THERMODYNAMIC ASSESMENT OF THE Cu - Ti SYSTEM IN MICROALLOYED COPPER BASE ALLOYS

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ABSTRACT

The correlations made between thermodynamic and kinetic data of the heterogeneous systems provided insight into the alloys properties. Experimental researches presented in this paper refer to the thermodynamics of Cu-Ti binary system for very low concentrations of titanium in copper from $0.006\cdot10^{-2} \div 0.340\cdot10^{-2}$ *mole fractions at 1372 K, at 1423 K temperatures. By electrochemical method the thermodynamics activities and activity coefficients at 1372 K, 1423 K were determined. The Associated Solution Model (ASM) parameters have been used to describe the thermodynamic properties of the Cu-Ti dilute solutions. Analytical expression has been derived to express the activity of titan in copper and the activity coefficient. The first and second order Wagner's self-interaction parameters were given as a function of ASM parameters.*

KEYWORDS: alloy, thermodynamics, activity.

1. Introduction

The copper based alloys feature very favourable thermal and electrical properties and also excellent mechanical characteristics therefore micro alloying copper with Ti, Cr, Al etc. may be used in all present and future technical fields. Kinetic and thermodynamic data of the melt alloys allow for the equilibrium conditions of the heterogeneous systems to be established and give a complete image upon the structure of the alloy and its properties [1, 2].

In the present study, liquid copper containing titanium at concentrations corresponding with concentration superior limits of authors papers [3-5] have been investigated and experiments have been carried out at two temperatures 1373 K and 1423 K, conditions which may be met at copper micro alloying. Liquid copper containing titanium was brought into equilibrium with molten $\{CuCl_2 + Ti_2O_3\}_{slag}$ saturated with Ti_2O_3 (s). The equilibrium oxygen partial pressure was measured by means of solid-oxygen galvanic cell of the type:

$$Mo/Mo + MoO_2/ZrO_2\,(MgO)/(Cu + Ti)_{alloy} + Ti_2O_{3(s)} + (CaCl_2 + Ti_2O_3)_{slag}/Mo$$

The thermodynamic activity of titan in copper and interaction parameters of the Cu-Ti binary liquid solutions was interpreted using the Associated Solution Model (ASM) Parameters [6].

2. Experimental method

The electrochemical methods based on the galvanic cells of the oxygen concentration with solid electrolytes are the most convenient methods for thermodynamics study of the high temperature metallic melts. The schematic draw of the electrochemical cell with solid oxide electrolyte is illustrated in figure 1.

The thermodynamic equilibrium of galvanic cell corresponds to the chemical reactions equilibrium:

$$2Ti_{(inCu)} + 3/2O_2 = Ti_2O_{3(s)} \quad (1)$$

$$\Delta G^0_{(1)} = -RT\ln K_{(1)} \quad (2)$$

$$\log K_{(1)} = \log a_{Ti_2O_3} - 2\log a_{Ti} - (3/2)\log P_{O_2} = 13{,}48 = 18500/T \quad (3)$$

where: the activities of Ti_2O_3, $a_{Ti_2O_3}$, referred to pure solid Ti_2O_3 are unity, since the $(CaCl_2 + Ti_2O_3)$ melts were saturated with pure solid Ti_2O_3.

From Eq (3) results that titanium activity can be determined by the oxygen potential measurements with the following relation:

$$E = \frac{RT}{F}\ln\frac{P^{14}_{O_2(Ref)} + P^{14}_{(-)}}{P^{14}_{O_2(slag)} + P^{14}_{(-)}} \quad (4)$$

where: E is electromotive force, F the Faraday constant and $P_{(-)}$ the oxygen partial pressure when both ionic and n-type electronic conductivity are equal.

