THERMODYNAMICS OF Cu-Ce-M(M=Sn, Zn, Pb)

LIQUID SOLUTIONS [1]

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ABSTRACT

The iso-activity of [Ce] of samples in multiple-hole graphite crucibles can be reached by controlling the equilibrium oxygen potential of the reaction $2[Ce]+3CO=Ce_2O_3+3C$ with C-CO. Using this principle and conjugate gradient method of solving ill-conditioned equations, the activity interaction coefficients between Ce and Sn, Zn, Pb alloying elements were determined. The equilibrium constant of the reaction $2[Ce]+3[O]=Ce_2O_3$ and the standard free energy of formation of Ce_2O_3 in liquid Cu were obtained at 1 200 C.

Key words: Cu-Ce-M(M=Sn, Zn, Pb)   liquid solutions   thermodynamic   properties

1   IINTRODUCTION

Rare-earth elements play important roles in purification, modification and alloying in copper-base solutions[1]. Sn, Zn, Pb are impurity elements in copper when their contents are lower, and alloying elements when higher. The interaction between added rare-earth elements and these elements can improve the properties of copper alloys, but the extent of the interaction is still unknown. Therefore, it is important to study the thermodynamics of the interaction between rare-earth elements and alloying elements as well as the deoxidation action by rare-earth elements in liquid copper.

2   IEXPERIMENTAL METHODS

The purity of Cu and Ce was 99. 99% and > 99. 95% respectively. Sn, Zn and Pb were chemically pure. Graphite crucibles were spectrally pure.

A furnace with molybdenum disilicide heater was adopted, and the working zone was 9 cm long. A DWK-720 controller was used to regulate the temperature within an accuracy of ± 2 C.

The experiments were done in a graphite crucible with six holes, each of which containing 50 g electrolytic copper under CO atomosphere. The equilibrium time was 3 h. First, the copper was melted at 1 200 C and kept at that temperature for 30 min to be predeoxidized. Cerium was added to each hole and the bath was stirred with a spectrally pure graphite bar. 30 min later. Sn (or Zn. Pb) was added to each hole according to the pre-determined quantities. The bathes were stirred every other 30 min. After 3 h equilibrium, the crucible was drawn out of the furnace and quenched in water. The equilibrium products of Ce were extracted from alloy samples by electrolysis, and the dissolved Ce was measured by spectrophotometry.

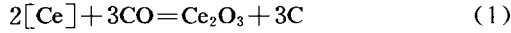## 3   EXPERIMENTAL THEORY AND DATA PROCESSING METHOD

3. 1   *Experimental Theory*

The [% C] in liquid copper was less than 0. 000 1[-2] at 1 200 C. so C was regarded as insolu-

ble in $Cu^{[3]}$.

The following chemical reaction reached equilibrium under the experimental condition:

$$2[Ce]+3CO=Ce_2O_3+3C \tag{1}$$

equilibrium constant $K = a_{Ce_2O_3} \cdot a_C^3/a_{Ce}^2 \cdot P_{CO}^3$ (2)

Using working pressure $P_{CO} = 0.1$ MPa, and taking pure substances of C and Ce_2O_3 as the activity standard, then $a_C = 1$, $a_{Ce_2O_3} = 1$,
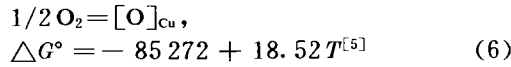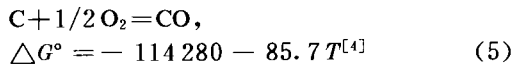
So $K = 1/a_{Ce}^2$ (3)

K was constant when the temperature kept unchanged. Therefore a_{Ce} was constant, so the activity of [Ce] in six bathes of the graphite crucible reached equality.

3.2 *Processing Data Method*

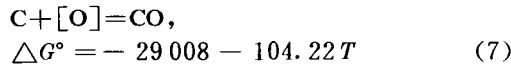The $a_{[O]}$ was determined by the following reaction:

$$C+[O]=CO \tag{4}$$

we know that

$C+1/2\,O_2=CO$,

$\triangle G^\circ = -114\,280 - 85.7\,T^{[4]}$ (5)

$1/2\,O_2=[O]_{Cu}$,

$\triangle G^\circ = -85\,272 + 18.52\,T^{[5]}$ (6)

Combining equations (5) and (6), we get

$C+[O]=CO$,

$\triangle G^\circ = -29\,008 - 104.22\,T$ (7)

when $T = 1\,473$ K, $P_{CO} = 0.1$ MPa, $a_{[O]} = 3.3 \times 10^{-7}$. Since $a_{[O]}$ is quite small, the quaternary system Cu-Ce-M-O can be regarded as a ternary system Cu-Ce-M.

