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THERMODYNAMICS OF Cu–Ce–I (I = Al, Si, Ti, Fe) LIQUID SOLUTIONS①

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ABSTRACT

The iso-activity of [Ce] of samples reached in multiple-hole-graphite crucibles by controlling the oxygen potential through the reaction $2[Ce]+3CO=Ce_2O_3+3C$. Combining conjugate gradient method of solving ill-conditioned equations, the activity interaction coeffients between Ce and Al, Si, Ti and Fe 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 ℃.

Key words: iso-activity interaction coefficient Cu–Ce–Al Cu–Ce–Si Cu–Ce–Ti Cu–Ce–Fe equilibrium constant standard free energy of formation

1 INTRODUCTION

Rare earth elements play important roles in purification, modification and improving the properties in copper-base solutions[1]. Al, Si, Ti and Fe are impurity elements when their contents are lower, and they are alloying elements when their contents are higher in copper. The interaction between the added rare earth elements and those elements can improve the properties of copper alloys, but the extents of the interactions are still unknown. Therefore, it is important to study the thermodynamics of the interactions between rare earth elements and those alloying elements as well as the deoxidation action by rare earth elements in liquid copper.

2 EXPERIMENTAL METHOD

2. 1 *Materials*

The purity of Cu and Ce were 99.99 % and 99.95 % respectively. Al, Si, Ti and Fe were chemically pure, and the graphite crucibles were spectrally pure.

2. 2 *Experimental Procedure*

A furnace with molybdenum disilicide heater was added, and the working zone was 9 cm long. A DWK−702 controller was used to regulate the temperature with an accuracy of ± 2 ℃. The experiments were done in a graphite crucible with six holes each of which contianed 50 g of electric copper under a CO atmosphere. The equilibrium time was 3h. First, the copper was melted at 120 ℃ and kept at that temperature for 30 minutes to pre-deoxidze it. Cerium was added to each hole and the bath was stirred with a spectro-pure graphite bar 30 minutes later, Al (or Si, Ti or Fe) was added to each hole according to the pre-determined quantities. The bathes were stirred and then given a 30 minutes vrest before being stirred again.

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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 ℃, so C was regarded as insoluble in Cu[3].

The following chemical reaction reaches equilibrium under the experimental condition:

$$2[\mathrm{Ce}]+3\mathrm{CO}=\mathrm{Ce_2O_3}+3\mathrm{C} \qquad (1)$$

equilibrium constant

$$k=a_{\mathrm{Ce_2O_3}}a_{\mathrm{c}}/a_{\mathrm{Ce}}^{2}p_{\mathrm{CO}}^{3} \qquad (2)$$

Assuming that $p_{\mathrm{CO}}=0.1$ MPa, and taking pure substance of C and $\mathrm{Ce_2O_3}$ as the activity standard, then $a_{\mathrm{c}}=1$, $a_{\mathrm{Ce_2O_3}}=1$,

So $$k=1/a_{\mathrm{Ce}}^{2} \qquad (3)$$

k was constant when the temperature was unchanged. Therefore, a_{Ce}^{2} was constant, so the activity of [Ce] in the six bathes of the graphite crucible reached equality.

3. 2 *Processing Data Method*

The $a_{[\mathrm{o}]}$ was determined by the following reaction:

$$\mathrm{C}+[\mathrm{O}]=\mathrm{CO} \qquad (4)$$

We know that

$$\left.\begin{array}{l}\mathrm{C}+\mathrm{O_2}/2=\mathrm{CO}\\ \triangle G^{\circ}=-114,280-85.7T\quad \mathrm{J/mol}\end{array}\right\}(5)$$

$$\left.\begin{array}{l}\mathrm{O_2}/2=[\mathrm{O}]_{\mathrm{Cu}}\\ \triangle G^{\circ}=-85,272+18.52T\quad \mathrm{J/mol}\end{array}\right\}(6)$$

