THERMODYNAMIC CALCULATIONS IN LIQUID Al-Sn ALLOYS SYSTEMS

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Lucrarea prezintă aspecte legate de calcularea activităţii în sistemele de aliaje Al-Sn, comparând din punct de vedere al exactităţii, două modele teoretice. Primul model, modelul soluţiilor subsubregulare parţial-ordonate propus de D. Taloi [1], iar cel de-al doilea, un model de predicţie al activităţilor componenţilor dezvoltat de T. Fan s.a. [2]. Ambele modele au merite şi pot fi utilizate cu succes, abaterile de la datele experimentale fiind acceptabile. Modelul soluţiilor subsubregulare parţial ordonate prezintă abateri medii abosolute mai mici decât cele ale modelului de predicţie, dar cel de-al doilea model are avantajul calculării activităţilor componenţilor în lipsa datelor experimenatale.

The paper presents aspects regarding the computation of activities in Al-Sn alloys systems, comparing two theoretical models from the accuracy point of view. The first one, the partially-ordered sub-sub-regular solution model proposed by D. Taloi [1], and the second one a prediction model of components' activities developed by T. Fan et al. [2]. Both models have merits and can be successfully used, the deviations from experimental data being acceptable. The partially-ordered sub-sub-regular solution model has smaller mean absolute deviations than those of prediction model, but the second model has the advantage of computing components activities independent of experimental data.

Keywords: Al-Sn alloys, components' activities

1. Introduction

Al-Sn alloys are extensively used in industry applications due to their excellent tribological and mechanical properties. They are commonly used for sliding bearing application, in plain bearings, combustion engines pistons and cylinder liners [3, 4, 5, 6]. They are also used in Al-battery systems [7] and thin films and oxide films formation [8, 9]. Aluminum alloyed with tin, indium, and zinc is used as sacrificial anodes and corrosion-proof anodic coatings for steel [10], while Al-Sn-Zn alloys are used as soldering materials [11]. As a result, thermodynamics of liquid Al-Sn alloys are currently studied by numerous researchers. The aim of this paper is to theoretically investigate the thermodynamic activities of liquid Al-Sn alloys, computed using the theoretical

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model of partially-ordered sub-sub-regular solution presented by D. Taloi [1], in comparison with the model prediction of thermodynamics activity presented by T. Fan et al. based on Miedema model combined with Wilson equation [2,12], and, in the same time with the experimental data obtained through electromotive force (EMF) method [13].

2. Theory

2.1 Partially-ordered sub-sub-regular solution model (POSSR)

According to this model the activity coefficients of both components are obtained based on the following equations:

$$\begin{aligned}\ln\gamma_1 = {} & \left(1-\lambda-\lambda'\right)\ln\left(1-\lambda-\lambda'\right)- \\ & \left(1-\lambda-\lambda'+\lambda x_2^2+2\lambda' x_2^3\right)\ln\left[1-\left(\lambda+\lambda'\right)x_1-\lambda x_2^2-\lambda' x_2^3\right]+ \\ & \lambda x_2^2\ln\left(\frac{x_1}{x_2^2}+1\right)+2\lambda' x_2^3\ln\left(\frac{x_1}{x_2^3}+1\right)-\lambda\ln\left(x_1+x_2^2\right)- \\ & \lambda'\ln\left(x_1+x_2^3\right)+\left(\omega_0'-\omega_1'\right)x_2^2+3\omega_2' x_2^4+2\left(\omega_1'-\omega_2'\right)x_2^3+ \\ & \left(\lambda x_2^2+2\lambda' x_2^3\right)\ln\left(x_2-\lambda x_2^2-\lambda' x_2^3\right)\end{aligned} \tag{1}$$

and

$$\begin{aligned}\ln\gamma_2 = {} & \omega_0' x_1^2+2\omega_1' x_1^2 x_2+3\omega_2' x_1^2 x_2^2+\ln\frac{1-\lambda x_2-\lambda' x_2^2}{1-\left(\lambda-\lambda'\right)x_1-\lambda x_2^2-\lambda' x_2^3}- \\ & \lambda x_2\left(2-x_2\right)\ln\left(\frac{x_1}{x_2^2}+1\right)-\lambda' x_2^2\left(3-2x_2\right)\ln\left(\frac{x_1}{x_2^3}+1\right)+ \\ & \left[\lambda x_2\left(2-x_2\right)+\lambda' x_2^2\left(3-2x_2\right)\right]\ln\frac{1-\left(\lambda-\lambda'\right)x_1-\lambda x_2^2-\lambda' x_2^3}{x_2-\lambda x_2^2-\lambda' x_2^3}\end{aligned} \tag{2}$$

where x_1 and x_2 are molar fractions of components 1 and 2 respectively. ω_0', ω_1', and ω_2' are energies of mixing, and λ and λ' are structural parameters ranging between 0 and 1. The parameters ω_0', ω_1', ω_2', λ and λ' are determined from experimental data using the least square method.

