УДК 621.01; 622.279

THERMODYNAMIC ASSESSMENT OF THE COPPER-OXYGEN SYSTEM

Cezar TOADER, Radu COTEȚIU, Anamaria DĂSCĂLESCU
North University of Baia Mare, Romania, Baia Mare 4800, st.Dr.Victor Babes NR 62A
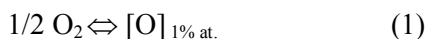
This work presents the study of some thermodynamic properties of the Cu-O system, which represent the base of several technological processes in the pyrometallurgy of copper. In the first part of the research have been determined several thermodynamic measurements activity and activity coefficient of oxygen in liquid copper-oxygen function on the temperature and oxygen concentration influence on them. The experimental results have been related to various thermodynamicals models refering to metallurgical melting for alloys the discovery of some structural information on the melting in the studied system.

Эта работа представляет изучение некоторых термодинамических свойств системы Cu-O, которые являются основой технологических процессов в пирометалургии меди. В первой части исследований определены измерения поведения термодинамических процессов и коэффициента действия кислорода в жидкой фазе медь- кислород на температуру и влияние концентрации кислорода на них. Экспериментальные результаты были связаны с различными термодинамическими моделями, относящимися к металлургическому плавлению сплавов в изучаемой системе.

The copper-oxygen system presents a challenging task for thermodynamic modelling. Extensive measurement of the thermodynamic properties of the liquid phase between the Cu and Cu_2O composition using electromotive force (e.o.m.). were made by Taskinen [1] in reasonable agreement with each other, Kulkarni [2] made measurements in a rather limited temperature interval (1513 to 1623 K), where as Taskinen [1] covered a considerably larger temperature interval (1373 to 1723 K). Osterwald [3] made measurement in the oxygen-rich liquid and of the Cu_2O -liquid and Cu_2O liquid equilibrium.

In contrast to the rather limited number of measurement at high oxygen content, a large number of thermodynamic investigations of the Cu-rich liquid have been made using electromotive force.

The binary intends to determine the activity and oxygen activity coefficient for different concentrations as a temperature function around 1150-1200^0 C.

Based on the dependence between the activity coefficient and the atomic ratio the activity limit coefficient for solutions at infinite dilution has been determined and with its help it was established the equation of the free standard enthalpy as a function of the reaction temperature:

$$1/2\ O_2 \Leftrightarrow [O]\ _{1\%\ at.} \qquad (1)$$

The experiments were realised using an electrochemical method based on the electromotive force of equilibrium measurements for a typical galvanic cell:

$$\text{Cromel, Cu}_{(l)} + [O] \mid ZrO_2 + Y_2O_3 \mid \text{NiO-Ni, Pt} \quad (2)$$
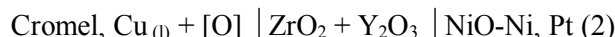
The difference between oxygen potential of the $Cu_{(l)} + [O]$ solution and $NiO + Ni$ mechanic mixture determines an electric potential difference between the two cell electrodes (E). Thermodynamically the cell equilibrium is in perfect agreement with the chemical equilibrium of reaction:

$$[O]_{Cu} + Ni_{(s)} \Leftrightarrow NiO_{(s)}. \qquad (3)$$

EXPERIMENTAL REZULTS

The reassert on the Cu-O system have been done at temperatures between 1150 and 1200^0 C. Based on the electromotive force measurements, the activity and activity coefficients as a function of the atomic ratio and temperature have been calculated.

Experimental data for activity and activity coefficients, determination as a function of the electromotive force, given by:

$$\ln a_O = 23211\frac{E}{T} + \frac{29416}{T} - 11,85 \qquad (4)$$

and

$$\gamma = \frac{a_O}{X_O}, \qquad (5)$$

where: E - represents the cell electromotive force; a_O - copper 's oxygen activity; γ_O - oxygen activity

coefficient; T - temperature; X_O - oxygen atomic ration.

