

MARIAN KUCHARSKI\*, MONIKA GLUZIŃSKA\*

## SURFACE TENSION OF LIQUID Cd-Zn-Sn ALLOYS

### NAPIĘCIE POWIERZCHNIOWE CIEKLYCH STOPÓW Cd-Zn-Sn

A model predicting the surface tension of multicomponent solutions from the knowledge of thermodynamic properties, densities and surface tensions for limiting binaries has been proposed. The model was tested for the surface tension of Cd-Zn-Sn alloys, which were determined by the maximum bubble pressure method. Surface tension and density data of Cd-Sn and Zn-Sn alloys were acquired from literature. A fairly good agreement between predicted and experimental data was obtained for Cd-Zn-Sn.

W pracy zaproponowano model do obliczania napięcia powierzchniowego wieloskładnikowych roztworów w którym wykorzystuje się znajomość własności termodynamicznych, gęstości i napięcia powierzchniowego dla granicznych roztworów podwójnych. Model wykorzystano do obliczenia wartości napięcia powierzchniowego stopów Cd-Zn-Sn, które również zmierzono metodą maksymalnego ciśnienia w pęcherzykach gazowych. Wartości gęstości, napięcia powierzchniowego oraz własności termodynamicznych dla granicznych układów podwójnych zaczerpnięto z literatury. Uzyskano dosyć dobrą zgodność między wartościami obliczonymi z modelu, a danymi eksperymentalnymi.

## 1. Introduction

The investigation of the physical properties such as surface tension, density and viscosity is of great importance from theoretical and practical point of view. These properties in conjunction with thermodynamic data can provide better understanding of processes occurring in extractive metallurgy. The surface tension is the property that influences the reaction rates taking place on interface of

\*INSTYTUT METALI NIEŻELAZNYCH AGH, 30-059 KRAKÓW, AL. MICKIEWICZA 30

phases because of adsorption phenomenon which is related to the surface tension. The paper presents the results of surface tensions measurements for Zn-Cd-Sn alloys as well as a model which attempts to describe the surface tension of multi-component solutions from the knowledge of thermodynamic properties, densities and surface tensions for limiting binaries.

## 2. The surface tension measurements of Cd-Zn-Sn alloys

The surface tension of Cd-Zn-Sn alloys has been measured with the maximum-bubble pressure method. The experimental set up used during these measurements has been described in paper [1]. This experimental set up is shown in Fig. 1. The apparatus consists of furnace, gas train, capillary, graphite container with investigated alloy placed in crucible, bellows system and micrometer screw. In order to limit evaporation of cadmium and zinc from the Cd-Zn-Sn alloy, the crucible contained the sample was placed in graphite container with lid wherein a hole for capillary introduction had been made.