2.2 Model prediction of thermodynamics activity (P)

In this model the activity coefficient of a component 1 can be calculated as:

$$\ln\gamma_1 = \frac{\alpha_{12}H_m^M}{RT}\left\{1+x_2\left[\begin{array}{l}\dfrac{1}{x_1}-\dfrac{1}{x_2}-\dfrac{u_1(\varphi_1-\varphi_2)}{1+u_2x_2(\varphi_1-\varphi_2)}+\dfrac{u_2(\varphi_2-\varphi_1)}{1+u_2x_1(\varphi_2-\varphi_1)}- \\ \dfrac{V_1^{\frac{2}{3}}\left[1+u_1(1-2x_1)(\varphi_1-\varphi_2)\right]}{x_1V_1^{\frac{2}{3}}\left[1+u_1x_2(\varphi_1-\varphi_2)\right]+x_2V_2^{\frac{2}{3}}\left[1+u_2x_1(\varphi_2-\varphi_1)\right]}+ \\ \dfrac{V_2^{\frac{2}{3}}\left[-1+u_2(1-2x_1)(\varphi_2-\varphi_1)\right]}{x_1V_1^{\frac{2}{3}}\left[1+u_1x_2(\varphi_1-\varphi_2)\right]+x_2V_2^{\frac{2}{3}}\left[1+u_2x_1(\varphi_2-\varphi_1)\right]}\end{array}\right]\right\} \quad (3)$$

In equation (3):

- α_{12} is denoted as $\alpha_{12} = 1-0.1T\left(\dfrac{1}{T_1^m}+\dfrac{1}{T_2^m}\right)$ (4)

  where T_1^m, T_2^m are the melting points of the two components and T is the temperature of the liquid melt;

- $H_m^M = f_{12}\dfrac{x_1\left[1+u_1x_2(\varphi_1-\varphi_2\right]x_2\left[1+u_2x_1(\varphi_2-\varphi_1\right]}{x_1V_1^{\frac{2}{3}}\left[1+u_1x_2(\varphi_1-\varphi_2)\right]+x_2V_2^{\frac{2}{3}}\left[1+u_2x_1(\varphi_2-\varphi_1)\right]}$ (5)

  is the molar enthalpy of mixing in (*kJ/mol*);

- $f_{12} = \dfrac{2pV_1^{\frac{2}{3}}V_2^{\frac{2}{3}}\left\{\dfrac{q}{p}\left[(n_{ws}^{\frac{1}{3}})_1-(n_{ws}^{\frac{1}{3}})_2\right]^2-(\varphi_1-\varphi_2)^2-b\dfrac{r}{p}\right\}}{(n_{ws}^{\frac{1}{3}})_1^{-1}+(n_{ws}^{\frac{1}{3}})_2^{-1}}$ (6)

- the rest of parameters are as follows (Table 1): φ is the electron density in (*volts*); V is the molar volume in (cm^3); n_{ws} is expressed in density units *(d.u.)*; $\frac{q}{p}$ is 9.4 ($volts^2/(d.u.)^{2/3}$) for all aloys; p equals 14.1 for alloys of two transition metals, 10.6 for two non-transition metals, and 12.3 for a transition metal with a non-transition metal; b equals 1.0 for solid alloys, 0.73 for liquid alloys of a transition metal with a non-transition metal, and 0 for all the other alloys.

Table 1

The values of some parameters used in calculations [10]

Element	$n_{ws}^{\frac{1}{3}}$ *((d.u.)$^{1/3}$)*	φ *(volts)*	$V^{\frac{2}{3}}$ *(cm)^3*	T^m *(K)*	u	$\frac{r}{p}$
Al	1.39	4.2	4.6	933	0.07	1.9
Sn	1.24	4.15	6.4	505	0.04	2.1

3. Results and discussion

In order to obtain the experimental values of the activities in the Al-Sn alloys systems, our experiments were conducted by means of electrochemical measurements, performing a reaction in an electrolytic cell at constant temperature of 1023 K. The electromotive force (EMF) produced is related to the activity through the relation:

$$\ln a_i = -\frac{zF}{RT}E \tag{11}$$

where z is charge number, F is Faraday's constant, E is the measured cell voltage, R is the gas constant, and T is the temperature.

In Table 2 are presented the outcomes of activities and activities' coefficients obtained using the two proposed models, as well as the experimental data at 1023 K.

Even if the two models proposed for analysis in this work are different in the sense that partially-ordered sub-sub-regular solution model can be developed based on experimental data while prediction model is independent of them, the comparison between them is still valid.

