

THERMODYNAMICS OF Cu-Y-M (M=Al, Si, Ti, Fe) LIQUID SOLUTIONS^①

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ABSTRACT

The iso-activity of [Y] of samples reached in multiple-hole-graphite crucibles by controlling the oxygen potential through the reaction $2[Y] + 3CO = Y_2O_3 + 3C$. Combining conjugate gradient method of solving ill-conditioned equations, the activity interaction coefficients between Y and Al, Si, Ti, Fe alloying elements were determined. The equilibrium constant of the reaction $2[Y] + 3[O] = Y_2O_3$ and the standard free energy of formation of Y_2O_3 in liquid Cu were obtained at 1200 °C.

Key words: iso-activity interaction coefficient Cu-Y-M (M=Al, Si, Ti, Fe)

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

The purities of Cu and Y were 99.90% and 99.95% respectively. Al, Si, Ti and Fe were chemical pure, and the graphite crucibles were spectrally pure.

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 °C. The experiments were done in a graphite crucible with six holes each of which contained 50 g of electric copper under a CO atmosphere. The equilibrium time was 3 h. First, the copper was melted at 1200 °C and kept at that temperature for 30 min to pre-deoxidize it. Yttrium was added to each hole and the bath was stirred with a spectro-pure graphite bar 30 min 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 min rest before being stirred again. After 3 h equilibrium, the crucible was drawn out of the furnace and quenched in water. The equilibrium products of Y were extracted from alloy samples by electrolysis, and the dissolved Y was measured by spectrophotometry.

3 EXPERIMENTAL THEORY AND DATA PROCESSING METHOD

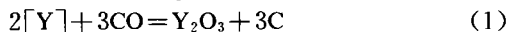
3.1 Experimental Theory

The [%C] in liquid copper was less than

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0.0001^[2] at 1200 °C, so C was regarded as insoluble in Cu^[3].

The following chemical reaction reaches equilibrium under the experimental condition:



The equilibrium constant is;

$$k = a_{\text{Y}_2\text{O}_3} a_{\text{C}}^3 / (a_{\text{Y}}^2 p_{\text{CO}}^3) \quad (2)$$

Using working pressure $p_{\text{CO}} = 0.1$ MPa, and taking pure substance of C and Y_2O_3 as the activity standard, then $a_{\text{C}} = 1$, $a_{\text{Y}_2\text{O}_3} = 1$,

$$\text{so } k = 1/a_{\text{Y}}^2 \quad (3)$$

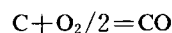
where k was constant when the temperature was unchanged. Therefore, a_{Y}^2 was constant, so the activity of $[\text{Y}]$ in the six bathes of the graphite crucible reached equality.

3.2 Data Processing Method

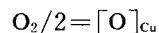
The $a_{[\text{O}]}$ was determined by the following reaction:



We know that



$$\Delta G^\circ = -114\,280 - 85.7T \quad \text{J/mol} \quad (5)$$



$$\Delta G^\circ = -85\,272 + 18.52T \quad \text{J/mol} \quad (6)$$

Combining Eqs. (5) and (6), we get



$$\Delta G^\circ = -29\,008 - 104.22T \quad \text{J/mol} \quad (7)$$

Where $T = 1437$ K, $p_{\text{CO}} = 0.1$ MPa, $a_{[\text{O}]} = 3.3 \times 10^{-7}$, so the quaternary system Cu-Y-M-O can be regarded as a ternary system Cu-Y-M.

$$\begin{aligned} \lg a_{\text{Y}} &= \lg f_{\text{Y}} + \lg [\% \text{Y}] \\ &= e_{\text{Y}}^{\text{Y}} [\% \text{Y}] + \gamma_{\text{Y}}^{\text{Y}} [\% \text{Y}]^2 + e_{\text{Y}}^{\text{M}} [\% \text{M}] \\ &\quad + \gamma_{\text{Y}}^{\text{M}} [\% \text{M}]^2 + \gamma_{\text{Y}}^{\text{M}, \text{Y}} [\% \text{M}] [\% \text{Y}] \\ &\quad + \lg [\% \text{Y}] \end{aligned} \quad (8)$$