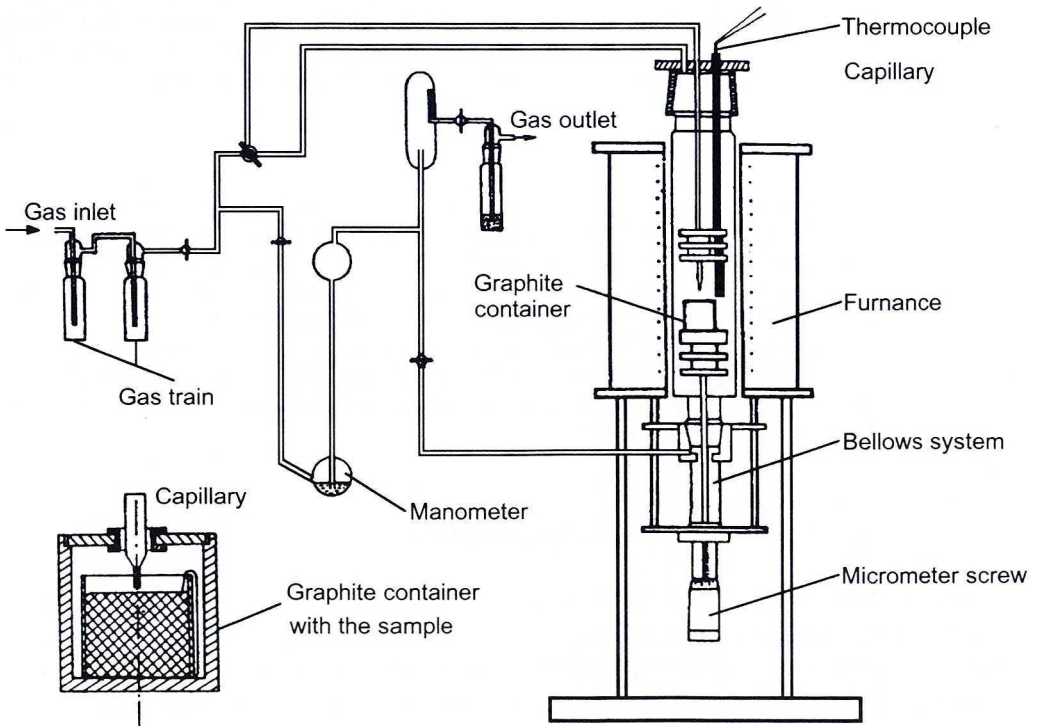


Fig. 1. Experimental apparatus

A sample of the investigated alloy was placed in the furnace which was then closed. Next the gas-train was switched on and purified argon was passing through the system for about 24 hrs. After flushing the system, the furnace was switched on to have the furnace heated up to the desired temperature. Then the capillary was immersed at one of three chosen depths. The maximum pressure required for forming and detaching several bubbles was measured. The bubble rate formation was about 60 seconds. The average value of these measurements was taken for surface tension computation, and the first approximation of the surface tension was determined with the equation:

$$\sigma = \frac{1}{2} r \cdot P_{\max}, \quad (1)$$

where:  $\sigma$  is the first approximated value of the surface tension,  $r$  is the capillary radius ( $r \approx 1.5$  mm),  $P_{\max}$  is the maximum pressure required for forming and detaching a bubble. The real value of measured surface tension was obtained with S u g d e n ' s corrective procedure [2]. Investigated alloys were prepared from Cd-99.999%, Zn-99.999%, and Sn-99.99% purity.

Results obtained for Cd-Zn-Sn alloys are enclosed in Table 1, and graphically illustrated in Fig. 2.

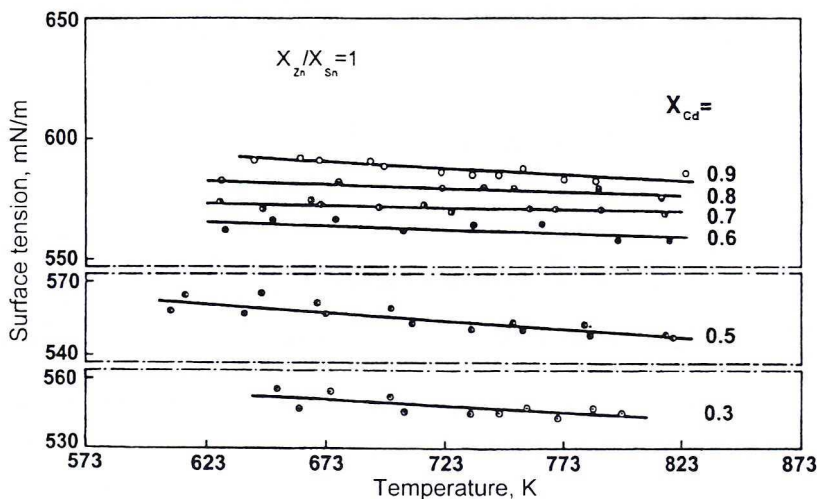


Fig. 2. Temperature dependence of the surface tension for Cd-Zn-Sn alloys

For all investigated alloys, the surface tension varies linearly with temperature despite the fact that surface tensions of zinc [3] and cadmium [1] show curvilinear dependencies vs. temperature.

Dependence of surface tension of Cd-Zn-Sn alloys on composition and temperature.  
For all alloys  $X_{Zn}/X_{Sn} = 1$

|                |                    |   |
|----------------|--------------------|---|
| $X_{Cd} = 0.9$ | $T$<br>[K]         | 643 662 669 691 697 721 734 745 755 773 785 825             |
|                | $\sigma$<br>[mN/m] | 591 592 591 591 590 578 586 596 590 583 583 586             |
| $X_{Cd} = 0.8$ | $T$<br>[K]         | 629 679 721 741 751 788 815                                 |
|                | $\sigma$<br>[mN/m] | 583 583 581 581 581 581 577                                 |
| $X_{Cd} = 0.7$ | $T$<br>[K]         | 628 646 665 671 695 715 727 759 770 788 815                 |
|                | $\sigma$<br>[mN/m] | 574 572 577 574 572 574 570 574 574 574 570                 |
| $X_{Cd} = 0.6$ | $T$<br>[K]         | 630 651 677 700 734 763 796 817                             |
|                | $\sigma$<br>[mN/m] | 562 567 567 562 565 565 557 557                             |
| $X_{Cd} = 0.5$ | $T$<br>[K]         | 608 614 638 645 668 673 700 709 734 751 756 781 783 815 819 |
|                | $\sigma$<br>[mN/m] | 559 565 559 564 561 556 559 552 549 554 549 554 547 551 546 |
| $X_{Cd} = 0.3$ | $T$<br>[K]         | 653 663 675 700 707 734 745 757 770 785 797                 |
|                | $\sigma$<br>[mN/m] | 555 547 555 554 547 546 547 551 545 548 547                 |

### 3. The model

#### 3.1. Surface tension of binary mixtures

The relation between the surface tension and the activities of component "i" in bulk and surface phase for a mixture is expressed by the equation [4]:

$$\sigma = \sigma_i^0 \frac{A_i^0}{A_i} + \frac{RT}{A_i} \ln \frac{a_i^{(s)}}{a_i^{(b)}}, \quad (2)$$

where  $a_i^{(s)}$ ,  $a_i^{(b)}$  are the activities of component "i" in the surface and bulk phase respectively,  $A_i^0$  is the molar surface of pure component "i",  $A_i$  is the partial surface area of component "i",  $\sigma_i^0$  is the surface tension of pure component "i". This equation was for the first time developed by Butler [5].