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

$$\left.\begin{array}{l}\mathrm{C}+[\mathrm{O}]=\mathrm{CO}\\ \triangle G^{\circ}=-29,008-104.22T\quad \mathrm{J/mol}\end{array}\right\}(7)$$

When $T=1473$ K, $p_{\mathrm{CO}}=0.1$ MPa, $a_{[\mathrm{o}]}=3.3\times 10^{-7}$, so the quaternary system Cu–Ce–I–O can be regarded as a ternary system Cu–Ce–I.

$$\lg a_{\mathrm{Ce}}=\lg f_{\mathrm{Ce}}+\lg[\%\mathrm{Ce}]=e_{\mathrm{Ce}}^{\mathrm{Ce}}[\%\mathrm{Ce}]+\gamma_{\mathrm{Ce}}^{\mathrm{Ce}}[\%\mathrm{Ce}]^{2}+e_{\mathrm{Ce}}^{\mathrm{I}}[\%\mathrm{I}]+\gamma_{\mathrm{Ce}}^{\mathrm{I}}[\%\mathrm{I}]^{2}+\gamma_{\mathrm{Ce}}^{\mathrm{I,Ce}}[\%\mathrm{I}][\%\mathrm{Ce}]+\lg[\%\mathrm{Ce}] \qquad (8)$$

The $\lg a_{\mathrm{Ce}}$ of the binary Cu–Ce with the same a_{Ce} as the ternary Cu–Ce–I is expressed as

$$\lg a_{\mathrm{Ce}}=e_{\mathrm{Ce}}^{\mathrm{Ce}}[\%\mathrm{Ce}]_{\mathrm{o}}+\gamma_{\mathrm{Ce}}^{\mathrm{Ce}}[\%\mathrm{Ce}]_{\mathrm{o}}^{2}+\lg[\%\mathrm{Ce}]_{\mathrm{o}} \qquad (9)$$

$[\%\mathrm{Ce}]_{\mathrm{o}}$ represents the concentration of Ce in the Cu–Ce system.

(9)–(8):

$$\lg[\%\mathrm{Ce}]_{\mathrm{o}}/[\%\mathrm{Ce}]=e_{\mathrm{Ce}}^{\mathrm{Ce}}([\%\mathrm{Ce}]-[\%\mathrm{Ce}]_{\mathrm{o}})+\gamma_{\mathrm{Ce}}^{\mathrm{Ce}}([\%\mathrm{Ce}]^{2}-[\%\mathrm{Ce}]_{\mathrm{o}}^{2})+e_{\mathrm{Ce}}^{\mathrm{I}}[\%\mathrm{I}]+\gamma_{\mathrm{Ce}}^{\mathrm{I}}[\%\mathrm{I}]^{2}+\gamma_{\mathrm{Ce}}^{\mathrm{I,Ce}}[\%\mathrm{Ce}] \qquad (10)$$

When $e_{\mathrm{Ce}}^{\mathrm{Ce}}=0.108$, and $r_{\mathrm{Ce}}^{\mathrm{Ce}}=-1.59\times 10^{-3}$[6], equation (10) becomes

$$\lg[\%\mathrm{Ce}]_{\mathrm{o}}/[\%\mathrm{Ce}]-0.108([\%\mathrm{Ce}]-[\%\mathrm{Ce}]_{\mathrm{o}})+1.59\times 10^{-3}([\%\mathrm{Ce}]^{2}-[\%\mathrm{Ce}]_{\mathrm{o}}^{2})=e_{\mathrm{Ce}}^{\mathrm{I}}[\%\mathrm{I}]+\gamma_{\mathrm{Ce}}^{\mathrm{I}}[\%\mathrm{I}]^{2}+\gamma_{\mathrm{Ce}}^{\mathrm{I,Ce}}[\%\mathrm{Ce}] \qquad (11)$$

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

4 RESULTS

4. 1 *Equilibrium Results*

The equilibrium products of the Cu–Ce–I system were identified as $\mathrm{CeOP_2}$(at 25℃) by X-ray diffraction.

$$\mathrm{Ce_2O_3}+\mathrm{CO}=2\mathrm{CeO_2}+\mathrm{C}$$

$$\triangle G^{\mathrm{o}}=-264\,636+222.79\,T\quad \mathrm{J/mol}$$

$$\triangle G=\triangle G^{\mathrm{o}}+\mathrm{R}\,T\ln(1/P_{\mathrm{CO}})$$

No $\mathrm{CeO_2}$ was formed under these experimental conditions, so the equilibrium products should be $\mathrm{Ce_2O_3}$ at high temperatures.