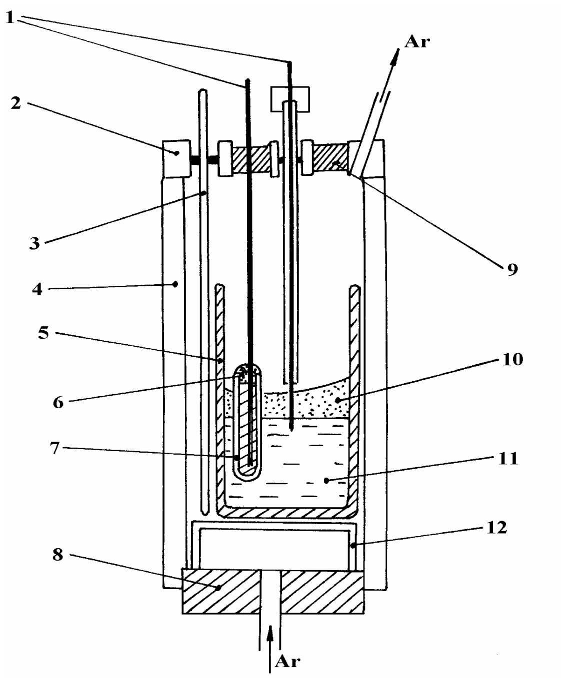

Fig.1. *Experimental cell. (1) molybdenum electrodes, (2) water cooled lid, (3) thermocouple, (4) mullite reaction tube, (5) alumina crucible, (6) zirconia cement, (7) zirconia tube, (8) rubber stopper, (9) rubber stopper, (10) Ti_2O_3 saturated ($CaCl_2$ + Ti_2O_3) melt, (11) Cu-Ti alloy, (12) pedestal.*

The oxygen partial pressure at the Mo+MoO_2, reference electrode, $P_{O_2(Ref)}$ was calculated by using the author’s previous results [2]:

$$RT\ln P_{O_2(Ref)} = -576.1 + 0.1692\,T \pm 0.3 \qquad (5)$$

A description of the thermodynamic characteristics of the liquid binary system to infinite dilution of one of the components could be achieved by using ASM (model).

3. Results and discussions

The activity and activity coefficients of the dissolution, respectively, were calculated on base of the measured electromotive forces, for each molar fraction of titanium in copper. The results are presented in Tables 1 and 2.

Analytical expressions of titan activity coefficient and interaction parameters were determined starting from Lupis and Eliot [4] relation’s -see equation (5), by the least square method:

$$\ln\gamma_B = \ln\gamma_B^0 + \varepsilon_B^0 X_B + \rho_B^0 X_B^2 \qquad (6)$$

Analytical expressions of titan activity coefficients are:

$$\log\gamma_{Ti} = -1.27 - 57.14X_{Ti} \quad \text{at 1373 K} \qquad (7)$$

$$\log\gamma_{Ti} = -1.26 - 37.14X_{Ti} \quad \text{at 1423 K}$$

Table 1. *Values of activity (a_{Ti}), activity coefficient (γ_i), titanium concentration X_{Ti} and electromotive force E of Cu-Ti binary system at 1373 K.*

Nr. crt.	$X_{Ti}\cdot 10^2$	***E*** **[mV]**	**log** a_{Ti}	**log** X_{Ti}	**log** γ_{Ti}	γ_{Ti}	$a_{Ti}\cdot 10^3$
1	0.312	714	-3.986	-2.503	-1.481	0.0330	0.1032
2	0.307	712	-3.987	-2.512	-1.475	0.0335	0.1030
3	0.304	710	-3.989	-2.517	-1.472	0.0337	0.1025
4	0.152	693	-4.170	-2.118	-1.352	0.0444	0.0676
5	0.148	692	-4.176	-2.830	-1.346	0.0451	0.0667
6	0.145	689	-4.178	-2.839	-1.339	0.0458	0.0663
7	0.117	673	-4.248	-2.932	-1.316	0.0483	0.0565
8	0.112	671	-4.262	-2.950	-1.312	0.0487	0.0547
9	0.107	669	-4.280	-2.971	-1.309	0.0491	0.0525
10	0.0579	648	-4.541	-3.240	-1.301	0.0500	0.0287
11	0.0136	628	-5.143	-3.866	-1.277	0.0528	0.00719
12	0.132	627	-5.152	-3.880	-1.272	0.0534	0.00704
13	0.00676	594	-5.420	-4.170	-1.250	0.0562	0.00380
14	0.00674	591	-5.423	-4.171	-1.242	0.0565	0.00377

Table 2. *Values of activity (a_{Ti}), activity coefficient (γ_i), titanium concentration X_{Ti} and electromotive force E of Cu-Ti binary system at 1423 K.*

