

KINETICS OF INTERACTION BETWEEN Cu_2S AND Cu_2O IN SOLID STATE UNDER NONISOTHERMAL CONDITION^①

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ABSTRACT The reaction mechanism and kinetics of the interaction between solid Cu_2O and Cu_2S under nonisothermal process were investigated by TG method. The result shows that the interaction takes place at 723 K and completes at 1 373 K, and in this temperature range the reaction rate of interaction has two maximum value at 873 K and 1 073 K respectively. The parameters that affect the rate of the interaction are flowrate of carrier inert gas, grain size of sample and concentration of Cu_2O . According to the experimental data the optimal conditions were obtained and the kinetics equation was derived.

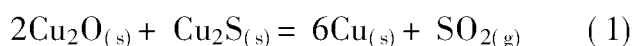
Key words kinetics of interaction nonisothermal process Cu_2S Cu_2O

1 INTRODUCTION

The producing copper with copper sulphide reduced by hydrogen and carbon monoxide is of interest in recent years. But it has not been reported that the kinetics and mechanism of the interaction between Cu_2O and Cu_2S in solid state. Byerley^[1] studied the interaction mechanism of Cu_2O and Cu_2S in liquid state. Liu^[2] researched the kinetics of the interaction at isotherm conditions in liquid state. In this paper, we report that in solid state and at nonisothermal condition the kinetics and mechanism of interaction of Cu_2O and Cu_2S . Because the interaction is the base for the producing copper directly from the solid Cu_2O and Cu_2S , it is very important not only in practice, but also in solid-solid reaction theory.

2 EXPERIMENTAL

The stoichiometric reaction of Cu_2S and Cu_2O interacted is shown as follows:



The measurement may be either by determining the weight loss of SO_2 from reaction by

TG method or iodimetric method. In order to measure the data accurately we designed a measuring system reported in Ref. [3].

The main parameters that influence the kinetics are flow rate of carrier gas, concentration of Cu_2O , particle size of the charge and temperature of the reaction. These parameters affected on the reaction rate are respectively shown in Figs. 1~4. From the Fig. 1 we can see that at the flowrate $Q_{\text{Ar}} > 600 \text{ mL/min}$ the external gas diffusion can be neglected. Thus the optimal flowrate determined is 600 mL/min.

At stoichiometric ratio of $2\text{Cu}_2\text{O}/\text{Cu}_2\text{S}$ the conversion reaction is the most efficient (Fig. 2). By Fig. 3 we know that the smaller the particle size is, the larger the conversion fraction is, and the optimal particle size is - 240 mesh.

From above discussion and Figs. 1~4, we get the optimal conditions: $\text{Cu}_2\text{O}/\text{Cu}_2\text{S} = 2:1$ (mol ratio), $Q_{\text{Ar}} > 600 \text{ mL/min}$, particle size - 240 mesh, temperature 1 373 K and charge mixed homogeneously.

3 MECHANISM AND KINETIC EQUATION

3.1 Mechanism of interaction

According to the reaction (1), the equilib-

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rium constant is

$$K = \frac{a_{\text{Cu}}^6 \cdot p_{\text{SO}_2}}{a_{\text{Cu}_2\text{O}}^2 \cdot a_{\text{Cu}_2\text{S}}} \quad (2)$$

and the activity of Cu, Cu_2O and Cu_2S in solid state may be considered as unit, then