It has been suggested [1, 6, 7] that the activity coefficients in the surface phase for binaries solutions can be written as follows:

$$\ln \gamma_i^{(s)} = \text{const} \cdot f_i(X_i^{(s)}), \quad (3)$$

where  $f_i$  is the same function, which describes the activity coefficient of the component “ $i$ ” in the bulk phase:

$$\ln \gamma_i^{(b)} = f_i(X_i^{(b)}). \quad (4)$$

It should be mentioned that in our model “const” does not represent a fraction of  $i - j$  bonds of  $i$ -th atom in surface phase in comparison with  $i$ -th atom in the bulk phase. To reach the surface  $i$ -th atom has to gain an extra energy, and therefore energy bonds in the surface phase would be much weaker than in the bulk phase. Therefore in our model “const” is rather related to  $i - j$  pair energies in surface and bulk phases.

$$\varepsilon_{i,j}^{(s)} - (\varepsilon_{i,i}^{(s)} + \varepsilon_{j,j}^{(s)}) / 2 = \text{const} \cdot [\varepsilon_{i,j}^{(b)} - (\varepsilon_{i,i}^{(b)} + \varepsilon_{j,j}^{(b)}) / 2]. \quad (5)$$

Some of the atoms would acquire such energy that can leave also the surface and pass to the gas phase. Because of it, thermodynamically this solution should be close to ideality, and hence “const” value should be closed to zero. It is understandable that there is also decrease of  $i - j$  bonds of  $i$ -th atom in the surface phase.

Taking into account “ $i$ ” and “ $j$ ” ( $i \neq j$ ) components of the binary mixture and using equations (2) – (4) one can obtained the following equation:

$$\frac{\sigma_i^0 A_i^0 - \sigma_j^0 A_j^0 \Theta_{ij}}{RT} + \Theta_{ij} \ln X_j^{(b)} - \ln X_i^{(b)} + \Theta_{ij} f_j(X_j^{(b)}) - f_i(X_i^{(b)}) = \Theta_{ij} \ln X_i^{(s)} - \ln X_i^{(s)} + \text{const} \cdot [\Theta_{ij} f_j(X_k^{(s)}) - f_i(X_k^{(s)})], \quad (6)$$

where  $\Theta_{ij} = A_i/A_j$ ,  $A_i = V_i/\tau$ ,  $V_i$  is partial molar volume of component “ $i$ ”,  $\tau$  is assumed thickness of the surface phase- we usually assume a monolayer surface phase. Equation (6) can be solved numerically for chosen “constant” value which “best” fits the Eq. (2) to experimental data. In Fig. 3, a flow chart for calculating the surface tension is presented. The constants as well as the surface compositions for Zn-Sn and Cd-Sn alloys were estimated with this algorithm. The experimental data for these systems were acquired form literature [1, 3].

The surface tensions of Zn-Cd system were measured by Ptak and Kucharski [8], however their data were obtained at an intensive zinc and cadmium evaporation. Measurements of the surface tension of the metals possessing high vapour pressure can give false results if equilibrium between the vapour and the liquid did not prevailed [9]. An attempt to describe these data by Eq. (2) shows rather poor fit. The surface tension from equation (2) for these systems was computed utilising the estimated data. Comparison between the experimental data and those computed from Eq. (2) are shown in Figs. 4 and 5.