Nr. crt.	$X_{Ti}\ 10^2$	E [mV]	$\log \cdot a_{Ti}$	$\log X_{Ti}$	$\log \gamma_{Ti}$	γ_{Ti}	$a_{Ti} \cdot 10^3$
1	0.331	704	-3.959	-2.480	-1.479	0.0324	0.1100
2	0.326	701	-3.962	-2.487	-1.475	0.0334	0.1090
3	0.164	692	-4.147	-2.785	-1.362	0.0434	0.0713
4	0.159	685	-4.166	-2.798	-1.356	0.0440	0.0682
5	0.153	681	-4.169	-2.816	-1.353	0.0443	0.0677
6	0.127	667	-4.220	-2.896	-1.324	0.0474	0.0602
7	0.120	662	-4.229	-2.920	-1.319	0.0479	0.0590
8	0.166	659	-4.250	-2.935	-1.315	0.0484	0.0562
9	0.0631	641	-4.497	-3.200	-1.307	0.0493	0.0318
10	0.0143	622	-5.132	-3.844	-1.288	0.515	0.00738
11	0.0141	618	-5.133	-3.850	-1.283	0.521	0.00736
12	0.00724	582	-5.405	-4.140	-1.265	0.0543	0.00393

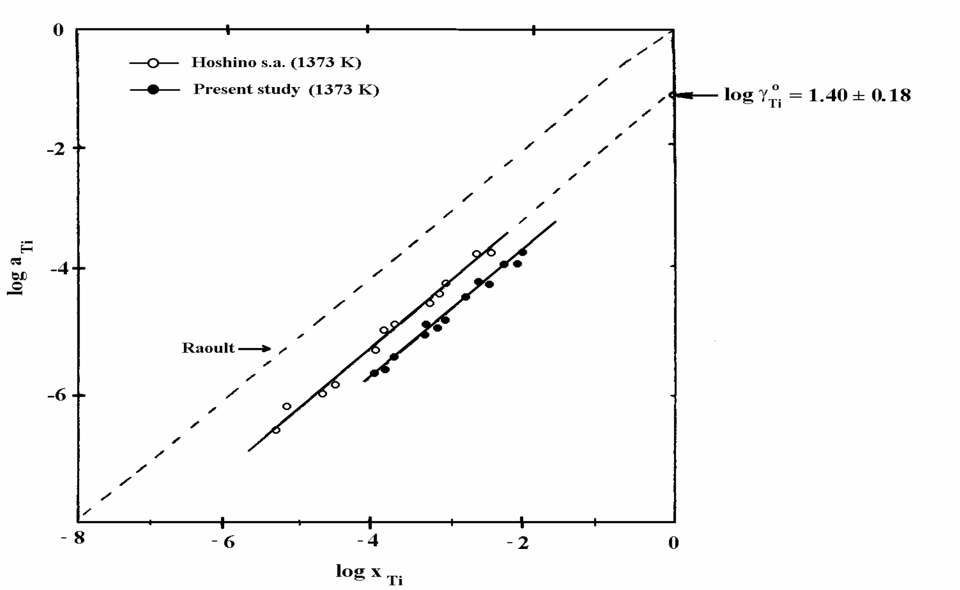

Fig. 2. *Relation between log a_{Ti}, and log X_{Ti}, in comparison with literature data [2].*

Figure 2 shows the study of logarithmic plots between activity a_{Ti} and concentration X_{Ti} for Cu-Ti binary system, in comparison with the literature data. It exhibits the high negative deviation from Raoult law. The negative deviations from ideal solution law indicate that titanium dissolution reaction in copper is exothermic; therefore copper and titan atomic bonding is stronger than those of similar atoms.

3.1. Analytical expression for the titan activity in binary dilute Cu- Ti alloys in terms of Associated Solution Model Parameters (ASM)

A binary solution made of A and B is modeled as a pseudo-ternary solution of “A”, “B”, and “ApBq” species, constrained by the internal equilibrium reaction:

p “A” + q “B” = “ApBq” (9)

The general analytical expression for $\ln a_B$ is:

$$\ln a_B = \frac{1}{q}[\ln X_B - \ln q + \frac{p+b}{q} X_B + \frac{p+2pq+b^2}{2q^2} X_B^2 - \ln k +$$
$$+1/2(w_{13}+w_{31})\{1-2\alpha X_B + [(1-p)\alpha^2 - 2\beta] X_B^2\} +$$
$$+1/2(w_{31}+w_{13})\{1-2\alpha X_B + [(1-p)\alpha^2 - 2\beta] X_B^2\} +$$
$$+1/2(w_{31}+w_{13})\{1-6\alpha X_B + [(9-3p)\alpha^2 - 6\beta] X_B^2\} +$$
$$+4v_{13}\{-2\alpha X_B + [(7-p)\alpha^2 - 2\beta] X_B^2\}] \tag{10}$$

where w_{13}, w_{31}, w_{32}, v_{13} are the solution parameters.