$$K = p_{\text{SO}_2} \quad (3)$$

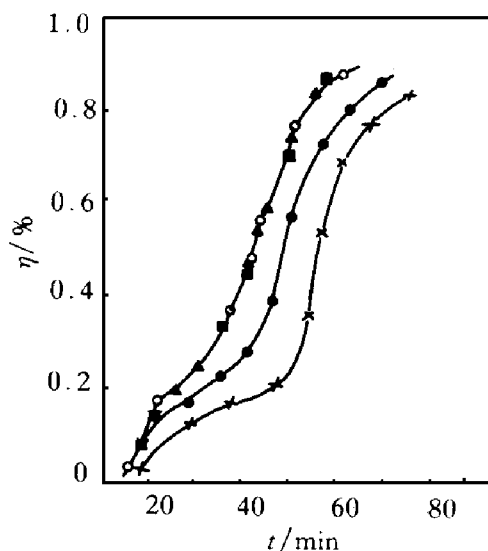


Fig. 1 Effect of flowrate on conversion fraction

○—600 mL/min; ▲—800 mL/min;
■—1 000 mL/min; ×—300 mL/min;
●—400 mL/min

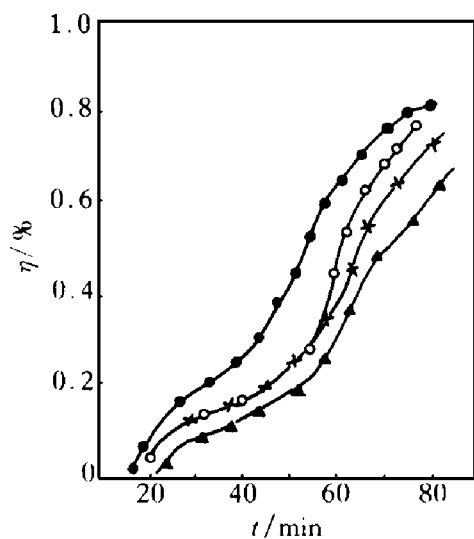


Fig. 2 Effect of Cu_2O concentration on conversion fraction

○—over 5% Cu_2O ; ▲—over 15% Cu_2O ;
×—over 10% Cu_2O ; ●— $\text{Cu}_2\text{O}/\text{Cu}_2\text{S} = 2$

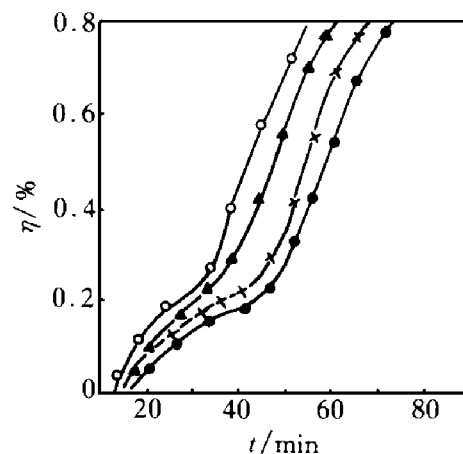


Fig. 3 Effect of particle size on Conversion fraction

○—600 mL/min; ▲—800 mL/min;
×—300 mL/min; ●—400 mL/min

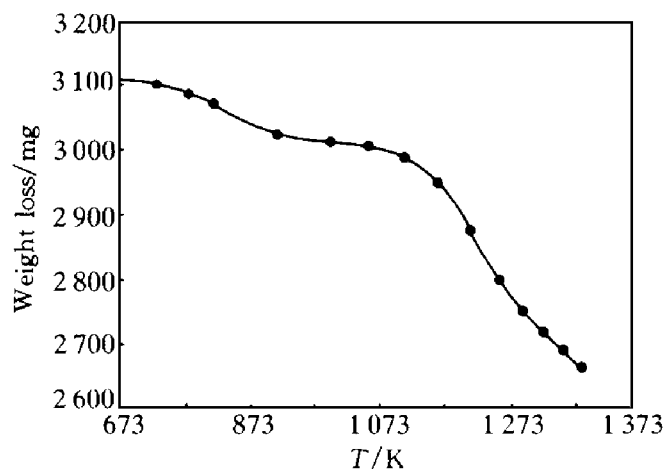


Fig. 4 Effect of temperature on weight loss of sample

($\text{Cu}_2\text{O}/\text{Cu}_2\text{S} = 2$; $Q_{\text{Ar}} = 600$ mL/min)

Thus, the criterion of K is based on the equilibrium pressure of SO_2 . According to the thermodynamic data the relationship of equilibrium constant with temperature is^[4]

$$\lg p_{\text{SO}_2} = -\frac{777.927}{T} + 4.449 \quad (4)$$

The experimental temperature is 800~ 1 773 K, so the equilibrium constant calculated from equation (4) is

$$K/10^5 \text{ Pa} = p_{\text{SO}_2} = 3.0 \times 10^3 - 1.02 \times 10^4$$

The larger equilibrium pressure of SO_2 indicates that the reaction (1) is very favorable to proceed toward the right.

At initial stage the contact surface of well mixed Cu_2O and Cu_2S is very large, the rate of chemical reaction depended on surface is quite fast and the diffusing from reaction region to the bulk gas current of SO_2 is always less than rate of chemical reaction, so the SO_2 gas diffusion becomes dominant step of the process. When the interacted reaction continuously proceed, the resistance of solid copper embeded in the charge becomes so large that the chemical reaction slows down and becomes a control step of the process. Thus the mechanism of the interaction process is a mixed control. The schematic diagram of mechanism model is shown in the Fig. 5 and the two stages of mechanisms may be expressed as follows: at initial stage, $V_c > V_d$ the control step is diffusion and at second stage, $V_d > V_c$ is a chemical control.