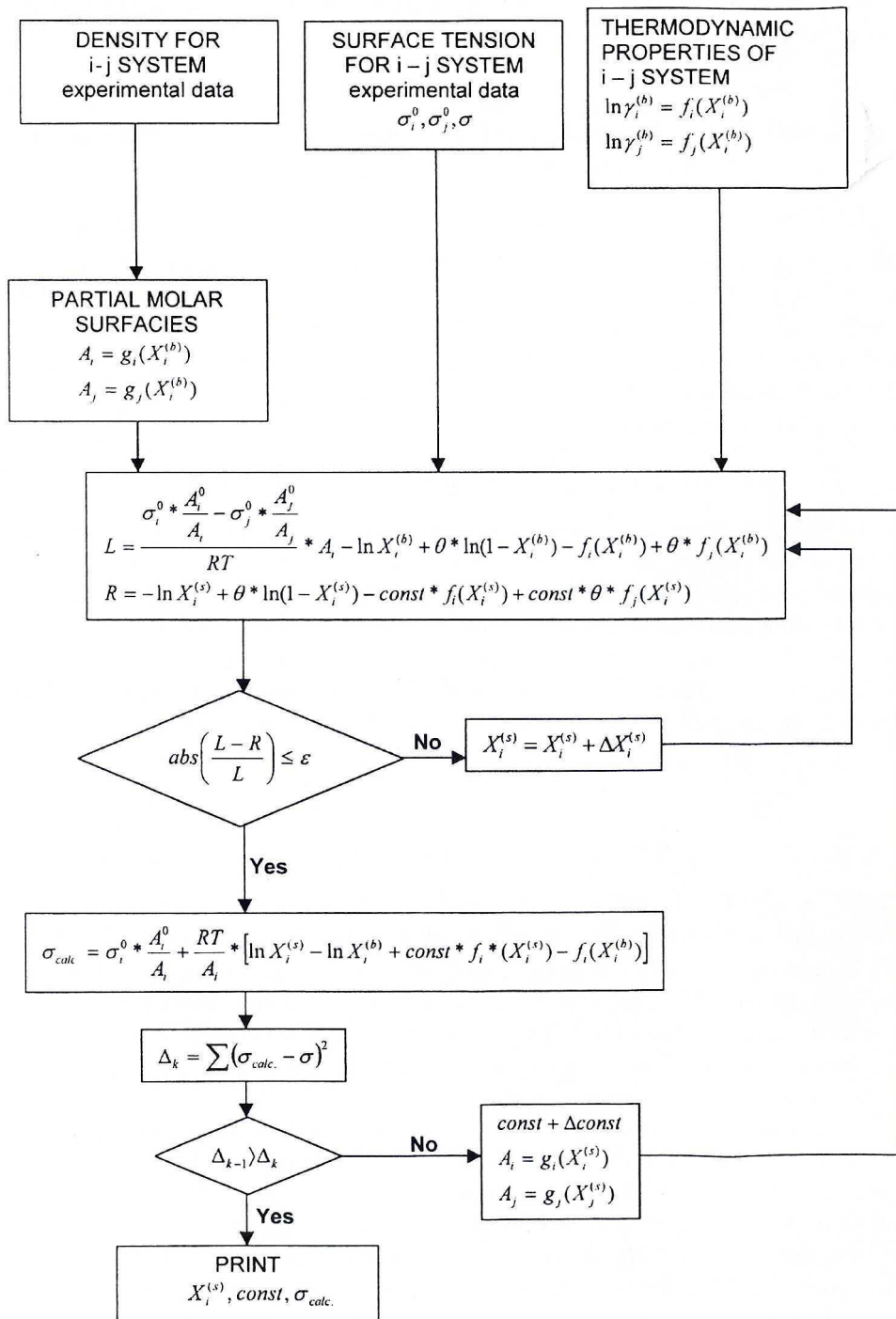


Fig. 3. Flow chart for calculating the surface tension of binary mixtures

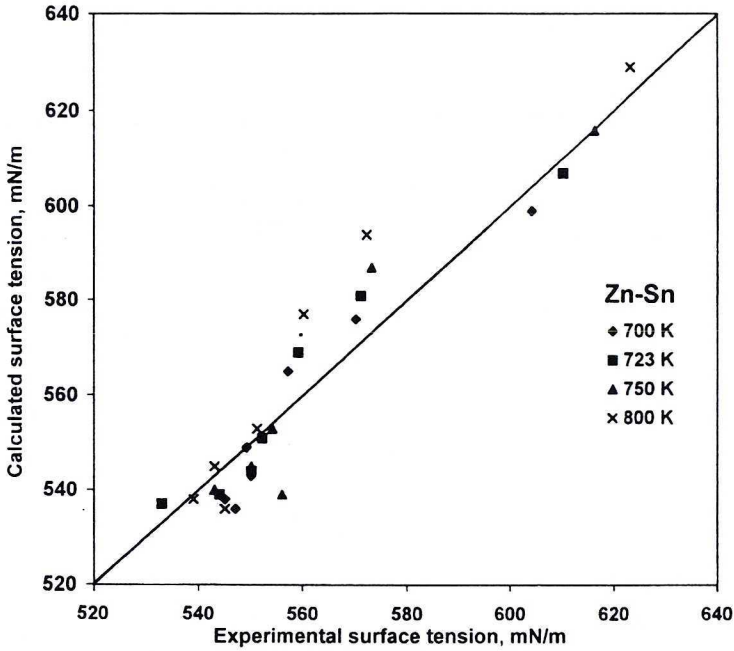


Fig. 4. Comparison between measured values of surface tension and values calculated with Eq. (2) with  $\text{const}_{\text{Zn,Sn}} = -0.03$  for Zn-Sn alloys. Experimental data were taken from literature [3]