4.2 *Activity Interaction Coefficients*

The experimental data for the Cu-Ce-I (I = Al, Si, Ti and Fe) systems are shown in Fig. 1–4, and the iso-activity equations were obtained through regression

For the Cu–Ce–Al system:

$$[\%Ce]=0.235+0.044[\%Al]+0.176[\%Al]^2$$

and $\gamma=0.96$

For the Cu–Ce–Si system:

$$[\%Ce]=0.226+0.080[\%Si]+0.076[\%Si]^2$$

and $\gamma=0.98$

For the Cu–Ce–Ti system:

$$[\%Ce]=0.242+0.348[\%Ti]-0.008[\%Ti]^2$$

and $\gamma=0.96$

For the Cu–Ce–Fe system:

$$[\%Ce]=0.217-0.207[\%Fe]+0.124[\%Fe]^2$$

and $\gamma=0.99$

By using the method explained in section 2.2 and the relationships between activity interaction coefficients[7], the interaction coefficients between I and Ce were evaluated.

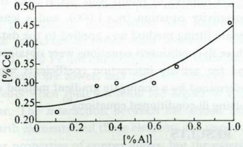

Fig. 1 Iso-activity curve of Ce in the Cu–Ce–Al system

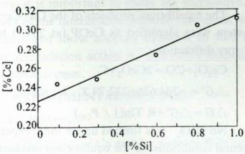

Fig. 2 Iso-actibity curve of Ce in the Cu–Ce–Si system

For the Cu–Ce–Al system:

$$e_{Ce}^{Al}=-0.251,\quad \gamma_{Ce}^{Al}=-0.378,\quad \gamma_{Ce}^{Al,Ce}=0.700,$$

$$e_{Al}^{Ce}=-0.045, \gamma_{Al}^{Ce}=0.154, \varepsilon_{Al}^{Ce}=\varepsilon_{Ce}^{Al}=-24.0$$

For the Cu–Ce–Si system:

$$e_{Ce}^{Si}=-0.281,\quad \gamma_{Ce}^{Si}=-0.162,\quad \gamma_{Ce}^{Si,Ce}=0.520,$$

$$e_{Si}^{Ce}=-0.053, \gamma_{Si}^{Ce}=0.119, \varepsilon_{Ce}^{Si}=\varepsilon_{Si}^{Ce}=-28.0$$

For the Cu–Ce–Fe system:

$$e_{Ce}^{Fe}=0.735,\quad \gamma_{Ce}^{Fe}=-0.335,\quad \gamma_{Ce}^{Fe,Ce}=-1.378,$$

$$e_{Fe}^{Ce}=0.296, \gamma_{Fe}^{Ce}=-0.631, \varepsilon_{Fe}^{Ce}=\varepsilon_{Ce}^{Fe}=148.7$$

For the Cu–Ce–Ti system:

$$e_{Ce}^{Ti}=-1.120,\quad \gamma_{Ce}^{Ti}=-0.462,\quad \gamma_{Ce}^{Ti,Ce}=2.043,$$

$$e_{Ti}^{Ce}=-0.380, \gamma_{Ti}^{Ce}=0.801, \varepsilon_{Ce}^{Ti}=\varepsilon_{Ti}^{Ce}=-193.9$$

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

Substituting the activity interaction coefficients to equation (8), the average value of a_{Ce} was obtained to be 0.243. Therefore, the equilibrium constant of the reaction 3[O]+2[Ce]=

