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MODELING AND EXPERIMENTAL MEASUREMENTS OF THE SURFACE TENSIONS OF Cu-Pb-Fe ALLOYS

MODELOWANIE I POMIAR NAPIĘCIA POWIERZCHNIOWEGO STOPÓW Cu-Pb-Fe

In the paper, a model enabling calculation of surface tensions of liquid ternary Cu-Pb-Fe alloys, on the basis of the densities (molar volumes) of the solution components as well as the surface tensions and the thermodynamic properties of the adequate binary alloys, has been proposed. Basing on the experimental results, obtained with the use of the sessile drop method for seven Cu-Pb-Fe alloy compositions, the proposed surface tension model has been verified.

W pracy zaproponowano model pozwalający na obliczanie napięcia powierzchniowego ciekłych trójskładnikowych stopów Cu-Pb-Fe na podstawie znajomości gęstości (objętości molowej) składników roztworu i napięcia powierzchniowego oraz właściwości termodynamicznych odpowiednich stopów podwójnych. Następnie dokonano weryfikacji zaproponowanego modelu napięcia powierzchniowego w oparciu o uzyskane metodą kropli leżącej wyniki eksperymentalne dla siedmiu różnych składów stopu Cu-Pb-Fe.

1. Introduction

The Cu-Pb-Fe alloy is a basic product of removing copper (in an electric furnace) from slag formed during the one-stage flash furnace copper smelting process, applied in the Głogów II Copper Plant. In the paper, a model enabling calculation of the surface tensions of liquid ternary Cu-Pb-Fe alloys, on the basis of the densities (molar volumes) of the solution components as well as the surface tensions and the thermodynamic properties of the adequate binary alloys, has been proposed. Basing on the experimental results, the proposed surface tension model has been verified.

2. Modeling of the surface tension of Cu-Pb-Fe alloys

If the equilibrium between the bulk of an A-B-C (Cu-Pb-Fe) solution and a monomolecular layer on the surface of this solution, which is treated as an individual phase [1], is assumed, the following relationships can be derived:

$$\sigma_{ABC} = \sigma_A + \frac{RT}{S_A} \ln \frac{a_A^{(s)}}{a_A^{(b)}} = \sigma_B + \frac{RT}{S_B} \ln \frac{a_B^{(s)}}{a_B^{(b)}} = \sigma_C + \frac{RT}{S_C} \ln \frac{a_C^{(s)}}{a_C^{(b)}} \quad (1)$$

This equation, in a simplified form, was first given by Batler [2].

Equation (1) can be presented in the form of two non-linear equations:

$$\frac{\sigma_A - \sigma_B}{RT} S_A - \ln a_A^{(b)} + \Theta_{AB} \ln a_B^{(b)} = \Theta_{AB} \ln a_B^{(s)} - \ln a_A^{(s)} \quad (2)$$

$$\frac{\sigma_A - \sigma_C}{RT} S_A - \ln a_A^{(b)} + \Theta_{AC} \ln a_C^{(b)} = \Theta_{AC} \ln a_C^{(s)} - \ln a_A^{(s)} \quad (3)$$

where:

S_A, S_B, S_C – molar surfaces of A-B-C solution components,

R – gas constant,

T – temperature,

$\sigma_A, \sigma_B, \sigma_C$ – surface tensions of A-B-C solution components,

$a_A^{(b)}, a_B^{(b)}, a_C^{(b)}$ – activities of A-B-C solution components in its bulk,

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$a_A^{(s)}, a_B^{(s)}, a_C^{(s)}$ – activities of A-B-C solution components in its surface layer

and:

$$\Theta_{AB} = \frac{S_A}{S_B}; \Theta_{AC} = \frac{S_A}{S_C}.$$

It can be easily seen that the unknowns in this system of equations are $x_A^{(s)}, x_B^{(s)}, x_C^{(s)}$ and the shape of functions describing the activity coefficients of the surface layer components ($\ln \gamma_A^{(s)}, \ln \gamma_B^{(s)}, \ln \gamma_C^{(s)}$). One of the variables can be eliminated in a simple way by the following equation:

$$x_A^{(s)} + x_B^{(s)} + x_C^{(s)} = 1 \quad (4)$$

The next problem is far more difficult to solve, because the shape of the function describing the thermodynamic data in the surface phase cannot be determined experimentally. Thus, it is assumed as follows:

- the mathematical shape of the functions describing the activity coefficients in the surface layer of the appropriate binary alloys ($\gamma_{Cu}^{(s)}, \gamma_{Sb}^{(s)}, \gamma_{Fe}^{(s)}$) is the same as the shape of the functions describing the activity coefficients in the bulk of the solution ($\gamma_{Cu}^{(b)}, \gamma_{Sb}^{(b)}, \gamma_{Fe}^{(b)}$)
- the atoms in the surface layer have fewer nearest neighbours than the atoms in the bulk of the solution.