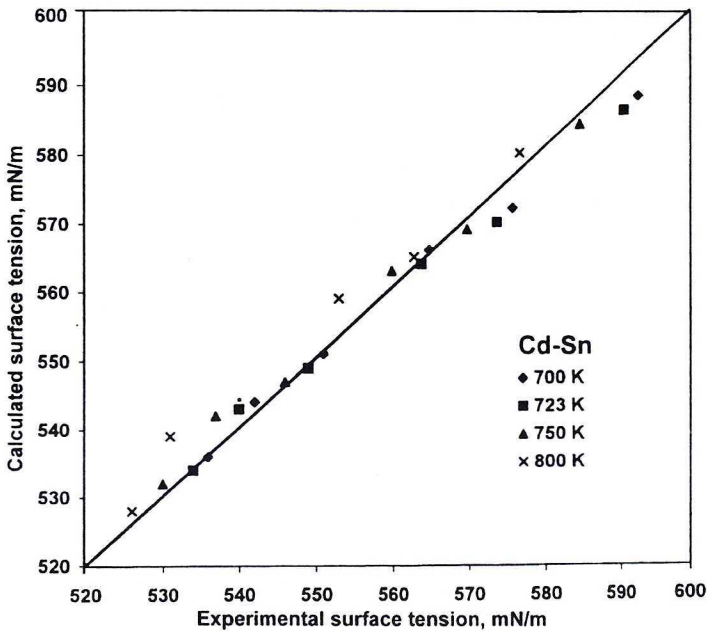


Fig. 5. Comparison between measured values of surface tension and values calculated with Eq. (1) with  $\text{const}_{\text{Cd,Sn}} = 0.23$  for Cd-Sn alloys. Experimental data were taken from literature [1]

3.2. Surface tension of multicomponent mixtures

Let us assume that our mixture is formed from  $n$ -components. According to Eq. (2), surface tension of the mixture, can be expressed by the  $n$ -relations:

$$\begin{aligned} \sigma &= \sigma_1^0 \frac{A_1^0}{A_1} + \frac{RT}{A_1} \ln \frac{a_1^{(s)}}{a_1^{(b)}}, \\ \sigma &= \sigma_2^0 \frac{A_2^0}{A_2} + \frac{RT}{A_2} \ln \frac{a_2^{(s)}}{a_2^{(b)}}, \\ \sigma &= \sigma_3^0 \frac{A_3^0}{A_3} + \frac{RT}{A_3} \ln \frac{a_3^{(s)}}{a_3^{(b)}}, \\ &\dots\dots\dots \\ \sigma &= \sigma_n^0 \frac{A_n^0}{A_n} + \frac{RT}{A_n} \ln \frac{a_n^{(s)}}{a_n^{(b)}}, \end{aligned} \tag{7}$$

where:  $a_1^{(b)}, a_2^{(b)}, a_3^{(b)}, \dots, a_n^{(b)}$  and  $a_1^{(s)}, a_2^{(s)}, a_3^{(s)}, \dots, a_n^{(s)}$  are activities of the solution components in bulk and surface phase respectively,  $A_1, A_2, A_3, \dots, A_n$  are partial molar surface of the solution components,  $A_1^0, A_2^0, A_3^0, \dots, A_n^0$  are molar surface of pure components,  $\sigma_1^0, \sigma_2^0, \sigma_3^0, \dots, \sigma_n^0$  are surface tensions of pure components.

By combination of these equations one can obtained  $(n - 1)$  independent non-linear equations:

$$\begin{aligned} &\frac{\sigma_1^0 A_1^0 - \sigma_2^0 A_2^0 \Theta_{12}}{RT} + \Theta_{12} \ln X_2^{(b)} - \ln X_1^{(b)} + \Theta_{12} F_2(X_1^{(b)}, X_2^{(b)}, \dots, X_n^{(b)}) \\ &\quad - F_1(X_1^{(b)}, X_2^{(b)}, \dots, X_n^{(b)}) = \Theta_{12} \ln X_2^{(s)} - \ln X_1^{(s)} \\ &\quad + \Theta_{12} F_2(X_1^{(s)}, X_2^{(s)}, \dots, X_n^{(s)}) - F_1(X_1^{(s)}, X_2^{(s)}, \dots, X_n^{(s)}), \\ &\frac{\sigma_1^0 A_1^0 - \sigma_3^0 A_3^0 \Theta_{13}}{RT} + \Theta_{13} \ln X_3^{(b)} - \ln X_1^{(b)} + \Theta_{13} F_3(X_1^{(b)}, X_2^{(b)}, \dots, X_n^{(b)}) \\ &\quad - F_1(X_1^{(b)}, X_2^{(b)}, \dots, X_n^{(b)}) = \Theta_{13} \ln X_3^{(s)} - \ln X_1^{(s)} \\ &\quad + \Theta_{13} F_3(X_1^{(s)}, X_2^{(s)}, \dots, X_n^{(s)}) - F_1(X_1^{(s)}, X_2^{(s)}, \dots, X_n^{(s)}), \end{aligned} \tag{8}$$