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

$$\begin{aligned} \lg a_{\text{Y}} &= e_{\text{Y}}^{\text{Y}} [\% \text{Y}]_0 + \gamma_{\text{Y}}^{\text{Y}} [\% \text{Y}]_0^2 \\ &\quad + \lg [\% \text{Y}]_0 \end{aligned} \quad (9)$$

where $[\% \text{Y}]_0$ represents the concentration of Y in the Cu-Y system. (9) - (8):

$$\begin{aligned} \lg \frac{[\% \text{Y}]_0}{[\% \text{Y}]} &= e_{\text{Y}}^{\text{Y}} ([\% \text{Y}] - [\% \text{Y}]_0) \\ &\quad + \gamma_{\text{Y}}^{\text{Y}} ([\% \text{Y}]^2 - [\% \text{Y}]_0^2) \\ &\quad + e_{\text{Y}}^{\text{M}} [\% \text{M}] + \gamma_{\text{Y}}^{\text{M}} [\% \text{M}]^2 \\ &\quad + \gamma_{\text{Y}}^{\text{M}, \text{Y}} [\% \text{Y}] \times [\% \text{M}]^2 \end{aligned} \quad (10)$$

when $e_{\text{Y}}^{\text{Y}} = 0.036$, and $\gamma_{\text{Y}}^{\text{Y}} = -2.04 \times 10^{-3}$ ^[6], Eq. (10) becomes

$$\begin{aligned} \lg \{ [\% \text{Y}]_0 / [\% \text{Y}] \} &= 0.108 ([\% \text{Y}] - [\% \text{Y}]_0) \\ &\quad + 2.04 \times 10^{-3} ([\% \text{Y}]^2 - [\% \text{Y}]_0^2) \\ &= e_{\text{Y}}^{\text{M}} [\% \text{M}] + \gamma_{\text{Y}}^{\text{M}} [\% \text{M}]^2 \\ &\quad + \gamma_{\text{Y}}^{\text{M}, \text{Y}} [\% \text{Y}] [\% \text{M}] \end{aligned} \quad (11)$$

A number of points were taken from the iso-activity equation ($n \geq 1000$), 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

The equilibrium products of the Cu-Y-M system were identified as Y_2O_3 by X-ray diffraction.

4.1 Activity Interaction Coefficients

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

For the Cu-Y-Al system:

$$[\% \text{Y}] = 0.733 + 0.083 [\% \text{Al}] + 0.038 [\% \text{Al}]^2$$

and $\gamma = 0.794$

For the Cu-Y-Si system:

$$[\% \text{Y}] = 0.772 + 0.314 [\% \text{Si}] - 0.00052 [\% \text{Si}]^2 \text{ and } \gamma = 0.95$$

For the Cu-Y-Ti system:

$$[\% \text{Y}] = 0.782 - 0.426 [\% \text{Ti}] + 0.180 [\% \text{Ti}]^2$$

and $\gamma = 0.978$

For the Cu-Y-Fe system:

$$[\% \text{Y}] = 0.751 - 0.691 [\% \text{Fe}] + 0.495 [\% \text{Fe}]^2$$

and $\gamma = 0.981$

By using the method explained in section 3.2 and the relationship between activity interaction coefficients^[7], the interaction coefficients between M and Y were evaluated.