Hence, for the appropriate binary systems, the following equations can be written:

– A-B solutions

$$\ln \gamma_{A(A-B)}^{(s)} = \frac{Z^{(s)}}{Z^{(b)}} f_{A(A-B)}(T, x_A^{(s)}) = \alpha_{A-B} f_{A(A-B)}(T, x_A^{(s)})$$

$$\ln \gamma_{B(A-B)}^{(s)} = \frac{Z^{(s)}}{Z^{(b)}} f_{B(A-B)}(T, x_A^{(s)}) = \alpha_{A-B} f_{B(A-B)}(T, x_A^{(s)})$$

– A-C solutions

$$\ln \gamma_{A(A-C)}^{(s)} = \frac{Z^{(s)}}{Z^{(b)}} f_{A(A-C)}(T, x_A^{(s)}) = \alpha_{A-C} f_{A(A-C)}(T, x_A^{(s)})$$

$$\ln \gamma_{A(A-C)}^{(s)} = \frac{Z^{(s)}}{Z^{(b)}} f_{C(A-C)}(T, x_A^{(s)}) = \alpha_{A-C} f_{B(A-B)}(T, x_A^{(s)}) \quad (5)$$

– B-C solutions

$$\ln \gamma_{B(B-C)}^{(s)} = \frac{Z^{(s)}}{Z^{(b)}} f_{B(B-C)}(T, x_C^{(s)}) = \alpha_{B-C} f_{B(B-C)}(T, x_C^{(s)})$$

$$\ln \gamma_{C(B-C)}^{(s)} = \frac{Z^{(s)}}{Z^{(b)}} f_{C(B-C)}(T, x_C^{(s)}) = \alpha_{B-C} f_{C(B-C)}(T, x_C^{(s)})$$

where:

$Z^{(s)}$ – the number of the nearest neighbours of the atom in the surface layer,

$Z^{(b)}$ – the number of the nearest neighbours of the atom in the bulk of the solution.

Functions $f_{A(X-Y)}, f_{B(X-Y)}, f_{C(X-Y)}$ are of the same shape as for the activity coefficients in the bulk of the appropriate binary solutions.

The determination of the surface tension for an A-B-C solution is possible if a system of the non-linear Equations (2) and (3) is solved, and then Equation (1) is applied. However, in order to determine the surface tension of a ternary system on the basis of the data related to the appropriate binary systems, a model used for predicting thermodynamic properties of multicomponent system should be applied.

Modeling of A-B-C alloys thermodynamic properties were based on the descriptions of binary systems with the use of a power series proposed by Redlich and Kister [3]:

$$\begin{aligned} \Delta G_{A-B}^{EX} &= x_A \times x_B \sum_0^n L_{A-B}^{(v)} (x_A - x_B)^v \\ \Delta G_{A-C}^{EX} &= x_A \times x_C \sum_0^n L_{A-C}^{(v)} (x_A - x_C)^v \\ \Delta G_{B-C}^{EX} &= x_B \times x_C \sum_0^n L_{B-C}^{(v)} (x_B - x_C)^v, \end{aligned} \quad (6)$$

where:

$\Delta G_{A-B}^{EX}, \Delta G_{A-C}^{EX}, \Delta G_{B-C}^{EX}$ – a change in excessive free energy of forming A-B, A-C and B-C solutions,

x_A, x_B, x_C – mole fractions of the A-B, A-C and B-C solution components,

$L_{A-B}^{(v)}, L_{A-C}^{(v)}, L_{B-C}^{(v)}$ – Redlich-Kister polynomial coefficients for the appropriate binary solutions A-B, A-C i B-C, $v = 0, 1, 2, \dots, n$.

The Redlich-Kister polynomial coefficients used in calculations are listed in Table 1.