.....  
.....

$$\begin{aligned} &\frac{\sigma_1^0 A_1^0 - \sigma_n^0 A_n^0 \Theta_{1n}}{RT} + \Theta_{1n} \ln X_n^{(b)} - \ln X_1^{(b)} + \Theta_{1n} F_n(X_1^{(b)}, X_2^{(b)}, \dots, X_n^{(b)}) \\ &\quad - F_1(X_1^{(b)}, X_2^{(b)}, \dots, X_n^{(b)}) = \Theta_{1n} \ln X_n^{(s)} - \ln X_1^{(s)} \\ &\quad + \Theta_{1n} F_n(X_1^{(s)}, X_2^{(s)}, \dots, X_n^{(s)}) - F_1(X_1^{(s)}, X_2^{(s)}, \dots, X_n^{(s)}). \end{aligned}$$



In order to solve this set of equations, the model utilising thermodynamic properties of limiting binary systems [10] was used to describe activity coefficients of the components in bulk and surface tension phases. The excess free energy of mixing according to this model is expressed by the equation:

$$G^E = (1-y_2) \left[ G^E(y_1) \right]_{1,2} + y_2(1-y_3) \left[ G^E(y_1) \right]_{1,3} + \dots + y_2 y_3 \dots y_{n-1} \left[ G^E(y_1) \right]_{1,n} + \sum_{i=2}^{n-1} \sum_{j=i+1}^n (X_i + X_j)^2 \left[ G^E \left( \frac{X_j}{X_i + X_j} \right) \right]_{i,j}, \quad (9)$$

where  $[G^E(y_1)]_{1,i}$  is the excess free energy of the limiting binary 1 -  $i$  mixture,  $\left[ G^{EX} \left( \frac{X_j}{X_i + X_j} \right) \right]_{i,j}$  is the excess free energy of the limiting binary  $i$  -  $j$  mixture ( $i \geq 2; j \geq i + 1$ ),  $X_i; X_j$  are the mole fractions, and

$$\begin{aligned} y_1 &= \frac{X_2 + X_3 + \dots + X_n}{X_1 + X_2 + \dots + X_n} = 1 - X_1, \\ y_2 &= \frac{X_3 + X_4 + \dots + X_n}{X_2 + X_3 + \dots + X_n}, \\ &\dots \dots \dots \\ y_{n-1} &= \frac{X_n}{X_{n-1} + X_n} \end{aligned} \quad (10)$$

are independent variables.

The relations express partial molar free energies of mixing:

$$\begin{aligned} G_1^E &= G^E - y_1 \frac{\partial G^E}{\partial y_1}, \\ G_2^E &= G_1^E + \frac{\partial G^E}{\partial y_1} - \frac{y_2}{y_1} \frac{\partial G^E}{\partial y_2}, \\ &\dots \dots \dots \\ G_n^E &= G_1^E + \frac{\partial G^E}{\partial y_1} + \frac{1-y_2}{y_1} \frac{\partial G^E}{\partial y_2} + \frac{1-y_3}{y_1 y_2} \frac{\partial G^E}{\partial y_3} + \dots + \frac{1-y_{n-1}}{y_1 y_2 y_3 \dots y_{n-2}} \frac{\partial G^E}{\partial y_{n-1}}. \end{aligned} \quad (11)$$

Thermodynamic properties for limiting binary systems of Zn-Cd-Sn alloys were taken from literature [11 - 13], and according to equations (11), the partial free energy of Zn in Zn-Cd-Sn alloys was computed (Zn = 1, Cd = 2, Sn = 3). The calculated values are compared with the experimental data [14] as can be seen in Fig. 6.

As can be easily seen the computed values are in a quite good agreement with the experimental data.

