THERMODYNAMICS AND PHASE EQUILIBRIUM OF

Cu-Y-O, Cu-Y-S, Cu-Y-O-S LIQUID SOLUTIONS[①]

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ABSTRACT   Thermodynamics of Cu-Y-O, Cu-Y-S and Cu-Y-O-S solutions at 1 200 ℃ were studied using solid electrolyte cell and chemical equilibrium method. The equilibrium constant of deoxidation, desulfurization and deoxysulfurization by Y, the Gibbs standard reaction free energies of the formation of Y_2O_3, YS and Y_2O_2S in Cu-base solution, activity interaction coefficients of S and Y, temperature dependence of standard free energy of solution of Y in Cu, self-interaction coefficients of Y in liquid Cu were obtained. The phase precipitation diagram for Cu-Y-O-S system was plotted. The thermodynamic condition of the existence of Y_2O_3, YS and Y_2O_2S in liquid Cu was determined.

Key words   Y, O, S and Cu liquid   thermodynamic property   phase diagram

1 INTRODUCTION

Rare earth elements in non-ferrous solutions play a role in purification, improving properties and alloying[1]. As inclusion element in Cu, the final contents of O and S are still high (O: 0. 05~%0. 2%, S: 0. 001%~ 0. 003%), even in refined Cu. Rare earth elements have properties of strong deoxidation and desulfurization in Fe or Ni liquid solution, as reported by some works[3-5]. But many thermodynamic parameters, such as equilibrium constants of deoxidation and desulfurization, activity interaction coefficient, the Gibbs standard reaction free energy of formation of the equilibrium products and condition of their steady existence in Cu liquid have not been known yet.

Thus it is very significant to investigate the equilibrium of deoxidation and desulfurization of rare earth elements. In this paper, as a studying object, Y has been selected.

2 EXPERIMENTAL

The purity of Cu and Y were 99. 9% and 99. 95%, respectively. CuS was chemically pure and Ni, NiO were analytically pure.

Cu-Y-O, Cu-Y-S system were investigated in molybdenum wire resistance furnace under high-purity argon atmosphere after dehydration and deoxidation.

MgO crucibles which are chemically stable were selected. Oxygen activity was measured using the sensor of NiCr | $[O]_{Cu}$ ‖ ZrO_2 (MgO)‖Ni,NiO|NiCr.

In our primary experiments, we found that as proper reference electrode Ni, NiO is preferable to Cr, Cr_2O_3 or Mo, MoO_2.

Thermodynamics and phase equilibrium for Cu-Y-O-S system were conducted in a $MoSi_2$ bar resistance furnace under CO gas at 1 200 ℃, using the spectrochemically pure graphite crucible with seven holes, and the equilibrium time was 2 h.

The equilibrium products were extracted from the samples by the electrolysis method, and then the content of the dissolved Y was determined by use of ICP spectrophotometry. The composition of the equilibrium products were identified by X-ray diffraction measurement.

3 RESULTS

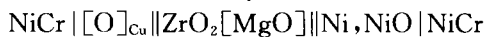### 3. 1 *Equilibrium Products*

The equilibrium products in Cu-Y-O, Cu-Y-S and Cu-Y-O-S solutions were identified as Y_2O_3, YS and Y_2O_2S, respectively.

3. 2 *Equilibrium Thermodynamic Properties of* Cu-Y-O *Solution*

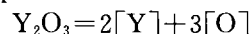The sensor used for measuring oxygen potential was as follows:

NiCr | $[O]_{Cu}$ || $ZrO_2[MgO]$ || Ni,NiO | NiCr

Sensor cell reaction is $Ni+[O]=NiO$ at 1 200 ℃, and α_0 was calculated by the following equation[6]:

$$\alpha_0 = 114.5[1.19 \times 10^{-2} \exp(-7.789E) -1.62 \times 10^{-7}]^2$$

The equilibrium reaction occurred at high temperature in Cu-base solution was:

$$Y_2O_3 = 2[Y] + 3[O]$$

The melt point of pure Y_2O_3 is 2 330 ℃, assuming pure substance as the standard state, then $\alpha_{Y_2O_3} = 1$.

Deoxidation constant $K = \alpha_Y^2 \cdot \alpha_O^3 = K' \cdot f_Y^2$, here K' is the apparent deoxidation constant. $K' = [\%Y]^2 \cdot \alpha_O^3$, thus:

$$lgK = lgK' + 2lgf_Y$$
$$-lgK' = lgK + 2(e_Y^Y[\%Y] + e_Y^O[\%O])$$

Since $[\%O]$ is low enough, so do α_0 and e_Y^O, the last two terms of the above equation may be neglected.