$\lg a_{Ce} = \lg f_{Ce} + \lg[\%Ce]$

$= e_{Ce}^{Ce}[\%Ce] + \gamma_{Ce}^{Ce}[\%Ce]^2 + e_{Ce}^{M}[\%M]$

$\quad + \gamma_{Ce}^{M}[\%M]^2 + \gamma_{Ce}^{M, \, Ce}[\%M][\%Ce]$

$\quad + \lg[\%Ce]$ (8)

The $\lg a_{Ce}$ of the binary Cu-Ce with the same a_{Ce} as the ternary Cu-Ce-M is expressed as

$\lg a_{Ce} = e_{Ce}^{Ce}[\%Ce]_0 + \gamma_{Ce}^{Ce}[\%Ce]_0^2 + \lg[\%Ce]_0$ (9)

where $[\%Ce]_0$ represents the concentration of $[\%Ce]$ in the Cu-Ce system.

Eq. (9) minus Eq. (8) is

$\lg([\%Ce]_0/[\%Ce]) = e_{Ce}^{Ce}([\%Ce] - [\%Ce]_0) +$

$\qquad\qquad \gamma_{Ce}^{Ce}([\%Ce]^2 - [\%Ce]_0^2)$

$\qquad\qquad + e_{Ce}^{M}[\%M] + \gamma_{Ce}^{M}[\%M]^2$

$\qquad\qquad + \gamma_{Ce}^{M, \, Ce}[\%M][\%Ce]$ (10)

when $e_{Ce}^{Ce} = 0.108$, $\gamma_{Ce}^{Ce} = -1.59 \times 10^{-3[6]}$, Eq.

(10) becomes

$\lg([\%Ce]_0/[\%Ce]) - e_{Ce}^{Ce}([\%Ce] - [\%Ce]_0) -$

$\gamma_{Ce}^{Ce}([\%Ce]^2 - [\%Ce]_0^2) = e_{Ce}^{M}[\%M] + \gamma_{Ce}^{M}[\%M]^2$

$+ \gamma_{Ce}^{M, \, Ce}[\%M][\%Ce]$ (11)

A number of points were taken from the iso-activity equation ($n \geqslant 1\,000$), and the least square method was applied to the data. Three ill-conditioned equations were obtained and the activity interaction coefficients were determined by the conjugate gradient method of solving ill-conditioned equations[6].

4 RESULTS

4.1 *Equilibrium Products*

The equilibrium products of Cu-Ce-M system were identified as CeO_2 (at 25 ℃) by X-ray diffraction.

From Ref. 4, we know that

$Ce_2O_3 + CO = 2CeO_2 + C$

$\triangle G^\circ = -264\,636 + 222.79\,T$ (J/mol)
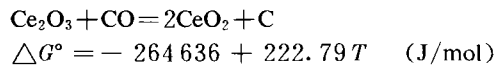
when $T = 1\,473$ K, $P_{CO} = 0.1$ MPa, $a_{Ce_2O_3} = 1$,

$a_{CeO_2} = 1$, $a_c = 1$,

$\triangle G^\circ = 63\,540$ J/mol

Therefore no CeO_2 was formed under these experimental conditions, the equilibrium products should be Ce_2O_3 at high temperatures. But Ce_2O_3 is unstable at room temperature, it can be easily oxidized into CeO_2. That explains the former X-ray diffraction results.

4.2 *Activity Interaction Coefficients*

The experimental data for the Cu-Ce-M (M = Sn, Zn, Pb) system are shown in Figs. 1—3, and the iso-activity equations were obtained through regression.

For the Cu—Ce—Sn system:

$[\%Ce] = 0.244 + 0.145[\%Sn]$

$\qquad + 0.015[\%Sn]^2$, $r = 0.99$;

For the Cu-Ce-Zn system:

$[\%Ce] = 0.206 + 0.273[\%Zn]$

$\qquad - 0.122[\%Zn]^2$, $r = 0.99$;

For the Cu-Ce-Pb system:

$[\%Ce] = 0.215 + 0.238[\%Pb]$

$\qquad - 0.150[\%Pb]^2$, $r = 0.95$.

