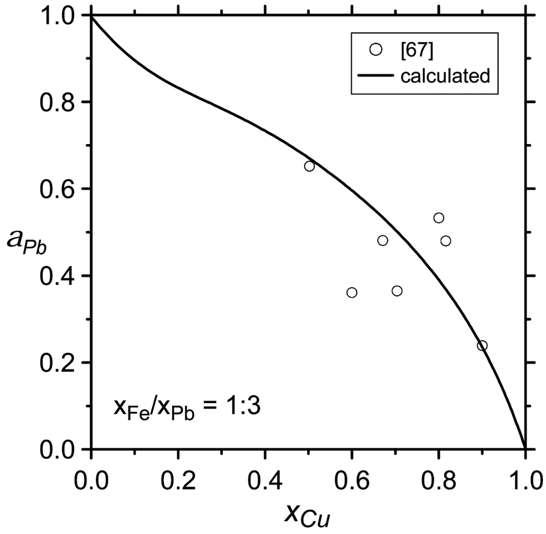

Fig. 6. The calculated activity of lead in Cu-Fe-Pb liquid solution for constant ratio x_{Fe}/x_{Pb} = 1:3 at 1723 K compared with the experimental data of Onderka et al. [67]

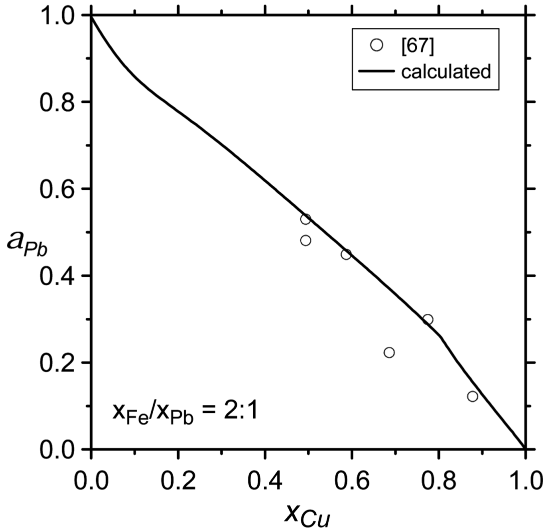

Fig. 7. The comparison of experimental [67] and calculated activity of lead in Cu-Fe-Pb liquid solution for constant ratio x_{Fe}/x_{Pb} = 2:1 at 1723 K

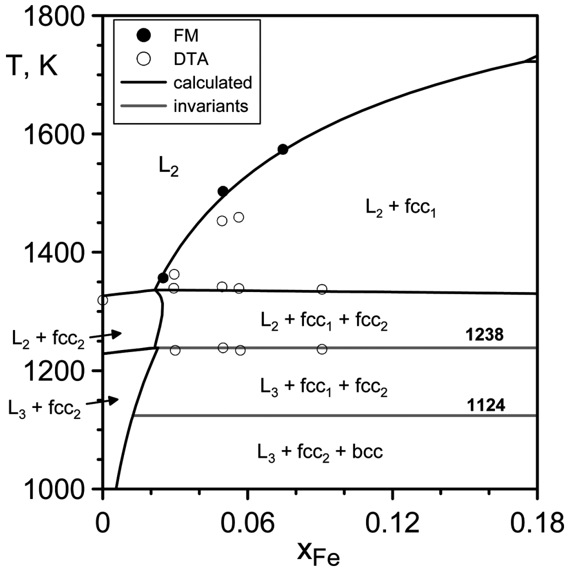

Fig. 8. The isopleth x_{Pb} = 0.06 of Cu-Fe-Pb system. The data of DTA analysis and freezing method (FM) form Moser et al. [65] were superimposed. fcc_1 and fcc_2 are iron rich and copper rich fcc solid solutions, respectively. L_2 and L_3 – copper and lead rich liquid solutions