The concentration dependence of $-lgK'$ on $[\%Y]$ is shown in Fig. 1; from Fig. 1 we can obtain the value of $-lgK$.

Deoxidation constant of Y in liquid Cu at 1 200 ℃ is:

$$lgK = -19.66$$
$$K = 2.19 \times 10^{-20}$$

Gibbs standard reaction free energy of the formation of Y_2O_3 in liquid Cu at 1 200 ℃ is:

$$\Delta G^0 = RTlnK = -554.44 \text{ kJ/mol}$$

Equilibrium relationship between Y and O in liquid Cu at 1 200 ℃ was obtained according to $lgK = lg\alpha_O^3 \cdot \alpha_Y^2$, as shown in Fig. 2.

Through calculation, we can get $lg\alpha_Y = -1.5lg\alpha_O - 9.83$.

From Fig. 2 we can conclude that, when $\alpha_Y = 0.145$, α_O can be decreased to $1 \times 10^{-4}\%$ lower. This indicates that Y has very strong ability of deoxidation.

3. 3 *Thermodynamic Properties of* Cu-Y-S *System*

Reaction of desulfurization in Cu-base solution is as follows:

$$YS_{(s)} = [Y] + [S]$$
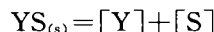
The melt point of pure YS is 2 060 ℃, assuming pure substance as the standard state, then $\alpha_{YS} = 1$ at 1 200 ℃.

Since apparent desulfurization constant $K' = [\%Y] \cdot [\%S]$, and desulfurization constant $K = \alpha_Y \cdot \alpha_S = K' \cdot f_Y \cdot f_S$, then:

$$lgK = lgK' + e_S^Y[\%Y] + e_Y^Y[\%Y] + e_Y^S[\%S] + e_S^S[\%S]$$

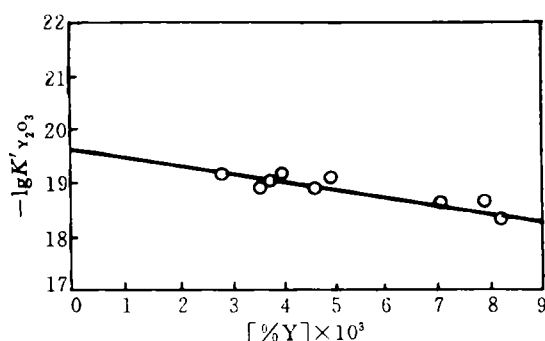Using the transforming formula of e_Y^S and e_S^Y, that is $e_Y^S = 2.773 e_S^Y$, then:

Fig. 1 $-lg\, K'_{Y_2O_3}$ **vs** $[\%Y]$ **in liquid Cu**
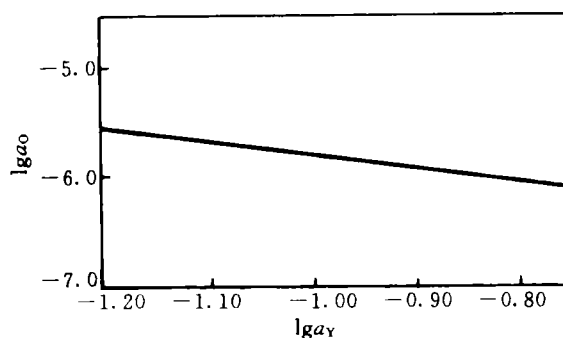

Fig. 2   Equilibrium diagram for $[Y]$-$[O]$ **in liquid Cu**

$-\lg K' - e_S^S[\%S] - e_Y^Y[\%Y]$

$\quad = -\lg K + e_S^Y([\%Y] + 2.773[\%S])$

Line of $-\lg K' - e_S^S[\%S] - e_Y^Y[\%Y]$ versus $[\%Y] + 2.733[\%S]$ was plotted in Fig. 3. Choosing $e_S^S = -0.143^{[7]}$, $e_Y^Y = 0.101^{[6]}$, from the regression curve in dilute liquid solutions, we obtained a linear equation. The intercept and the starting tangent of the linear equation are $\lg K = -5.37$ and $e_S^Y = -7.89$ respectively. So the linear equation obtained is as follows:

$-\lg K' - 0.143[\%S] - 0.101[\%Y] = -5.37$

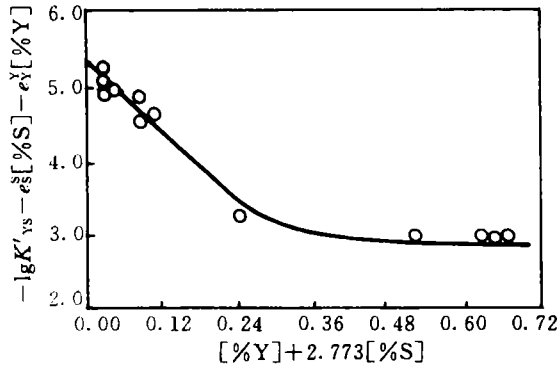$-7.89([\%Y] + 2.773[\%S])$, $r = 0.97$

Fig. 3 Concentration dependence of
$-\lg K'_{YS} - e_S^S[\%S] - e_Y^Y[\%Y]$ **in liquid Cu**

Desulfurization constant of Y in liquid Cu at 1 200 ℃ is:

$\lg K = -5.37$, $K = 4.27 \times 10^{-6}$

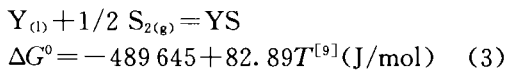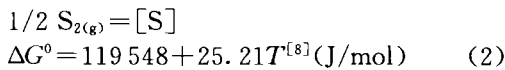Interaction coefficient between Y and S in liquid Cu at 1 200 ℃ is $e_S^Y = -7.89$.

From the transforming formula of activity interaction coefficient, we determined that:

$e_Y^S = -21.2$, $\varepsilon_S^Y = \varepsilon_Y^S = -2540$

Gibbs standard reaction free energy of formation of YS in liquid Cu at 1 200 ℃ is:

$\Delta G^0 = RT\ln K = -151.26 \text{ kJ/mol}$ 　　(1)

Now we calculate the standard free energy of solution of Y and activity coefficient of Y in liquid Cu. For the following reactions we have:

$1/2\ S_{2(g)} = [S]$

$\Delta G^0 = 119\,548 + 25.21T^{[8]}(\text{J/mol})$ 　　(2)

$Y_{(l)} + 1/2\ S_{2(g)} = YS$

$\Delta G^0 = -489\,645 + 82.89T^{[9]}(\text{J/mol})$ 　(3)

Combining (1), (2) and (3), when $T = 1\,473\,\text{K}$, then:

$Y_{(l)} = [\%Y]$

$\Delta G_S^0 = -133.87\,\text{kJ/mol}$

From $\Delta G_S^0 = RT\ln(\gamma_Y^0 \cdot M_{Cu}/100M_Y)$, we can obtain that at 1 200 ℃ the activity coefficient is:

$\gamma_Y^0 = 2.47 \times 10^{-3}$

Assuming Cu-Y system as a regular solution, $RT\ln\gamma_i^0$ is a constant, then the dependence of γ_Y^0 and ΔG_S^0 on temperature can be given as follows:

$\ln\gamma_Y^0 = -8\,835/T$

$\Delta G_S^0 = -73\,405 - 41.04T$

As a property of regular solution, $\varepsilon_i^i = -2\ln\gamma_i^0$. So the self-interaction coefficient of Y can be calculated:
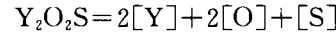
$\varepsilon_Y^Y = 17\,676/T$

From the transforming formula of ε_i^i and e_i^i, we get:

$e_Y^Y = 54.93/T + 1.24 \times 10^{-3}$

3.4　*Thermodynamic Property for* Cu-Y-O-S *System*

Deoxysulfurization reaction:

$Y_2O_2S = 2[Y] + 2[O] + [S]$

The melt point of pure Y_2O_2S is 2 120 ℃; assuming pure substance as the standard state, then at 1 200 ℃, $a_{Y_2O_2S} = 1$. The apparent desulfurization constant $K' = [\%Y]^2 \cdot a_O^2 \cdot [\%S]$, and desulfurization constant $K = a_Y^2 \cdot a_O^2 \cdot a_S = K' \cdot f_Y^2 \cdot f_S$, so we have:

$-\lg K' = -\lg K + 2(e_Y^Y[\%Y] + e_Y^S[\%S])$

$\quad + e_S^S[\%S] + e_S^Y[\%Y]$

$\quad + 2e_Y^O[\%O] + e_S^O[\%O]$ 　　　(4)

Taking $e_S^S = -0.143^{[7]}$, $e_Y^Y = 0.101^{[6]}$, a_O can be determined by the reaction $C + [O] = CO$. At 1 200 ℃, $a_O = 3.3 \times 10^{-7}$.