For the Cu-Y-Al system:

$$\begin{aligned} e_{\text{Y}}^{\text{Al}} &= -0.106, \gamma_{\text{Y}}^{\text{Al}} = -0.029, \\ \gamma_{\text{Y}}^{\text{Al}, \text{Y}} &= -0.066, e_{\text{Al}}^{\text{Y}} = -0.017, \\ \gamma_{\text{Al}}^{\text{Y}} &= -0.014, e_{\text{Al}}^{\text{Y}} = e_{\text{Y}}^{\text{Al}} = -9.9 \end{aligned}$$

For the Cu-Y-Si system:

$$e_{\text{Y}}^{\text{Si}} = -0.414, \gamma_{\text{Y}}^{\text{Si}} = -0.059,$$

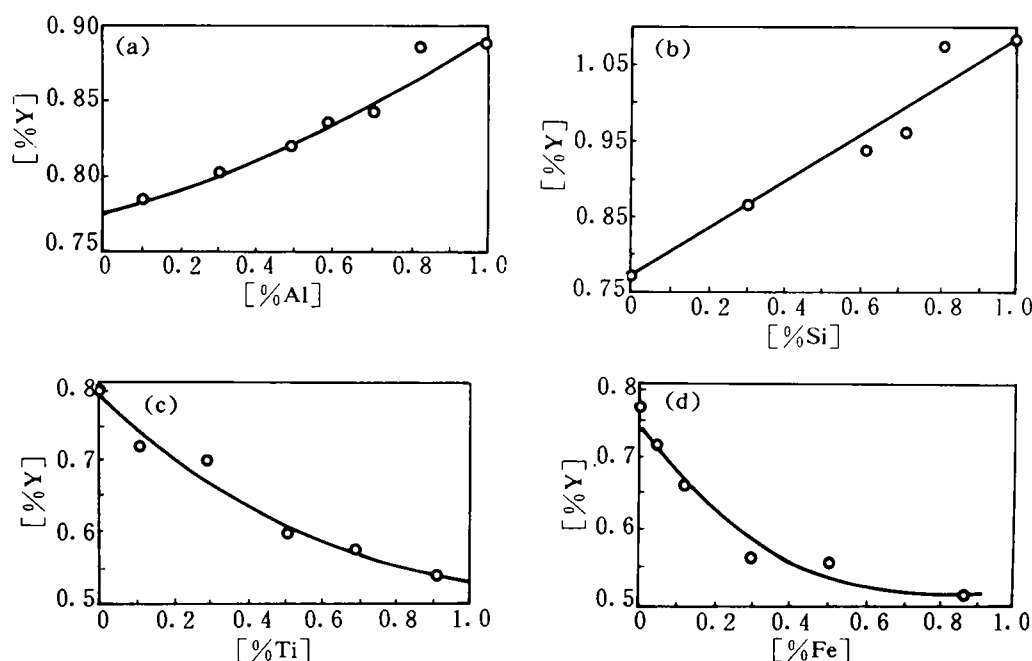


Fig. 1 Iso-activity curves of Cu-Y-M system

(a)—M = Al; (b)—M = Si; (c)—M = Ti; (d)—M = Fe

$$\gamma_{Y}^{Si,1} = 0.272, e_{Si}^1 = -0.128,$$

$$\gamma_{Si}^1 = 0.097, \varepsilon_{Si}^1 = \varepsilon_{Si}^1 = -41.5$$

For the Cu-Y-Fe system;

$$e_{Fe}^{Fe} = 0.711, \gamma_{Fe}^{Fe} = -0.392,$$

$$\gamma_{Fe}^{Fe,Y} = -0.318, e_{Fe}^Y = 0.448,$$

$$\gamma_{Fe}^Y = -0.342, \varepsilon_{Fe}^Y = \varepsilon_{Fe}^Y = 143.9$$

For the Cu-Y-Ti system;

$$e_{Ti}^{Ti} = 0.414, \gamma_{Ti}^{Ti} = -0.145,$$

$$\gamma_{Ti}^{Ti,Y} = -0.225, e_{Ti}^Y = -0.247,$$

$$\gamma_{Ti}^Y = -0.158, \varepsilon_{Ti}^Y = \varepsilon_{Ti}^Y = 79.0$$

4.2 The Equilibrium Constant of the Reaction Between Yttrium and Oxygen and the Standard Free Energy of Formation of Y_2O_3 in Liquid Cu