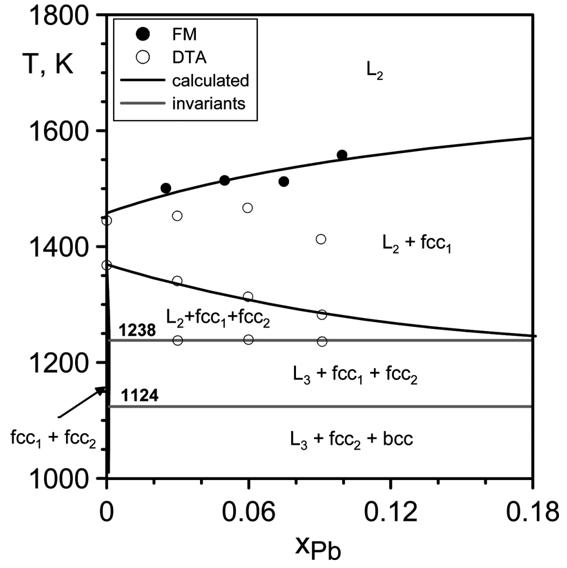

Fig. 9. The isopleth x_{Fe} = 0.05 of Cu-Fe-Pb system. The data of DTA analysis and freezing method (FM) from Moser et al. [65] were superimposed. fcc_1 and fcc_2 are iron rich and copper rich fcc solid solutions, respectively. L_2 and L_3 – copper and lead rich liquid solutions

5. Analytical Activity Description for Cu-rich Liquid Alloys

In order to provide simple formulas for components activity in the solution, optimized functions were used to convert activity data into functional dependence. Taking into account that Pb and Fe concentrations in copper ($x_{Pb} = x_{Fe} < 0.07$) are in fact in dilute solution range, we used the following approach:

- activity coefficient of copper was expressed by regular solution model, which should hold in this range very well due to the tendency towards immiscibility,

- activity coefficients of Fe and Pb were described by the interaction coefficients formalism as suggested by Wagner [70].

Consequently, using regular solution formalism [71, 72] one can arrive at the expression:

$$RT\ln\gamma_{Cu} = b_{CuPb}x_{Pb}^2 + b_{CuFe}x_{Fe}^2 + (b_{CuPb} + b_{CuFe} - b_{FePb})\,x_{Pb}x_{Fe} \tag{13}$$

which after recalculation of the activity data supplied by Pandat software [73] yields the following dependence:

$$\ln\gamma_{Cu} = \left(\frac{5335.6}{T} - 1.825\right)x_{Pb}^2 + \left(\frac{6006.5}{T} - 0.807\right)x_{Fe}^2 + \\ + \left(\frac{-18009}{T} + 11.08\right)x_{Pb}x_{Fe} \tag{14}$$

In turn, logarithms of lead and iron activity coefficients can be expressed as:

$$\ln\gamma_{Fe} = ln\gamma_{Fe}^0 + x_{Fe}\varepsilon_{Fe}^{Fe} + x_{Pb}\varepsilon_{Fe}^{Pb} \tag{15}$$

$$\ln\gamma_{Pb} = ln\gamma_{Pb}^0 + x_{Pb}\varepsilon_{Pb}^{Pb} + x_{Fe}\varepsilon_{Pb}^{Fe} \tag{16}$$

which again after recalculations yield the following dependencies:

$$\ln\gamma_{Fe} = \left(\frac{5665.5}{T} - 0.716\right) + x_{Fe}\left(\frac{-19268}{T} + 4.246\right) + \\ + x_{Pb}\left(\frac{24647}{T} - 13.363\right) \tag{17}$$

$$\ln\gamma_{Fe} = \left(\frac{4088.4}{T} - 0.988\right) + x_{Fe}\left(\frac{-7847.5}{T} + 1.392\right) + \\ + x_{Pb}\left(\frac{25052}{T} - 14.238\right) \tag{18}$$

Suggested expressions (14), (17) and (18) enable calculations of activities for all three components in the considered temperature and concentration range.

6. Discussion

The minimization of copper loss in slags produced by copper smelters is an old problem being steadily optimized in time. On the other hand, the studies on removal of lead and iron from Cu-Fe-Pb alloys had been performed [74]. Recently, Coursol *et al.* [75] came to the conclusion that minimum soluble copper content in the electric furnace slag is expected to be about 0.55 wt% Cu ranging up to about 1.3 wt%. However, good understanding of the achievable theoretical limits will allow one to assess the discrepancy between the real situation and ideal conditions of phase equilibrium. To be able to do such a prediction however, a reliable thermodynamic data and the model are required to calculate metal-slag equilibrium under variable conditions. In this work using the available and critically evaluated literature data, the complete thermodynamic description of ternary Cu-Fe-Pb system was done. The parameter values of the solution models were assessed using ThermoCalc software package version S [76], Pandat software version 8.1 [73] and SGTE unary database [77]. The Gibbs energy excess parameters of the solution phases were expressed using the Redlich-Kister polynomials. The calculated ternary Cu-Fe-Pb equilibrium diagram shows small range of homogeneous liquid solutions existing in the temperature range from 1473 to 1673 K. For this range, simple functions describing activity coefficients of all three components are also given. Still, some problems remain and should be mentioned.