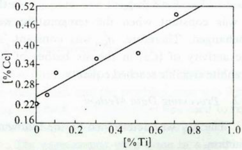

Fig. 3 Iso-activity curve of Ce in the Cu–Ce–Ti system

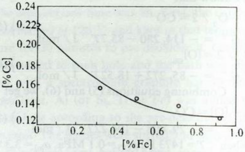

Fig. 4 Iso-activity curve of Ce in the Cu–Ce–Fe system

Ce_2O_3 is found to be:

$$k=(a_o^3a_{Ce}^2)^{-1}=(3.3\times10^{-7})^{-3}\times 0.243^{-2}$$
$$=4.71\times10^{-21}$$

The deoxidation constant of cerium is $k_{Ce_2O_3}=1/k=2.13\times10^{21}$

The standard free energy of formation of Ce_2O_3 is

$$\triangle G^{o}{}_{Ce_2O_3}=RT\ln k=-582.95\ \mathrm{kJ/mol}$$

5 DISCUSSION

Checking of iso-activity:

Taking five concentration points from the iso-activity lines of the Cu–Ce–I (I = Al, Si, Ti and Fe) systems and using the activity interaction coefficients, the a_{Ce} were calculated from equation (8) and listed in Table 1.

Table 1 Checking of iso–activity

Cu–Ce–I	[%I]				
	0.1	0.3	0.5	0.7	0.9
Cu–Ce–Al	0.249	0.249	0.249	0.249	0.249
Cu–Ce–Si	0.239	0.239	0.239	0.239	0.239
Cu–Ce–Ti	0.258	0.257	0.256	0.258	0.258
Cu–Ce–Fe	0.229	0.229	0.229	0.229	0.229

From Table 1, it can be seen that [%Ce] has reached iso-activity for all the systems.

6 CONCLUSIONS

(1) The equilibrium products of Cu–Ce–I (I = Al, Si, Ti or Fe) system were identified as Ce_2O_3 at, 1,200℃,

(2) The activity interaction coefficients between I and Ce in liquid copper solutions at 1,200℃ were obtained by an iso-activity method and the use of conjugate gradients for solving ill-conditioned equations:

For Cu–Ce–Al:

$$e_{Ce}^{Al}=-0.251,\ \ \gamma_{Ce}^{Al}=-0.378,\ \ \gamma_{Ce}^{Al,Ce}=0.700,$$
$$e_{Al}^{Ce}=-0.045, \gamma_{Al}^{Ce}=0.154, \varepsilon_{Ce}^{Al}=-24.0$$

For Cu–Ce–Si:

$$e_{Ce}^{Si}=-0.281,\ \ \gamma_{Ce}^{Si}=-0.162,\ \ \gamma_{Ce}^{Si,Ce}=0.520,$$
$$e_{Si}^{Ce}=-0.053, \gamma_{Si}^{Ce}=0.119, \varepsilon_{Ce}^{Si}=\varepsilon_{Si}^{Ce}=-28.0$$

For Cu–Ce–Ti:

$$e_{Ce}^{Ti}=-1.120,\ \ \gamma_{Ce}^{Ti}=-0.462,\ \ \gamma_{Ce}^{Ti,Ce}=2.043,$$
$$e_{Ti}^{Ce}=-0.380, \gamma_{Ti}^{Ce}=0.801, \varepsilon_{Ce}^{Ti}=\varepsilon_{Ti}^{Ce}=-193.9$$

For Cu–Ce–Fe:

$$e_{Ce}^{Fe}=0.735,\ \ \gamma_{Ce}^{Fe}=-0.335,\ \ \gamma_{Ce}^{Fe,Ce}=-1.378,$$
$$e_{Fe}^{Ce}=0.296, \gamma_{Fe}^{Ce}=-0.631, \varepsilon_{Ce}^{Fe}=\varepsilon_{Fe}^{Ce}=148.7;$$

(3) The equilibrium constant of the reaction $3[O]+2[Ce]=Ce_2O_3$ is 4.71×10^{20} and the standard free energy of formation of Ce_2O_3 in liquid Cu is −587.95 kJ / mol.

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