TABLE 1
The Redlich-Kister polynomial coefficients used in calculation [4, 5]

Alloy	Redlich-Kister coefficients
Cu-Fe	$L_{Cu-Fe}^{(0)} = 45180 - 8,05 T$
	$L_{Cu-Fe}^{(1)} = -6400 + 4,09 T$
	$L_{Cu-Fe}^{(2)} = 12500 - 5,35 T$
Cu-Pb	$L_{Cu-Pb}^{(0)} = 31007,6 - 7,19493 T$
	$L_{Cu-Pb}^{(1)} = 15345,1 - 10,82599 T$
	$L_{Cu-Pb}^{(2)} = 6492,6 + 5,94737 T$
	$L_{Cu-Pb}^{(3)} = 18416 + 13,160467 T$
Pb-Fe	$L_{Fe-Pb}^{(0)} = 110921,8 - 9,36674 T$
	$L_{Fe-Pb}^{(1)} = 29234,6 - 6,84981 T$

The excessive energy of the A-B-C solution mixing can be described by the following equation [6]:

$$\Delta G_{A-B-C}^{EX} = (1 - y_2) [\Delta G_{A-B}^{EX}] + y_2 [\Delta G_{A-C}^{EX}] + y_1^2 [\Delta G_{B-C}^{EX}], \quad (7)$$

where:

$$y_1 = 1 - x_A$$

The use of equation (1) requires the partial functions of free energy for the considered ternary A-B-C solution which are obtained from the following equation:

$$y_2 = \text{frac}x_Cx_B + x_C. \quad (8)$$

$$\begin{aligned} \Delta G_{A(A-B-C)}^{EX} &= RT \ln \gamma_{A(A-B-C)} = \Delta G_{A-B-C}^{EX} - y_1 \frac{\partial \Delta G_{A-B-C}^{EX}}{\partial y_1} \\ \Delta G_{B(A-B-C)}^{EX} &= RT \ln \gamma_{B(A-B-C)} = \Delta G_{A-B-C}^{EX} + \frac{\partial \Delta G_{A-B-C}^{EX}}{\partial y_1} - \frac{y_2}{y_1} \frac{\partial \Delta G_{A-B-C}^{EX}}{\partial y_2} \\ \Delta G_{C(A-B-C)}^{EX} &= RT \ln \gamma_{C(A-B-C)} = \Delta G_{B(A-B-C)}^{EX} + \frac{1}{y_1} \frac{\partial \Delta G_{A-B-C}^{EX}}{\partial y_2} \end{aligned} \quad (9)$$

Similar equations can be proposed for a ternary solution in the surface layer:

$$\begin{aligned} \Delta G_{A(A-B-C)}^{EX(s)} &= RT \ln \gamma_{A(A-B-C)}^{(s)} = \Delta G_{A-B-C}^{EX(s)} - y_1^{(s)} \frac{\partial \Delta G_{A-B-C}^{EX(s)}}{\partial y_1^{(s)}} \\ \Delta G_{B(A-B-C)}^{EX(s)} &= RT \ln \gamma_{B(A-B-C)}^{(s)} = \Delta G_{A-B-C}^{EX(s)} + \frac{\partial \Delta G_{A-B-C}^{EX(s)}}{\partial y_1^{(s)}} - \frac{y_2^{(s)}}{y_1^{(s)}} \frac{\partial \Delta G_{A-B-C}^{EX(s)}}{\partial y_2^{(s)}} \\ \Delta G_{C(A-B-C)}^{EX(s)} &= RT \ln \gamma_{C(A-B-C)}^{(s)} = \Delta G_{B(A-B-C)}^{EX(s)} + \frac{1}{y_1^{(s)}} \frac{\partial \Delta G_{A-B-C}^{EX(s)}}{\partial y_2^{(s)}}, \end{aligned} \quad (10)$$

where:

$$\Delta G_{A-B-C}^{EX(s)} = (1 - y_2^{(s)}) [\alpha_{A-B} \Delta G_{A-B}^{EX(s)}] + y_2^{(s)} [\alpha_{A-C} \Delta G_{A-C}^{EX(s)}] + y_1^{(s)2} [\alpha_{B-C} \Delta G_{B-C}^{EX(s)}] \quad (11)$$

$$\frac{\partial \Delta G_{A-B-C}^{EX(s)}}{\partial y_1^{(s)}} = (1 - y_2^{(s)}) \alpha_{A-B} \frac{\partial \Delta G_{A-B}^{EX(s)}}{\partial y_1^{(s)}} + y_2^{(s)} \alpha_{A-C} \frac{\partial \Delta G_{A-C}^{EX(s)}}{\partial y_1^{(s)}} + 2y_1^{(s)} \alpha_{B-C} \Delta G_{B-C}^{EX(s)} \quad (12)$$

$$\frac{\partial \Delta G_{A-B-C}^{EX(s)}}{\partial y_2^{(s)}} = \alpha_{A-C} \Delta G_{A-C}^{EX(s)} - \alpha_{A-B} \Delta G_{A-B}^{EX(s)} + y_1^{(s)2} \alpha_{B-C} \frac{\partial \Delta G_{B-C}^{EX(s)}}{\partial y_2^{(s)}}. \quad (13)$$