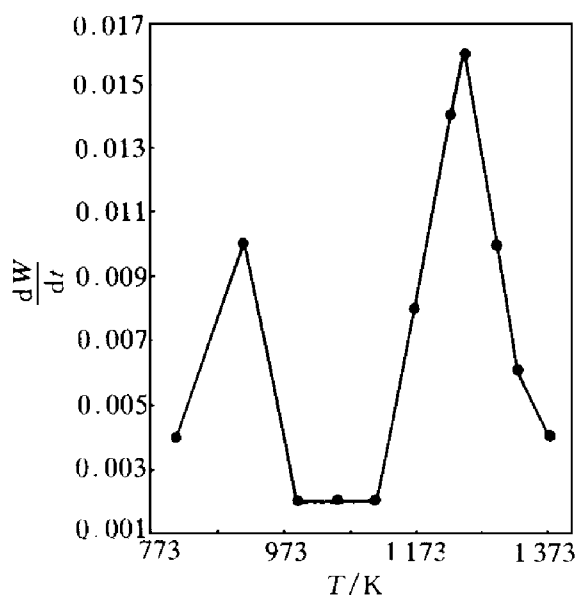


Fig. 5 The relation of reaction rate with temperature

3.2 Derivation of kinetic equation

In the nonisothermal condition the reaction rate is a function of the reaction extent and temperature^[5], namely

$$\frac{d\alpha}{dt} = \Phi(\alpha, T) \quad (5)$$

According to experimental measurement the relationship between reaction temperature and time is nonlinear and the equation determined is

shown as follows:

$$\ln t = -\frac{a}{T} + b \quad (6)$$

where a and b are constant determined by experiment.

In a solid-solid interaction system of non-isothermal process the reaction rate at a definite condition changes with contact surface. Taking unit mass of reactant contact surfaces as main parameter of the reaction, the equation can be expressed as follows:

$$-\frac{dW_s}{dt} = kFC^n \quad (7)$$

where W_s is the weight of solid reactant in the reaction system, C is the concentration of the reactant, F is the area of unit mass of the reactant surface, k is the specific rate constant, and n is the reaction orders. The charge with definite mesh size may be considered as a homogeneous globe with radius R_0 , and after time t the radius R_0 is reduced to R due to the interaction. The relation between rate of weight change and radius R of globular granule may be obtained from following equation:

$$-\frac{dW_s}{dt} = -\frac{d}{dt}\left(N \frac{4}{3}\pi R^3 \rho\right) \quad (8)$$

$$-\frac{dW_s}{dt} = 4N\pi R^2 \rho \left(-\frac{dR}{dt}\right) \quad (9)$$

where ρ is the density of granule, N is the number of granule in the unit mass.

$$N = \frac{1}{(4/3)\pi R_0^3 \rho} \quad (10)$$

If the change of globular granule is expressed by conversion fraction, then the following equation holds true:

$$\alpha \frac{d\alpha}{dt} = \frac{1}{\ln} \left[\frac{(4/3)\pi R^3 \rho N}{(4/3)\pi R_0^3 \rho N} \right] = 1 - \left[\frac{R}{R_0} \right]^3 \quad (11)$$

$$\text{or } (1 - \alpha)^{1/3} = \frac{R}{R_0} \quad (12)$$

Thus, the conversion fraction in globular granule is function of the ratio of R/R_0 . By differentiation with respect to t we get

$$\frac{dR}{dt} = -\frac{R_0^3}{3R^2} \frac{d\alpha}{dt} \quad (13)$$

Substituting equations (10) and (13) into equation (9), the rate of weight change of the interaction becomes

$$-\frac{dW_s}{dt} = \frac{4\pi R^2 \rho}{(4/3)\pi R_0^3 \rho} \left| \frac{R_0^3}{3R^2} \frac{d\alpha}{dt} \right| \quad (14)$$

As stated above, the reaction surface is defined as unit mass contact surface, so the reaction area is as follows:

$$F = \frac{N4\pi R^2}{(4/3)N\pi R_0^3 \rho} = \frac{3R^2}{R_0^3 \rho} = \frac{3}{R_0 \rho} (1 - \alpha)^{2/3} \quad (15)$$

When granular size is definite and R_0 is constant, the equation (15) becomes

$$F = B(1 - \alpha)^{2/3} \quad (16)$$

in which B is a constant, $B = 3/R_0 \rho$.

The rate of weight change can be expressed in terms of conversion fraction α , then the equation (7) becomes

$$\frac{d\alpha}{dt} = kB(1 - \alpha)^{2/3} C^n \quad (17)$$

where n is the reaction orders, about 2.7~3.0, which is agreeable with the value of references [6-7]. The ratio Cu₂O/Cu₂S at any time maintains 2:1, so it may be considered as constant. Therefore the equation (17) can be written as follows:

$$\frac{d\alpha}{dt} = km(1 - \alpha)^{2/3} \quad (18)$$

where $m = BC^n$, and k is the specific rate constant expressed with Arrhenius empirical formula, we get

$$\frac{d\alpha}{dt} = A e^{-E/RT} m(1 - \alpha)^{2/3} \quad (19)$$

In a nonisothermal process the reaction temperature changes with time, their relationship determined by experimental data is a nonlinear curve.