Substituting the activity interaction coefficients to Eq. (8), the average value of a_Y was obtained to be 0.918. Therefore, the equilibrium constant of the reaction $3[O] + 2[Y] = Y_2O_3$ is found to be;

$$k = (a_O^3 a_Y^2)^{-1} = (3.3 \times 10^{-7})^{-3} \times 0.981^{-2}$$

$$= 3.30 \times 10^{19}$$

The deoxidation constant of Yttrium is

$$k_{Y_2O_3} = 1/k = 3.03 \times 10^{-20}$$

The Gibbs standard free energy of formation of Y_2O_3 is

$$\Delta G^\circ_{Y_2O_3} = RT \ln k = -550.53 \text{ kJ/mol}$$

5 CHECKING OF ISO-ACTIVITY

Taking five concentration points from the iso-activity lines of the Cu-Y-M (M = Al, Si, Ti and Fe) systems and using the activity interaction coefficients, the a_Y were calculated from Eq. (8) and listed in values of Table 1, it can be seen that the [%Y] has reached iso-activity for all the systems.

Table 1 Checking of iso-activity

Cu-Y-M	[%M]				\bar{a}_Y
	0.1	0.3	0.5	0.7	
Cu-Y-Al	0.922	0.922	0.922	0.922	0.918
Cu-Y-Si	0.921	0.922	0.921	0.921	
Cu-Y-Ti	0.933	0.936	0.936	0.936	
Cu-Y-Fe	0.892	0.892	0.891	0.892	

6 CONCLUSIONS

(1) The equilibrium products of Cu-Y-M (M = Al, Si, Ti or Fe) system were identified as Y_2O_3 at 1200 °C.

(2) The activity interaction coefficients between M (M = Al, Si, Ti or Fe) and Y in liquid copper solutions at 1200 °C were obtained by an iso-activity method and the use of conjugate gradients for solving ill-conditioned equations.

For the Cu-Y-Al:

$$e_Y^{Al} = -0.106, \gamma_Y^{Al} = -0.029, \\ \gamma_Y^{Al,Y} = -0.066, e_{Al}^Y = -0.017, \\ \gamma_{Al}^Y = -0.014, \varepsilon_{Al}^Y = \varepsilon_Y^{Al} = -9.9$$

For the Cu-Y-Si:

$$e_Y^{Si} = -0.414, \gamma_Y^{Si} = -0.059, \\ \gamma_Y^{Si,Y} = 0.272, e_{Si}^Y = -0.128, \\ \gamma_{Si}^Y = 0.097, \varepsilon_Y^{Si} = \varepsilon_{Si}^Y = -41.5$$

For the Cu-Y-Fe:

$$e_Y^{Fe} = 0.711, \gamma_Y^{Fe} = -0.392, \\ \gamma_Y^{Fe,Y} = -0.318, e_{Fe}^Y = 0.448, \\ \gamma_{Fe}^Y = -0.342, \varepsilon_{Fe}^Y = \varepsilon_Y^{Fe} = 143.9$$

For the Cu-Y-Ti:

$$e_Y^{Ti} = 0.414, \gamma_Y^{Ti} = -0.145, \\ \gamma_Y^{Ti,Y} = -0.225, e_{Ti}^Y = -0.247, \\ \gamma_{Ti}^Y = -0.158, \varepsilon_{Ti}^Y = \varepsilon_Y^{Ti} = 79.0$$

(3) The equilibrium constant of the reaction $3[O] + 2[Y] = Y_2O_3$ is 3.30×10^{19} and the Gibbs standard free energy of formation of Y_2O_3 in liquid Cu is -550.53 kJ/mol.

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