Equations (1-13) unequivocally indicate that the presented model is only based on the information regarding the properties of the appropriate binary solutions which can be obtained using components for a ternary solution, namely:

– thermodynamic properties allowing the determination of activity coefficients for binary solutions,

– surface tensions of binary solutions necessary for the determination of required constants (α_{A-B} , α_{A-C} , α_{B-C}),

– densities (molar volumes) of the solution components.

For example, the surface tensions of Cu-Pb-Fe alloys can be calculated using the following equation:

$$\sigma_{Cu-Pb-Fe} = \sigma_{Cu} + \frac{RT}{S_{Cu}} \ln \frac{a_{Cu}^{(s)}}{a_{Cu}} = \sigma_{Cu} + \frac{RT}{S_{Cu}} \ln \frac{1 - y_1^{(s)}}{1 - y_1} + \frac{1}{S_{Cu}} \left(\Delta G_{Cu(Cu-Pb-Fe)}^{EX(s)} - \Delta G_{Cu(Cu-Pb-Fe)}^{EX} \right) \quad (14)$$

The data regarding densities and surface tensions of pure components (Table 2), used for the model calculations, were taken from the papers by Keen [7] as well as Nizenko and Fłoka [8], while in case of the binary systems, the papers [9, 10, 11] were used.

TABLE 2

The surface tensions and densities of Cu, Pb and Fe [7, 8]

Metall	The surface tensions and densities
Cu	$\sigma = 1330 - 0,26 (T - 1358)$ $\rho = 8,039 - 9,6 \cdot 10^{-4} (T - 1356)$
Pb	$\sigma = 1330 - 0,26 (T - 1358)$ $\rho = 10,71 - 13,9 \cdot 10^{-4} (T - 600)$
Fe	$\sigma = 1862 - 0,39 (T - 1803)$ $\rho = 6,99$

3. Surface tension measurements

The measurements of surface tension at 1373 K, 1473 K and 1573 K were carried out for the alloys of the following compositions:

- 90 wt % Cu, 5 wt % Pb, 5 wt % Fe ($x_{Cu}=0.9257$, $x_{Pb}=0.0158$, $x_{Fe}=0.0585$)
- 90 wt % Cu, 7.5 wt % Pb, 2.5 wt % Fe ($x_{Cu}=0.9459$, $x_{Pb}=0.0242$, $x_{Fe}=0.0299$)
- 85 wt % Cu, 10 wt % Pb, 5 wt % Fe ($x_{Cu}=0.9066$, $x_{Pb}=0.0327$, $x_{Fe}=0.0607$)
- 85 wt % Cu, 12.5 wt % Pb, 2.5 wt % Fe ($x_{Cu}=0.9272$, $x_{Pb}=0.0418$, $x_{Fe}=0.0310$)
- 80 wt % Cu, 15 wt % Pb, 5 wt % Fe ($x_{Cu}=0.8860$, $x_{Pb}=0.0510$, $x_{Fe}=0.0630$)
- 75 wt % Cu, 20 wt % Pb, 5 wt % Fe ($x_{Cu}=0.8638$, $x_{Pb}=0.0706$, $x_{Fe}=0.0656$)
- 70 wt % Cu, 25 wt % Pb, 5 wt % Fe ($x_{Cu}=0.8398$, $x_{Pb}=0.0920$, $x_{Fe}=0.0682$)

In the measurements, the sessile drop method was used. A high-temperature microscope and a camera, both coupled with a computer equipped with a program enabling regulation and control of the device work parameters as well as recording and analyzing the picture were applied. The protective gas during the measurements was argon of 99.9999% purity.

For determination of the surface tension, a computational procedure of the least square estimation of the parameters of the system of equations describing the shape of a sessile drop of liquid was used. A detailed

description of the experimental apparatus and measurement method is presented in the literature mentioned in the references [12]. For the sessile drop volume calculating, necessary for determining the densities of the investigated alloys, a method based on dividing a given drop picture into segments was used [13]. In Fig.1, a sample shape (observed and recorded during the measurements) of a liquid metal drop is presented. For each alloy type used for surface tension investigations, six independent measurements, under identical experimental conditions, were performed.