All three binary systems, which were optimized first, are characterized with uncertainties which can affect optimized parameters of the ternary system. New data on the binary Cu-Pb system reported by Khairoulin and Stankus [22] shift two-melt phase boundary in the range of immiscibility. In their work phase boundaries were obtained by the γ-ray densitometer developed by the authors. It is doubtful if the authors were able to derive equilibrium compositions of the liquid phases as a function of temperature so precisely. Moreover, it is known that radiation brings about defects in the solid structure. Therefore, it cannot be excluded that γ-rays will influence also demixing process in the liquid state. Consequently, our optimization of the Cu-Pb binary system was based on the fit to thermodynamic properties of the liquid solutions and liquidus data ranging to practically pure lead.

The next binary system which was considered is Fe-Pb. Since the range of the gap is in this system in fact unknown, the whole optimization must be based on the data available up to monotectic temperature. Again, since mutual solubility of Fe and Pb is very small, there is a question if these data are satisfactory to reproduce the whole system. The assessed monotectic temperature of 1809.8 K and the eutectic temperature of 600.6 K differ less than 1 K from the previous assessments by Vaajamo and Taskinen [54] and Hämäläinen *et al.* [55], even though the experimental data used in these studies were a bit different.

For the description of the last binary Cu-Fe system the assessment of Ansara and Jansson [63] was chosen. It exhibits two peritectic reactions at 1762 and 1371 K respectively, as well as one eutectoid reaction at 1116 K.

The assessment of ternary Cu-Fe-Pb system is in good agreement with the experimental data of Onderka *et al.* [67] and with the data reported by Moser *et al.* [65]. The experimental values of lead activity by Pomianek and Golonka [68] differ from the current assessment. The dissolution of a graphite crucible they used in experiments in the Cu-Fe-Pb samples seems to influence their results. This would also explain the larger difference of activity values at higher temperatures.

The isopleths of Cu-Fe-Pb system calculated for constant $x_{Fe} = 0.05$ and $x_{Pb} = 0.06$ are shown in Figs.8 and 9 together with experimental data of Moser et al. [65] obtained by DTA analysis and freezing method. Generally, experimental data agree very well with calculated lines of phase diagram. Especially, invariant reaction of U_1: $L_2 + fcc_1 = L_3 + fcc_2$ at temperature 1238 K fits the experimental data very well. Such invariant reaction was missing in the previous work of Vaajamo and Taskinen [46]. It seems that it is the evidence of higher critical temperature of the miscibility gap in Cu-Pb system. If this temperature is too low, the extent of copper-lead miscibility gap in not wide enough to reach the equilibrium between iron – rich fcc phase (fcc_1) and two liquid solutions: copper–rich (L_2) and lead-rich (L_3). The calculated cross-sections of the liquidus surface fit the freezing point data of Moser *et al.* [65] for all experimental isopleths compositions. To improve the assessment some additional thermodynamic experiments of the system Cu-Fe-Pb are necessary.

Finally, making use of optimized parameters, activities of copper, iron and lead were recalculated and activity coefficients are given with simple equations (10), (13) and (14).

The estimation of the mutual interaction coefficients between iron and lead in copper over dilute solution range at fixed temperature 1523 K showed that cross-coefficients are found to be $\varepsilon_{Pb}^{Fe} = 2.21$ and $\varepsilon_{Fe}^{Pb} = 2.82$, i.e. they are almost equal. This result is compatible with Wagner's formalism $\varepsilon_i^j = \varepsilon_j^i$, and suggests that the addition of the third component (either Fe or Pb) to the binary solution increases activity coefficient of the solute at fixed temperature.

The derived expressions are valid in the considered concentration range and enable reliable and off-hand calculations of activities for all components of the ternary solution. This in turn may facilitate analysis of metal/slag equilibrium, and the calculation of copper solubility in the FeO-CaO-SiO_2 slag under variable external conditions.

When this paper has been finished the fast track announcement of new experimental data on solubility study of the copper–lead system together with assessment of Cu-Pb system will be published by Vaajamo et al. [78]. These data were not taken into account in the present paper.

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