The experimental data are shown in Table 2 in comparison with the calculated ones by means of the two theoretical models.

Figs 1 and 2 present the experimental activities in comparison with the calculated ones using the two models proposed, at different atom fractions of Sn.

Table 2

Activities and activities' coefficients at 1023 K

x_{Al}	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Experimental data											
a_{Al}	0.000	0.178	0.333	0.460	0.572	0.668	0.748	0.812	0.866	0.923	1.000
γ_{Al}	1.687	1.776	1.663	1.534	1.430	1.336	1.246	1.160	1.082	1.026	1.000
a_{Sn}	1.000	0.899	0.809	0.727	0.647	0.571	0.498	0.427	0.351	0.239	0.000
γ_{Sn}	1.000	0.999	1.011	1.039	1.079	1.141	1.244	1.422	1.755	2.386	6.563
Computed values using P model											
a_{Al}	0.000	0.253	0.435	0.564	0.655	0.720	0.770	0.813	0.859	0.918	1.001
γ_{Al}	2.956	2.530	2.175	1.880	1.638	1.440	1.283	1.162	1.074	1.020	1.001
a_{Sn}	1.000	0.908	0.829	0.761	0.703	0.651	0.600	0.541	0.457	0.308	0.000
γ_{Sn}	1.000	1.008	1.036	1.088	1.172	1.302	1.500	1.805	2.287	3.084	1.002
Computed values using POSSR model											
a_{Al}	0.000	0.174	0.345	0.503	0.636	0.739	0.812	0.860	0.894	0.932	1.000
γ_{Al}	1.717	1.738	1.726	1.675	1.590	1.478	1.353	1.228	1.117	1.035	1.000
a_{Sn}	1.000	0.899	0.801	0.708	0.625	0.553	0.494	0.443	0.395	0.306	0.000
γ_{Sn}	1.000	0.999	1.001	1.011	1.041	1.106	1.234	1.481	1.973	3.063	6.385

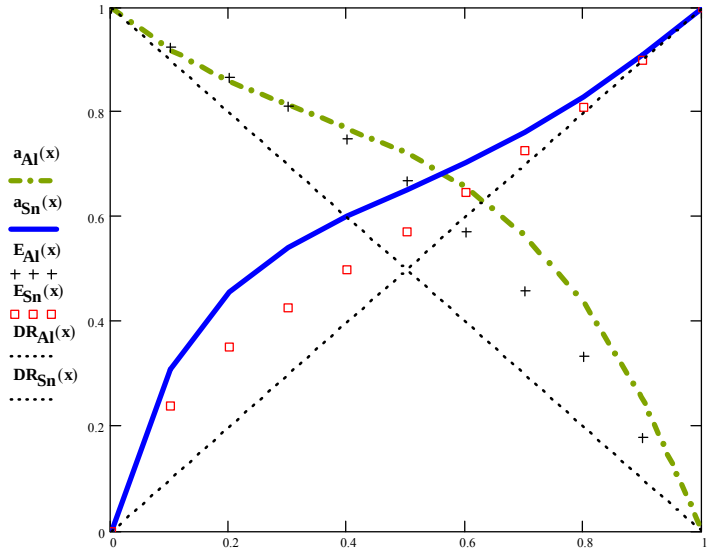

Fig. 1 Experimental (E) and calculated activities (a) with prediction model in liquid Al-Sn alloys at 1023 K

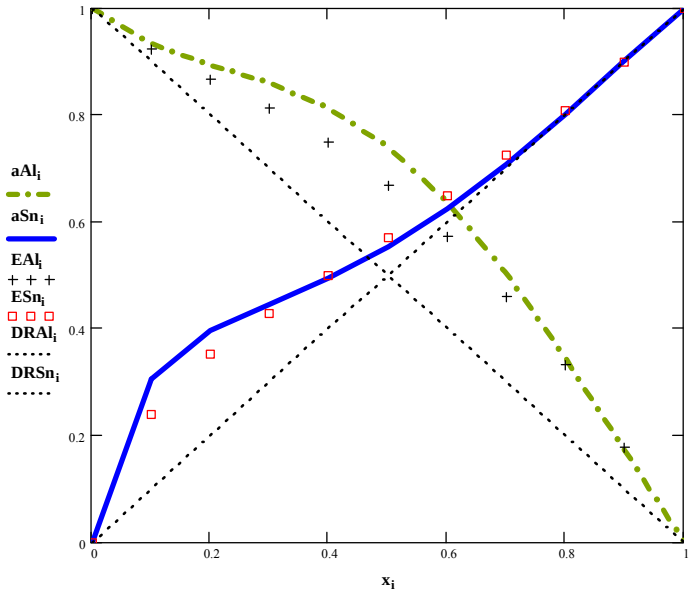

Fig. 2 Experimental (E) and calculated activities (a) with partially-ordered sub-sub-regular solution model in liquid Al-Sn alloys at 1023 K

A good consistency between experimental and calculated data for both models can be observed from Table 2 and Fig. 1 and Fig. 2. However, while P model shows some deviations for both components' activities between 0.1 to 0.6 atom fractions, the POSSR model seems to have better findings, at least for Sn activities.