Fig. 1. An alloy drop of 70 wt % Cu, 25 wt % Pb, 5 wt % Fe at 1373 K

4. Results and discussion

In Table 3, the measured surface tension values for Cu-Pb-Fe alloys as well as the values obtained through model calculations are presented:

Column 1 – the alloy composition in wt %,

Column 2 – temperature T in K, at which the experiment

was conducted,

Column 3 – the density ρ in kgm^{-3} , used for the surface tension calculations,

Column 4 – mean values of the surface tension σ in mNm^{-1} , calculated on the basis of measurement series, carried out under the same conditions,

Column 5 – the standard deviation $S(\sigma)$ in $mN \cdot m^{-1}$,

Column 6 – the surface tension σ_M in mNm^{-1} , calculated on the basis of the proposed model.

TABLE 3

The surface tensions of liquid Cu-Pb-Fe alloys

Alloy wt %	T K	$\rho \cdot 10^{-3}$ kgm^{-3}	σ $mN \cdot m^{-1}$	$S(\sigma)$ $mN \cdot m^{-1}$	σ_M $mN \cdot m^{-1}$
Cu90%-Pb5%-Fe5%	1373	8.03	765	16	757
	1473	7.94	802	10	797
	1573	7.85	816	13	833
Cu90%-Pb7.5%-Fe2.5%	1373	8.09	743	18	692
	1473	8.00	764	6	727
	1573	7.90	787	15	748
Cu85%-Pb10%-Fe5%	1373	8.10	652	14	633
	1473	8.00	703	17	669
	1573	7.91	743	14	701
Cu85%-Pb12.5%-Fe2.5%	1373	8.16	649	18	607
	1473	8.06	675	5	641
	1573	7.96	704	13	672
Cu80%-Pb15%-Fe5%	1373	8.16	620	16	565
	1473	8.07	634	10	599
	1573	7.97	664	13	630
Cu75%-Pb20%-Fe5%	1373	8.23	532	22	518
	1473	8.13	574	19	549
	1573	8.04	592	15	579
Cu70%-Pb25%-Fe5%	1373	8.30	477	8	482
	1473	8.20	532	18	512
	1573	8.10	553	16	540

For the Cu-Pb-Fe alloys, the measurement results show that within the increase in the amount of Pb in the alloy, the values of surface tension decrease significantly. Although they are ternary alloys, we can assume that lead is the component responsible for the surface tension values. This can be proved by the fact that the surface tension changes, as a function of the Pb content in the alloy (Table 3), are similar to the changes (mentioned in the references [10, 11, 14]) for binary Cu-Pb alloys. Lead, which is a surface-active element [15-17], shows the tendency to accumulate at the liquid meta-gas interface. The measurement results show that the temperature rise weakens lead's influence on the decrease in the surface tensions of the investigated Cu-Pb-Fe alloys (a positive coefficient $\frac{d\sigma}{dT}$). The observed tendency can be confirmed in many publications [10, 14-20] whose authors notice that for surface-active substances (oxygen, sulphur, antimony, lead, bismuth), the temperature coefficient of surface tension can have positive values contrary to those for pure liquid metals and the majority of alloys. This probably results from desorption (caused by temperature rise) of lead from the interfacial surface of liquid alloys, or replacing of lead atoms by iron and copper atoms in the surface phase of the Cu-Pb-Fe al-

loys, as well as, to some extent, lead evaporation from the alloy.

The data obtained with the use of the proposed model and the experimental data show a satisfactory agreement. In some cases, there are discrepancies due to the fact that the data for model calculations were taken from various literature sources. Thus, it can be expected that, for instance, during the investigations regarding the surface properties of pure metals or binary alloys, some experimental errors different from those in the present paper were made.

5. Summary

In the present paper, a model enabling calculation of surface tensions of Cu-Pb-Fe alloys formed during the one-stage flash furnace copper smelting process was proposed. Next, the model was verified on the basis of the obtained data for seven various alloy compositions.

The obtained results show that lead is the component demonstrating the strongest influence on the surface tension values of liquid Cu-Pb-Fe alloys. The greater amount of Pb in the alloy, the lower values of the surface

tension. The temperature rise weakens lead's influence on the decrease in surface tensions of the investigated alloys.

The results obtained from the proposed model and the experimental data show a satisfactory agreement. They are supplementary data for the very little information to be found in literature regarding the surface properties of liquid Cu-Pb-Fe.

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