We get $t = L e^{-\alpha/T}$ from the equation (6), then we rewrite the equation (19) in the form of

$$\frac{d\alpha}{dT} \frac{dT}{dt} = A e^{-E/RT} m(1 - \alpha)^{2/3} \quad (20)$$

or

$$\frac{d\alpha}{dT} = \frac{dT}{dt} m A e^{-E/RT} (1 - \alpha)^{2/3} \quad (21)$$

According to Eqn. (19) we obtain

$$\frac{dT}{dt} = L e^{-\alpha/T} \frac{\alpha}{T^2} \quad (22)$$

Substituting Eqn. (22) into Eqn. (21) we get

$$d\alpha = mLA e^{-(E + \alpha R)/RT} \cdot (1 - \alpha)^{2/3} (\alpha/T^2) dT \quad (23)$$

Rearranging Eqn. (23) we obtain

$$\frac{d\alpha}{(1 - \alpha)^{2/3}} = \frac{mLAR}{E + \alpha R} e^{-(E + \alpha R)/RT} d\left(-\frac{E + \alpha R}{T}\right) \quad (24)$$

Integrating Eqn. (24) we get

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^{2/3}} = \int_{T_0}^T \frac{mLAR}{E + \alpha R} e^{-(E + \alpha R)/RT} d\left(-\frac{E + \alpha R}{T}\right)$$

$$\text{i. e. } 1 - (1 - \alpha)^{1/3} = \frac{mLAR}{3(E + \alpha R)} e^{-(E + \alpha R)/RT} \quad (25)$$

Taking logarithm of both side in Eqn. (25), the equation becomes

$$\ln[1 - (1 - \alpha)^{1/3}] = \ln \frac{mLAR}{3(E + \alpha R)} - \frac{E + \alpha R}{RT} \quad (26)$$

Equation (26) is the nonisothermal kinetic equation of solid-solid interaction process.

Making a plot of $\ln[1 - (1 - \alpha)^{1/3}]$ vs $1/T$, we get two straightlines as shown in Fig. 6.

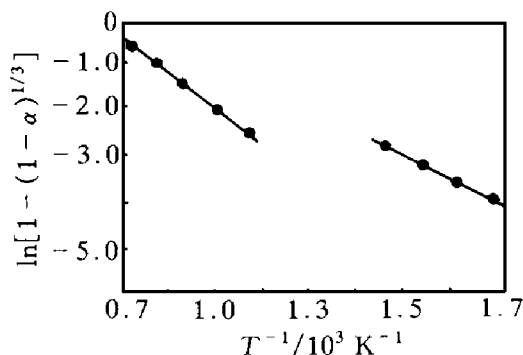


Fig. 6 Plot of transform function against $1/T$

The peaks in the Fig. 5 and the straightlines in Fig. 6 represent the same things, which indicates the different mechanism existing in the interaction process. At initial stage the temperature is from 723 K to 873 K, the rate of process is controlled by SO₂ gas diffusion. At the second stage when temperature attains 1073~1373 K, the rate of process turns to be controlled by chemical reaction. The changed causes of mechanism were already described in the former para-

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Si film has been observed. When the surface of the amorphous SiO₂ layer is not smooth, the small protruding points will cause stress fields around them in the ZMR Si film.

4 CONCLUSIONS

(1) Using a RF-induced graphite strip heater system, defects in the heat-sink structure SOI specimen can be confined in the Si film on the thicker SiO₂ layer. Silicon film on thin SiO₂ strips is defect-free. In our experiments, defect-free Si single crystal region with about 50 μm wide can be obtained by the process. The Si film has [100] orientation and a thickness of about 0.55 μm.

(2) Commonly observed defects in the defect localized regions are SGBs. Most of SGBs observed are of the mixed type, and have an ori-

entation difference of less than 3°.

(3) The dislocations and dislocation networks have been also observed in the defect localized regions of the SOI material. The Burgers vectors of the dislocations are $a/2\langle 110 \rangle$. A few interface dislocations in the Si substrate have no influence on the ZMR Si film, due to the existence of the amorphous SiO₂ separating layer.

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graph. It is beyond the argument that the values of diffusion and chemical activation energies (E_D and E_C) calculated from Arrhenius formula are coincident with the common values of diffusion and chemically controlled process.

Let the conversion function $f = 1 - (1 - \alpha)^{2/3}$, then

$$E = \frac{R \ln(f_1/f_2)}{1/T_1 - 1/T_2} \quad (27)$$

According to figure 6, substituting respectively the data of two straight lines into formula (27), we get $E_D = 39.935$ kJ/mol and $E_C = 78.854$ kJ/mol.

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