The graphic representation of the activity coefficient logarithm as a function of the oxygen atomic ratio at constant temperature (figure 1 and 2) emphasises a linear variation, which suggests a typical equation [4]:

$$\ln \gamma_O = \ln \gamma_O^0 + \varepsilon_O^0 X_O, \qquad (6)$$

where: γ_O^0 - represent the activity limit coefficient; ε_O^0 - first order autointeraction thermodynamic parameter.

For the oxygen limit activity coefficient and first autointeraction thermodynamic parameter determination, a typical linear has been considered:

$$y = ax + b$$

where: $y = \ln \gamma_O$, $x = X_O$ (atomic ratio).

From these notation, we obtain $b = \ln \gamma_O^0$ and $a = \varepsilon_O^0$.

To establish the analytical equations, the least-squares optimisation was used [5].

After finishing the calculus, the following equation which shown the variation of the activity coefficient as a function of the oxygen atomic ratio for:

T = 1423 K $\ln \gamma_O = -1,1647 - 2,2932 X_O$. (7)

T = 1473 K $\ln \gamma_O = -0,7403 - 1,8617 X_O$. (8)

Relation (7) and (8) were obtained by using medium values determined for each experiment and are graphically represented in figures 1 and 2.

From the expressions of the variation equation of the activity coefficient logarithm, activity coefficient values and first orders interaction thermodynamic parameters values were obtained and they are given in table 1.

For determination of analytical equation of these functions, the least-squares optimisation

method was used, on the base of the following equations were obtained:

$$\gamma_O^0 = -\frac{17600}{T} + 6,63. \qquad (9)$$

$$\varepsilon_O^0 = -\frac{20400}{T} + 6,89. \qquad (10)$$

CONCLUSIONS

The equations, which express the dependence of the activity, limit coefficient as a function of the atomic ratio established in the present work (7-8) allowed the determination of the activity limit coefficient and the thermodynamic interaction parameters.

The values of the activity limit coefficient presented in table 3 are in a very good agreement with the values obtained by Kulkarni [2] and who indicated the following values: 0,310 at 1150^0 C and 0,492 at 1200^0 C.

Taskinen [5] used an electrochemical method with a reference electrode from air and established the following values for the activity coefficient: $\ln \gamma_O = -1,757$ at 1150^0 C and $\ln \gamma_O = -0,991$ at 1200^0 C which are in very good agreement with the values presented in table 3.

Regarding the first order interaction coefficient of oxygen in liquid copper-oxygen, the present work shows an increase of this one from -2,2932 to -1,8617 once the temperature grows from 1150 to 1200^0 C.

Sigworth and Elliott [6] have established the following dependence of the first order coefficient of oxygen in liquid copper-oxygen:

$$\varepsilon_O^0 = -\frac{24000}{T} + 7,8. \qquad (11)$$

The equation established in the present work (10) is in a good agreement with Sigworth and Elliott.

Thus, the obtained values in the present work for the first order interaction coefficient of oxygen are a bit smaller if experimental errors are considered which can get to 30 % or even more, and become significantly close.

Table 1

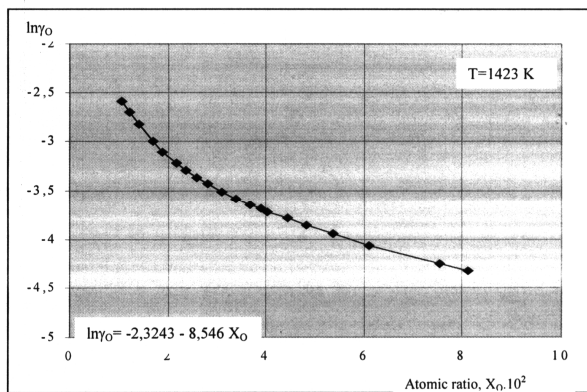| Nr. crt.	T (K)	$x = \dfrac{1}{T}.10^4$, K^{-1}	$y = \ln \gamma_O^0$	γ_O^0	$z = \varepsilon_O^0$
1	1423	7,0274	-1,1647	0,312	-2,2932
2	1473	6,7889	-0,7403	0,476	-1,8617