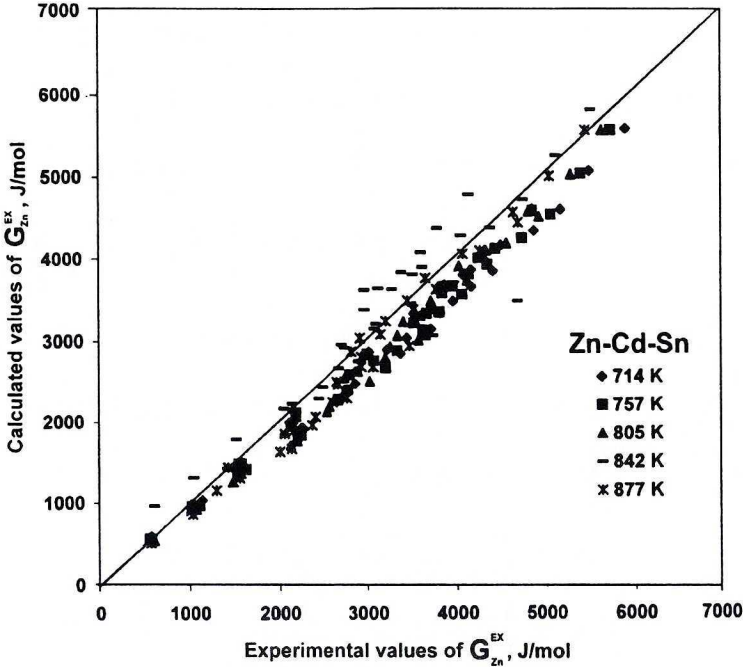


Fig. 6. Comparison between measured values of the partial free energy of zinc in Zn-Cd-Sn alloys and values calculated from the model

To solve the set of equation (8), the following assumptions have been made:

• The excess free energy of mixing for the “surface phase” is expressed by the equation:

$$\begin{aligned}
 G^{E(s)} = & (1 - y_2^{(s)}) \left[ \text{const}_{1,2} G^{E(s)}(y_1^{(s)}) \right]_{1,2} + \\
 & y_2^{(s)} (1 - y_3^{(s)}) \left[ \text{const}_{1,3} G^{E(s)}(y_1^{(s)}) \right]_{1,3} + \dots + \\
 & y_2^{(s)} y_3^{(s)} \dots y_{n-1}^{(s)} \left[ \text{const}_{1,n} G^{E(s)}(y_1^{(s)}) \right]_{1,n} + \\
 & \sum_{i=2}^{n-1} \sum_{j=i+1}^n (X_i^{(s)} + X_j^{(s)})^2 \left[ \text{const}_{i,j} G^{E(s)} \left( \frac{X_j^{(s)}}{X_i^{(s)} + X_j^{(s)}} \right) \right]_{i,j}, \quad (12)
 \end{aligned}$$

where  $\text{const}_{1,2}$ ,  $\text{const}_{1,3}$ , ...,  $\text{const}_{1,n}$  are constants estimated for  $1 - i$  binary systems,  $\text{const}_{i,j}$  are constants estimated for  $i - j$  binary systems ( $i \neq j$ ,  $j \neq 1$ ) are independent parameters for the “surface phase”.

• Mathematical form of the  $\left[ G^{E(s)} \right]_{k,l}$  functions is identical with those for the bulk phase of the  $k - l$  binary systems  $\left[ G^E \right]_{k,l}$ .

Utilising Eq. (12), the partial molar free energies of mixing for “surface phase” can be estimated:

$$\begin{aligned}
 G_1^{E(s)} &= G^{E(s)} - y_1^{(s)} \frac{\partial G^{E(s)}}{\partial y_1^{(s)}}, \\
 G_2^{E(s)} &= G_1^{E(s)} + \frac{\partial G^{E(s)}}{\partial y_1^{(s)}} - \frac{y_2^{(s)}}{y_1^{(s)}} \frac{\partial G^{E(s)}}{\partial y_2^{(s)}}, \\
 &\dots\dots\dots \\
 G_n^{E(s)} &= G_1^{E(s)} + \frac{\partial G^{E(s)}}{\partial y_1^{(s)}} + \frac{1 - y_2^{(s)}}{y_1^{(s)}} \frac{\partial G^{E(s)}}{\partial y_2^{(s)}} + \frac{1 - y_3^{(s)}}{y_1^{(s)} y_2^{(s)}} \frac{\partial G^{E(s)}}{\partial y_3^{(s)}} + \dots \\
 &\quad + \frac{1 - y_{n-1}^{(s)}}{y_1^{(s)} y_2^{(s)} y_3^{(s)} \dots y_{n-2}^{(s)}} \frac{\partial G^{E(s)}}{\partial y_{n-1}^{(s)}}.
 \end{aligned}
 \tag{13}$$

The set of equation (8) can be solved through Eqs. (11) and (13) providing that all  $const_{k,l}$  were determined from experimental data for  $k - l$  binary systems. In case of Zn-Cd-Sn alloys  $const_{Zn,Sn} = -0.03$  and  $const_{Cd,Sn} = 0.23$  were estimated. The value of  $const_{Zn,Cd}$  was assumed to be 0.2 or  $-0.2$ . Using these data two independent equations (8), which may be derived for Zn-Cd-Sn alloys were solved.