The activity of B diluted substance, of very low concentration, could have normally be expressed by self-interaction parameters in according to relation:

$$\ln a_B = \ln X_B + \ln\gamma_B^0 + \varepsilon_B^0 X_B + \rho_B^0 X_B^2 \quad (11)$$

where γ_B^0 is activity coefficient of B at infinite dilution and ε_B^0 and ρ_B^0 are the first and second order Wagner's self interaction parameter, respectively.

3.1.1. Results

The thermodynamics characteristics of the binary system of Cu-Ti, with infinite dilution of titanium in copper, could be described considering the two metals an associated species of CuTi. As result $p = q = 1$, $p + q - 1 = 1$, $\alpha = \beta = 1$.

Replacing these values in Eq (10) it has been obtained:

$$\begin{aligned} \ln a_{Ti} &= \ln X_{Ti} + 2X_{Ti} + 2X_{Ti}^2 - \ln k + \\ &+ 1/2(w_{13} + w_{32})(1 - 2X_{Ti} - 2X_{Ti}^2) + \\ &+ 1/2(w_{31} - w_{13})(1 - 6X_{Ti}) + 4v_{13}(-2X_{Ti} + 4X_{Ti}^2) \end{aligned} \quad (12)$$

$$\begin{aligned} \ln a_{Ti} &= \ln X_{Ti} + w_{Ti} - \ln k - \\ &- (2 + 2w_{13} - 4w_{31} - 8v_{13})X_{Ti} + \\ &+ (2 - w_{13} + 16v_{13})X_{Ti}^2 \end{aligned} \quad (13)$$

Comparing Eqs (11) and (12) it results that:

$$\ln\gamma_{Ti}^0 = w_{31} - \ln k \quad (14)$$

$$\varepsilon_{Ti}^0 = 2 + 2w_{13} - 4w_{31} - 6v_{13} \quad (15)$$

$$\rho_{Ti}^0 = 2 - w_{13} - w_{31} + 16v_{13} \quad (16)$$

The equations (14), (15) and (16) are the analytical expressions for $\ln\gamma_{Ti}^0$, ε_{Ti}^0, ρ_{Ti}^0, representing the ASM parameters.

The analytical expressions of the titanium activity in copper are determined using iterative method and are presented in Table 3.

They were used to study logarithmic plot between a_{Ti} and variation X_{Ti}, at 1373 K (see figure3), and at1423 K (see figure 4).