Using the method explained in section 3. 2 and the relationships between activity interaction coefficients[7], the interaction coefficients between M and Ce were evaluated as follows:

For the Cu-Ce-Sn system:

$e_{Ce}^{Sn} = -0.131$, $\gamma_{Ce}^{Sn} = -0.284$,

$\gamma_{Ce}^{Sn, Ce} = 1.660$, $e_{Sn}^{Ce} = -0.110$,

$\gamma_{Sn}^{Ce} = 1.616$, $\varepsilon_{Sn}^{Ce} = \varepsilon_{Ce}^{Sn} = -57.2$;

For the Cu-Ce-Zn system:

$e_{Ce}^{Zn} = -0.794$, $\gamma_{Ce}^{Zn} = 0.162$,

$\gamma_{Ce}^{Zn, Ce} = 1.053$, $e_{Zn}^{Ce} = -0.368$,

$\gamma_{Zn}^{Ce} = 0.563$, $\varepsilon_{Ce}^{Zn} = \varepsilon_{Zn}^{Ce} = -187.9$;

For the Cu-Ce-Pb system:

$e_{Ce}^{Pb} = -0.680$, $\gamma_{Ce}^{Pb} = 0.247$,

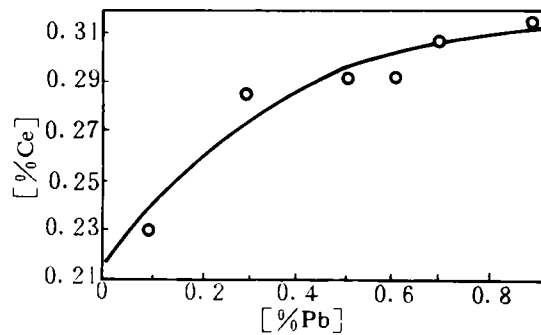**Fig. 3 Iso-activity curve of Ce for Cu-Ce-Pb system**

$\gamma_{Ce}^{Pb, Ce} = 0.875$, $e_{Pb}^{Ce} = -1.01$,

$\gamma_{Pb}^{Ce} = 1.483$, $\varepsilon_{Pb}^{Ce} = \varepsilon_{Ce}^{Pb} = -512.3$

4. 3 The Equilibrium Constant of the Reaction Between Cerium and Oxygen and the Gibb's Standard Free Energy of Formation of Ce_2O_3 in Liquid Cu

Substituting the activity interaction coefficients into Eq. (8), the average value of a_{Ce} was obtained to be 0. 234. Therefore, the equilibrium constant of the reaction $3[O] + 2[Ce] = Ce_2O_3$ is

$K = 1/a_0^3 \cdot a_{Ce}^2$

$= 1/[(3.3 \times 10^{-7})^3 \times (0.234)^2]$

$= 5.08 \times 10^{20}$

So the deoxidation constant of cerium is

$K_{Ce_2O_3} = 1/K = 1.97 \times 10^{-21}$

And the Gibb's standard free energy of formation of Ce_2O_3 is

$\triangle G^{\circ}_{Ce_2O_3} = -RT\ln K$

$= -583.87 \text{ kJ/mol}$

5 DISCUSSION

Taking five concentration points from the iso-activity lines of the Cu — Ce — M (M = Sn, Zn, Pb) system and using the activity interaction coefficients, values for a_{Ce} were calculated from Eq. (8) and listed in Table 1.

From Table 1, it can be seen that $[\%Ce]$ has reached iso-activity for every system.
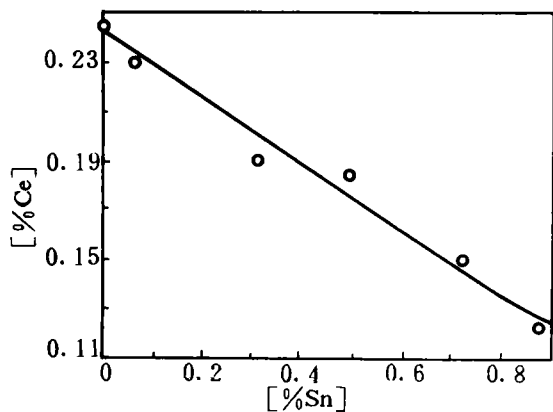

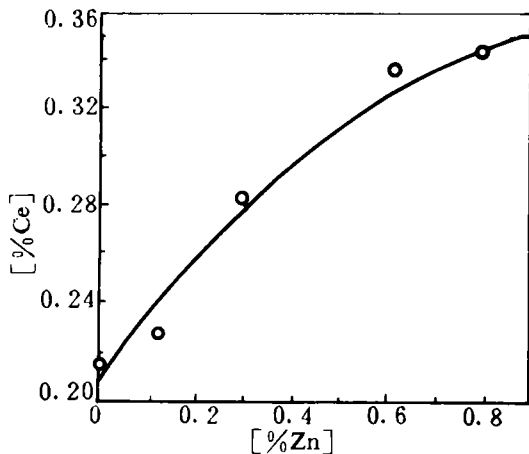**Fig. 1 Iso-activity curve of Ce for Cu-Ce-Sn system**

Fig. 2 Iso-activity curve of Ce for Cu-Ce-Zn system

Table 1   Checking of iso-activity

Cu-Ce-M	%M					$\bar{a}_{Ce}$
	0.1	0.3	0.5	0.7	0.9	
Cu-Ce-Sn	0.259	0.259	0.259	0.259	0.259	
Cu-Ce-Zn	0.217	0.217	0.217	0.217	0.217	0.234
Cu-Ce-Pb	0.227	0.227	0.228	0.225	0.225	

6   CONCLUSIONS

(1) The equilibrium products of Cu-Ce-M(M =Sn, Zn, Pb) systems were identified as Ce_2O_3 at 1 200 C.