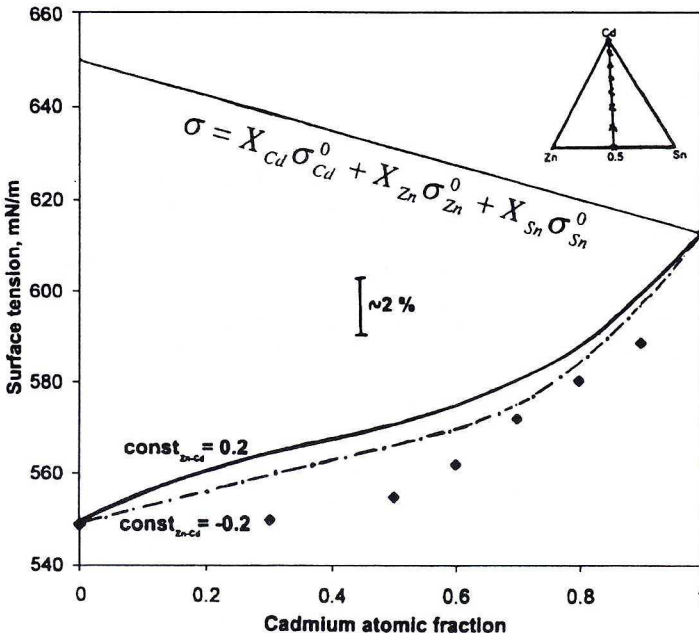


Fig. 7. Comparison between calculated from the model and measured values of the surface tension of Zn-Cd-Sn alloys

From this computation value  $y_1^{(s)}$  and  $y_2^{(s)}$ , and then surface tension of this system were calculated. Comparison between computed and experimental values is shown in Fig. 7.

As it can be seen in Fig. 7 a fairly good agreement between predicted and experimental data was obtained for Cd-Zn-Sn alloys.

#### 4. Conclusions

The surface tension of Zn-Cd-Sn alloys was measured by the maximum bubble pressure method over temperature and composition range. For the alloys with  $X_{Zn}/X_{Sn} = 1$ , and varied  $X_{Cd}$ , surface tension shows a linear dependence with temperature within experimental range.

A new predictive model for surface tension of multicomponent solutions was put forward. The model is capable to predict surface tension of multicomponent mixture from the knowledge of experimental data for limiting binary solutions. This model was tested for Zn-Cd-Sn alloys and a reasonable agreement between the values calculated from the model and measured data were observed.

#### REFERENCES

- [1] M. Kucharski, Density and surface tension of Sn-Cd alloys, *Arch. Hutnictwa* **22** (2), 181-194 (1977).
- [2] S. Sugden, The Determination of Surface Tension from the Maximum Pressure in Bubbles, *Journ. Chem. Soc.* 121, 858-866 (1922).
- [3] M. Kucharski, Density and surface tension of Sn-Zn alloys, *Zeszyty Naukowe AGH, Metalurgia i Odlewnictwo* **3** (3), 329-345 (1977).
- [4] Z. Moser, M. Kucharski, Sn-Zn system. Correlation between thermodynamic properties, physical properties, structure and phase diagram, *Journal of Non-Crystalline Solids* **156**, 369-373 (1933).
- [5] J. A. V. Butler, The Thermodynamics of the Surfaces of Solutions *Proc. Roy. Soc.* **135A**, 348-375 (1932).
- [6] Z. Moser, M. Kucharski, K. Rzyman, Activity and Surface Tension of Liquid AgCl-KCl Solutions., *J. Electrochem. Soc.* **125**, 692-697 (1978).
- [7] E. Yemu, R. Speiser, D. R. Poirier, Estimation of the Surface Tensions of Binary Liquid Alloys, *Metall. Trans.* **20B**, 693-703 (1989).
- [8] W. Ptak, M. Kucharski, Napięcie powierzchniowe stopów cynk-kadm i kadm-bizmut, *Archiwum Hutnictwa* **19** (3), 301-317 (1974).
- [9] D. W. G. White, The Surface tension of Zinc, *Trans. Met. Soc. AIME*, **236**, 796-803 (1966).
- [10] M. Kucharski, C. Acuna, Thermodynamic Properties of Multi-component Solutions, *Arch. Metall.* **41** (3), 271-281 (1966).
- [11] J. Dutkiewicz, W. Zakulski, The Cd-Zn (Cadmium-Zinc) System, *Bulletin of Alloy Phase Diagram* **5** (1), 30-36 (1984).
- [12] Z. Moser, J. Dutkiewicz, W. Gąsior, J. Salawa, The Sn-Zn (Tin-Zinc) System, *Bulletin of Alloy Phase Diagram* **6** (4), 330-334 (1985).

- [13] J. Dutkiewicz, L. Zabdyr, Z. Moser, J. Salawa, The Cd-Sn (Cadmium-tin) System, *Bulletin of Alloy Phase Diagram* **10** (3), 223-229 (1989).
- [14] W. Ptak, Z. Moser, Własności termodynamiczne ciekłych roztworów Zn-Sn-Cd, *Arch. Hutnictwa* **12** (1), 81-108 (1967).

REVIEWED BY: PROF. DR HAB. INŻ. WŁODZIMIERZ DERDA

*Received: 20 March 2001.*