Fig. 1 Activity coefficient logarithm as a function of the oxygen atomic ratio at 1423 K
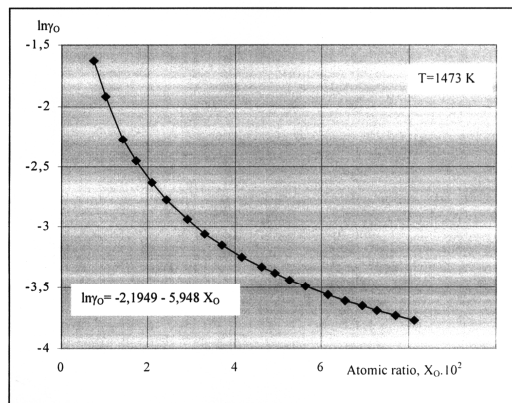

Fig. 2 Activity coefficient logarithm as a function of the oxygen atomic ratio at 1473 K

REFERENCES

1. TASKINEN, P. Scanned. J. Metallurgy, vol.8, 1979, (39-42)
2. KULKARNI ,A.D., Met.Trans., vol.4, 1973, 1973, (1713-1721)
3. OSTERWALD, J., Thesis, Technical University of Berlin, 1965
4. LUPPIS, C.H.P., ELLIOTT, J.E., Acta Met., vol.14, 1966, (529)
5. HOTEA, V., Dissertation, Bucharest, 1998
6. TASKINEN, P., Acct Politehnica Scandinavica, No.145, 1981, (45-72)
7. SIGWORTH, G.K., ELLIOTT, J.F., Canadian Metall. Quart, vol.13, 1974, (455-461)

STUDY OF GALVANIC CORROSION FOR TITANIUM AND ALLOYS USED IN DENTAL IMPLANTOLOGY

Cezar TOADER, Nicolae BĂNCILĂ, Anamaria DĂSCĂLESCU, Radu COTEȚIU
North University of Baia Mare, Romania, Baia Mare 4800, st.Dr.Victor Babes NR 62A

Эта статья представляет оценку гальванической коррозии для титана и сплавов, используемых в зубной имплантации. Экспериментально определено изменения потенциала во времени для различных зубных материалов: Ti5Al2,5Fe,Gaudor, Gaudent, Wisil, сталь 10NiCr18, чистый коммерческий титан.

This paper present evaluation of galvanic corrosion for titanium and alloys used in dental implantology. It's been determined experimentally the potential change in time for different dental materials: Ti5Al2,5Fe, Gaudor, Gaudent, Wisil, steel 10NiCr18, pure commercial titanium.

The conjoint degradation processes of corrosion and wear of metal surfaces is clearly of great importance in the design of orthopedic and dental prostheses. It is also clear that in a situation in which corrosion and wear are both possible degradation mechanisms each could have a profound effect on the other. Both processes will be controlled to a certain extent by the properties of the oxide layer on the surface of the material and the interaction of the environment which that surface. The passivation process will depend on the properties of the oxide formed, and thus the alloy composition, and the constituents of the environment.

In terms of wear without corrosion the amount of wear or the susceptibility of a surface to wear will be controlled to a certain by the hardness of the surface oxide. The depth of the wear scar, however, will depend on the wear mechanism that is occurring. If the main mechanism is wear of a softer material by a harder material in abrasive wear then one would expect the softies material to wear to the greatest depth.

Titanium and titanium alloys are now widely used in dental implantology because of their excellent characteristics such as chemical inertia, mechanical resistance, low density absence of toxicity, and above all for their biocompatibility.