Because value of a_O is very small, $[\%O] = a_O$. So the last two terms in equation (4) can be neglected. Using the transforming formula of e_Y^S and e_S^Y, we have:

$-\lg K' - 2e_Y^Y[\%Y] - e_S^S[\%S]$

$\quad = -\lg K + e_S^Y[\%Y] + 5.546[\%S]$ 　(5)

According to the experimental data for both $[\%Y]$ and $[\%S]$, regression process was carried out to equation (5). The follow-

ing equation was obtained:

$$-\lg K - 2e_Y^Y[\%Y] - e_S^S[\%S]$$
$$= 18.01 - 8.33([\%Y] + 5.546[\%S]) \quad (6)$$

From equation (6), $\lg K$ and e_S^Y can be obtained:

$$\lg K = -18.01, \quad e_S^Y = -8.33$$

At 1 200 ℃ deoxysulfurization constant of Y in liquid Cu is:

$$\lg K = -18.01, \quad K = 9.77 \times 10^{-19}$$

Gibbs standard reaction free energy of formation of Y_2O_2S in liquid Cu is:

$$\Delta G^0 = RT\ln K = -507.35 \text{ kJ/mol}$$

Interaction coefficient between Y and S is:

$$e_S^Y = -8.33, \quad e_Y^S = -23.1,$$
$$\varepsilon_S^Y = \varepsilon_Y^S = -2682$$

3. 5 *Precipitation Phase Diagram for* Cu-Y-O-S

Under a certain thermodynamic condition, two or more phases can exist in a same reaction system. We can predict the equilibrium product and control its formation for a system according to phase precipitation diagram under a certain thermodynamic condition.

Basic thermodynamic parameters are shown in Table 1. In terms of data in Table 1, we obtained some equations for $\lg a_O, \lg a_S$

and $\lg a_Y$, and the coordinates of each important point(See Table 2.)

3. 6 *The Planar Precipitation Phase diagram for* [Y]-[S]-[O] *in Liquid* Cu

The planar precipitation diagram for [Y]-[S]-[O] in liquid Cu at 1 200 ℃ is shown in Fig. 4. Dashed lines are the iso-activity lines of Y, which are horizontal in oxide district,
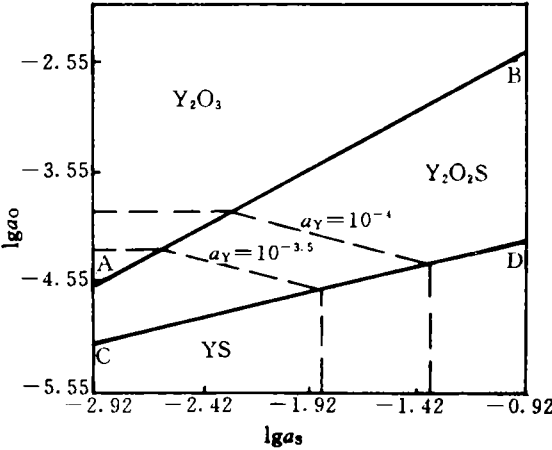

Fig. 4 Planar precipitation diagram for [Y]-[S]-[O] in liquid Cu

Table 1   Equilibrium constants of deoxidation, desulfurization and deoxysulfurization by Y in liquid Cu(1 200 ℃)

Reaction	ΔG^0/kJ • mol^{-1}	$\lg K$	K
$Y_2O_3 = 2[Y] + 3[O]$	-553.83	-19.66	2.19×10^{-20}
$YS = [Y] + [S]$	-151.26	-5.37	4.27×10^{-6}
$Y_2O_2S = 2[Y] + 2[O] + [S]$	-507.35	-18.01	9.77×10^{-19}

Table 2   Equations between $\lg a_O, \lg a_S$ and $\lg a_Y$ and coordinates of some important points

Geometric factors	Equations and coordinates	Projection on plane
Plane Y_2O_3	$\lg a_Y = -1.5\lg a_O - 9.83$	
Y_2O_2S	$\lg a_Y = -\lg a_O - 0.5\lg a_S - 9.01$	
YS	$\lg a_Y = -\lg a_S - 5.37$	
Line AB	$\lg a_Y = -1.5\lg a_O - 9.83$	$\lg a_O = \lg a_S - 1.64$
	$\lg a_Y = -\lg a_O - 0.5\lg a_S - 9.01$	$a_S/a_O = 43.7$
Line CD	$\lg a_Y = -\lg a_O - 0.5\lg a_S - 9.01$	$\lg a_O = 0.5\lg a_S - 3.64$
	$\lg a_Y = -\lg a_S - 5.37$	$a_S/a_O^2 = 1.91 \times 10^7$
Point B	$(\lg a_Y, \lg a_S, \lg a_O) = (-1.50, -3.92, -5.55)$	$(\lg a_S, \lg a_O) = (-3.92, -5.55)$
Point A	$(\lg a_Y, \lg a_S, \lg a_O) = (-3.0, -2.92, -4.55)$	$(\lg a_S, \lg a_O) = (-2.92, -4.55)$
Point C	$(\lg a_Y, \lg a_S, \lg a_O) = (-2.45, -2.92, -5.10)$	$(\lg a_S, \lg a_O) = (-2.92, -5.10)$