The last statement is sustained by the mean absolute deviation (MAD) which shows better values for POSSR model than for P model (Table 3).

Table 3

Mean absolute deviation for the two analyzed models

MAD_{Al}^{P}	**0.041091**
MAD_{AL}^{POSSR}	**0.031182**
MAD_{Sn}^{P}	**0.053636**
MAD_{Sn}^{POSSR}	**0.018**
MAD_{Total}^{P}	**0.094727**
MAD_{Total}^{POSSR}	**0.049182**

4. Conclusions

In regards of computing thermodynamic activities in Al-Sn alloys systems, there were investigated two theoretical models: the partially-ordered sub-sub-regular solution model and the prediction model.

From their reliability point of view, both analyzed models proved to have a good consistency with experimental data. Nevertheless, the partially-ordered sub-sub-regular solution model having smaller deviations from the experimental data proved to be a better alternative than the prediction model.

However, prediction model proposed by T. Fan et. al has the great advantage over the others models including POSSR model, through the fact that it does not require to have experimental data. Using only the physical parameters of pure metals, the component activities in binary alloys systems can be theoretically calculated and the calculations results agree well with the measured data.

R E F E R E N C E S

[1] *D. Taloi,* New considerations regarding the thermodynamic of binary alloy systems, UPB Sci. Bull., Series B, Vol. 68 No. 3, 2006, pp. 55-66.

[2] *T. Fan, G. yang, J. Chen, and Di Zhang,* Model prediction of thermodynamics activity in multicomponent liquid alloy, Key Engineering Materials Vol. 313, 2006, pp 19-23.

[3] *W.R.. Osario, J.E. Spinelli, N. Cheung, and A. Garcia,* Secondary dendrite arm spacing and solute redistribution effects on the corrosion resistance of Al-10 wt.%Sn and Al-20 wt.%Zn Alloys, Mat. Sc. and Eng. A 420, 2006, pp 179-186.

[4] *C.J. Kong, P.D. Brown, S.J. Harris, and D.G. McCartney*, The microstructure of a termally sprayed and heat treated Al-20 wt.%Sn-3 wt.%Si alloy, Mat. Sc. and Eng. A 403, 2005, pp 205-214.

[5] *A. Perone, A Zocco, H. de Rosa, R Zimmermann, and M. Bersani,* Al-Sn thin films deposited by pulsed laser ablation, Mat. Sc. and Eng., C 22, 2002, pp 465-468.

[6] *XU Guang-ming, LI Bao-mian, and CUI Jian-zhong*, Effect of heat treatment on microstructure and property of Al-Sn-Pb bearing material, Journal of Iron and Steel Research, International, 2006, 13(2), pp 73-76.

[7] *M. Kliskic, J. Radosevic, and S. Gudic,* Yield of hydrogen during cathodic polarization of Al-Sn alloys, Electrochimica Acta 48, 2003, pp 4167-4174.

[8] *C. Eisenmenger-Sittner, H. Bangert, C Tomastik, P.B. Barna, A. Kovacs, and F. Misiak*, Solid state diffusion of Sn in polycrystalline Al films, Thin Solid Films, 433, 2003, pp 97-102.

[9] *S. Gudic, J. Radosevic, and M. Kliskic*, Study of passivation of Al and Al-Sn alloys in borate buffer solutions using electrochemical impedance spectroscopy, Electrochemica Acta, 47, 2002, pp 3009-3016.

[10] *Yu. Ya. Andreev, and A.V. Goncharov,* Thermodynamic calculation and experimental investigation of the surface enrichment of electrochemically activated Al-Me (Sn, In, Zn) alloys, Electrochimica Acta 50, 2005, pp 2629-2637.

[11] *L.C. Prasad and A. Mikula,* Thermodynamics of liquid Al-Sn-Zn alloys and concerned binaries in the light of soldering characteristics, Physica B 373, 2006, pp 64-71.

[12] *T. Fan, G. Yang, and Di Zhang,* Prediction of chemical stability in SiC_p/Al composites with alloying element addition using Wilson equation and an extended Miedema model, Mat. Sc. and Eng. A 394, 2005 pp 327-338.

[13] *C. Popescu, F. Pereteanu, L Vladutiu, I. Constantin, D. Taloi,* New thermodynamic model for determination of compounds activities in binary alloys, Bull. of the Transilvania Univ. of Brasov, Supplement Bramat 2007, CD pp 351-354.