(2) The activity interaction coefficients between M and Ce in liquid copper solutions at 1 200 C were obtained by use of iso-activity method and conjugate gradient method of solving ill-conditioned equations.

For the Cu-Ce-Sn system:

$e_{Ce}^{Sn} = -0.131$, $\gamma_{Ce}^{Sn} = 0.284$, $\gamma_{Ce}^{Sn \cdot Ce} = 1.660$, $e_{Sn}^{Ce} = -0.110$, $\gamma_{Sn}^{Ce} = 1.616$, $\varepsilon_{Ce}^{Sn} = \varepsilon_{Sn}^{Ce} = -57.2$;

For the Cu—Ce—Zn system:

$e_{Ce}^{Zn} = -0.794$, $\gamma_{Ce}^{Zn} = 0.162$, $\gamma_{Ce}^{Zn \cdot Ce} = 1.053$, $e_{Zn}^{Ce} = -0.368$, $\gamma_{Zn}^{Ce} = 0.563$, $\varepsilon_{Ce}^{Zn} = \varepsilon_{Zn}^{Ce} = -187.9$;

For the Cu-Ce-Pb system:

$e_{Ce}^{Pb} = -0.680$, $\gamma_{Ce}^{Pb} = 0.247$, $\gamma_{Ce}^{Pb \cdot Ce} = 0.875$, $e_{Pb}^{Ce} = -1.01$, $\gamma_{Pb}^{Ce} = 1.483$, $\varepsilon_{Ce}^{Pb} = \varepsilon_{Pb}^{Ce} = -512.3$.

(3) The equilibrium constant of the reaction $3[O] - 2[Ce] = Ce_2O_3$ in liquid copper at 1 200 C is 5.08×10^{20}, and the Gibb's standard free energy of formation of Ce_2O_3 is $-583.87 \, kJ/mol$.

REFERENCES

1 Du, Ting. Bulletin of Science, 1963, (7): 13—22.
2 American Society for Metals. Metals Handbook. Metals Park, Ohio: 1973. 274.
3 Zou, Yuanxi; Zhao, Pengnian; Cao, Zhaomin. Acta Metall Sinica, 1963, 6: 121.
4 Turkdogan, E T. Physical Chemistry of High Temperature technology. New York: Academic press, 1980. 5 —24.
5 Sigworth, G K; Elliott, J F. Can Met Quart, 1974, 13: 455.
6 Li, Guodong; Du, Ting. Transactions of Nonferrous Metals Society of China, 1992, 2(4): 45.
7 Lupis, C H P; Elliott, J F. Acta Metall, 1966, 14: 529.

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efficiently in the roasting operation in the temperature range of 680 C to 720 C.

(4) There are lower content of sulphur and higher porosities in the residues. As a consequence, this is beneficial for the extraction of gold and silver in the residues.

(5) The residues can be sured as hematite concentrate after the removal of lead and zinc by reducing roasting.

(6) Direct metallurgical treatment of the ores can avoid the difficulties of beneficiation and improve the comprehensive utilization.

REFERENCES

1 Cauwe, PH; Minet, PH; Sheridan R. In: Sohn HY et al(eds), Bao, Xiaobo; Deng, Wenji ctrans, Progress of Sulphide Ore Metallurgy(Vol two) Beijing, Publishing House of Metallurgical Industry, 1991, 24—50.
2 Demarthe, J M; Georgeaux A. In: Jones M. J. (ed), Complex Metallurgy'78, Bad Harzburg, F. R. Germany, 1978, 113—120.
3 Limpo, J L; Figueiredo, J M; Amer, S et al. Hydrometallurgy, 1992, 28: 149—161.
4 Handbook of Mineral Processing Design, Beijing: Publishing House of Metallurgical Industry, 1988, 28.
5 Handbook of Mineral Processing Design, Beijing: Publishing House of Metallurgical Industry, 1988, 37.
6 Schulze, R G. In: Torma, A E and Gundiler, 1 H (eds), Proceedings of Process Metallurgys: Precious and Rare Metal Technologies. Albuquerque, New Mexico, USA, 1988, 201—207.
7 Yu Bingquan. In: A Collection of Thesis Presented in the Forth National Academic Conference on the Mineral Processing and Metallurgy of Gold and Silver, 1993, Zhengzhou, 1993, 8—186.