oblique in oxy-sulfide district and vertical in sulfide district. From the two lines, $\alpha_Y = 10^{-3.5}$ or 10^{-4}, we can read the values of α_O, α_S and α_Y directly, equilibrium between molten mass and one or two correlative precipitation phases is approached. The equilibrium relationship of [Y]-[S]-[O] in liquid Cu can be seen clearly in Fig. 4 and Table 2. So the condition for steady existence of Y_2O_3 is determined as follows:

$$\alpha_S/\alpha_O < 43.7$$
$$\alpha_O^3 \cdot \alpha_Y^2 > 2.19 \times 10^{-20}$$

The condition of steady existence for Y_2O_2S is:

$$\alpha_O^3 \cdot \alpha_Y^2 < 2.19 \times 10^{-20}$$
$$\alpha_O^2 \cdot \alpha_Y^2 \cdot \alpha_S > 9.77 \times 10^{-19}$$
$$\alpha_S/\alpha_O^2 < 1.91 \times 10^7$$

And that for YS is:

$$\alpha_S/\alpha_O^2 > 1.91 \times 10^7$$
$$\alpha_Y \cdot \alpha_S > 4.27 \times 10^{-6}.$$

4　CONCLUSIONS

(1) The equilibrium products for deoxidation, desulfurization, and deoxysulfurization by Y in liquid Cu at 1 200 ℃ were identified as Y_2O_3, YS and Y_2O_2S, respectively.

(2) The constants of deoxidation, desulfurization, deoxysulfurization and Gibbs reaction standard free energy of equilibrium products in liquid Cu at 1 200 ℃ have been determined:

$$K_{Y_2O_3} = 2.19 \times 10^{-20}$$
$$K_{YS} = 4.27 \times 10^{-6}$$
$$K_{Y_2O_2S} = 9.77 \times 10^{-19}.$$
$$2[Y] + 3[O] = Y_2O_3$$
$$\Delta G^0 = -554.44 \text{ kJ/mol}.$$
$$[Y] + [S] = YS$$
$$\Delta G^0 = -151.26 \text{ kJ/mol}.$$
$$2[Y] + 2[O] + [S] = Y_2O_3S$$
$$\Delta G^0 = -507.35 \text{ kJ/mol}.$$

(3) Dependence of the Gibbs standard free energy of solution of Y, self-interaction coefficient and activity coefficient of Y on temperature in liquid Cu are as follows:

$$\Delta G^0 = -73\,405 - 41.04T$$
$$\varepsilon_Y^Y = 17\,676/T$$

$$e_Y^Y = 54.93/T + 1.24 \times 10^{-3}$$
$$\ln \gamma_Y^0 = -8\,835/T.$$

(4) Interaction coefficients between Y and S in liquid Cu at 1 200 ℃ have been obtained.

For Cu-Y-S system:
$$e_S^Y = -7.89, \quad e_Y^S = -21.2,$$
$$\varepsilon_S^Y = \varepsilon_Y^S = -2\,540$$

For Cu-Y-O-S system:
$$e_S^Y = -8.33, \quad e_Y^S = -23.10,$$
$$\varepsilon_S^Y = \varepsilon_Y^S = -2\,682, \quad \gamma_S^Y = -16.86.$$

On an average:
$$e_S^Y = -8.11, \quad e_Y^S = -22.2,$$
$$\varepsilon_S^Y = \varepsilon_Y^S = -2\,611.$$

(5) Y has strong ability of deoxidation and desulfurization in the liquid Cu; when $\alpha_Y = 0.145$, [%O] can be decreased to lower than 1×10^{-4}%. Under the condition of low [%O] and [%S] content in liquid Cu, [%O] and [%S] can be further decreased by Y, forming the product Y_2O_2S.

(6) Planar precipitation phase diagram has been plotted at 1 200 ℃, which is the theoretical basis for predicting the forming sequence and the type of inclusions. The thermodynamic conditions for steady existence of Y_2O_3, YS and Y_2O_2S have been determined.

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