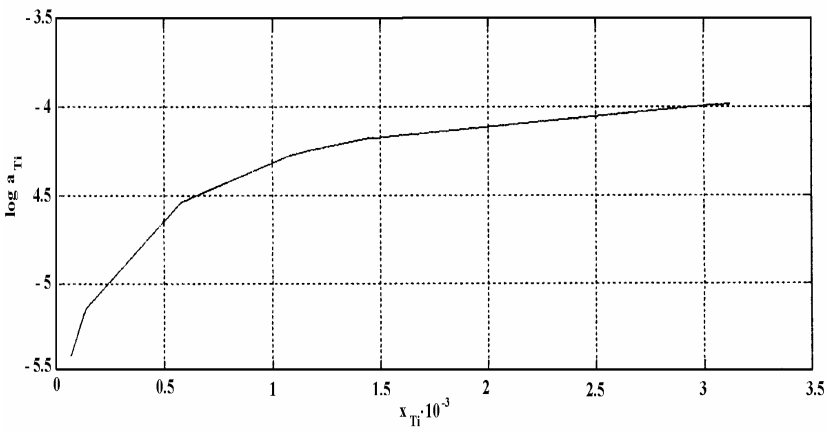

Fig.3. *Relation between log a_{Ti}, and X_{Ti} at 1373 K.*

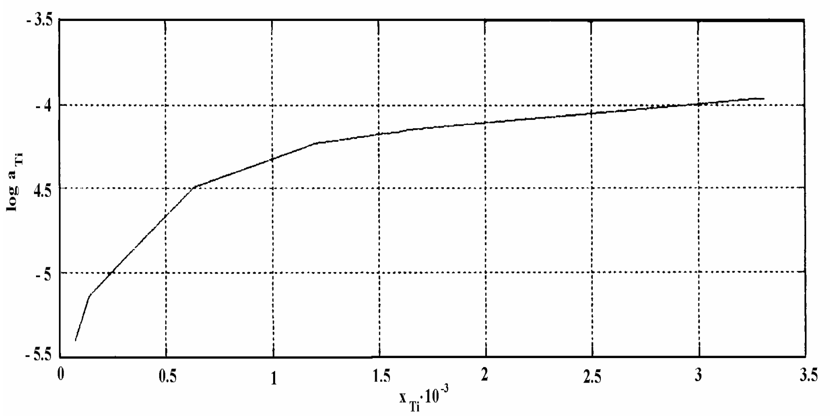

Fig.4. *Relation between log a_{Ti}, and X_{Ti} at 1423 K.*

***Table 3**. Analytical expressions of log a_{Ti} at 1373 K and 1423 K*

log $a_{Ti} = y$	$10^3\ X_{Ti} = x$	Analytical expressions
at 1373 K		
-3.959	3.310	$y = a_0 + a_1 X_{Ti}^2 + \log X_{Ti}$ $a_0 = \log\gamma_{Ti}^0 = -1.280$ $a_1 = \varepsilon_{Ti}^0 = -55.727$ $a_2 = \rho_{Ti}^0 = -2958.1731$ $\log a_{Ti} = -1.260 - 55.737X_{Ti} - 2956.1731X_{Ti}^2 + \log X_{Ti}$
-3.962	3.260	
-4.147	1.640	
-4.166	1.590	
-4.169	1.530	
-4.220	1.270	
-4.229	1.200	
-4.250	1.160	
-4.497	0.631	
-5.132	0.143	
-5.133	0.141	
-5.405	0.072	
at 1423 K		
-3.986	3.120	$y = a_0 + a_1 X_{Ti} + a_2 X_{Ti}^2 + \log X_{Ti}$ $a_0 = \log\gamma_{Ti}^0 = -1.2465$ $a_1 = \varepsilon_{Ti}^0 = -50.3097$ $a_2 = \rho_{Ti}^0 = -7898.26$ $\log a_{Ti} = -1.2465 - 50.3097X_{Ti} - 7898.26X_{Ti}^2 + \log X_{Ti}$
-3.986	3.070	
-3.987	3.040	
-4.170	1.520	
-4.176	1.480	
-4.178	1.450	
-4.248	1.170	
-4.262	1.120	
-4.280	1.070	
-4.541	1.579	
-5.141	0.136	
-5.152	0.132	
-5.420	0.066	
-5.419	0.067	

4. Conclusions

The following could be drawn:

1. Kinetic and thermodynamic data of melts allow establishing the process equilibrium conditions during alloy processing in order to reach the desired characteristics.
2. The experimental research on the thermodynamics of Cu-Ti system with low concentrations of titanium in liquid copper, at 1373 K and 1423 K, showed negative deviations from Raoult’s law. In this case, the dissolution reaction of solid titanium in copper is exothermic.
3. The analytical expression of the titanium activity in copper derived with Associated Solution Model (ASM) parameters are used to express the titan activity, activity coefficient, and the first and second order interaction parameters

References

[1]. L. J. Pan Wei, *Materials Science and Engineering. A* **269**, 104 (1999)

[2]. T. K. Inouye, H. Fujiwara, M. Iwase, *Metallurgical Transactions*, **22B**, 475 (1991)

[3]. H. Hoshino, T. Shimada, M. Yamamoto, M. Iwase, *Metallurgical Transactions*, **23B**, 160 (1992)

[4]. J. P. Hara, M. G. Frahberg, *Metallurgical Transaction*, **23B**, 23 (1992)

[5]. R.Arroyave, T.W. Eagar and L. Kaufman, *Journal of Alloys and Compounds*, **351** (2003) 158-170

[6]. R. C. Sharma, *Metallurgical Transaction*, **18A**, 1641 (1987).