

THERMOGRAVIMETRIC STUDY OF THE OXIDATION KINETICS OF COPPER

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ABSTRACT

The oxidation kinetics of copper in air has been studied at various temperatures in the range 500 °C to 924 °C by thermogravimetry. In that range of temperatures the oxidation leads to copper I oxide and the system shows diffusion controlled kinetics according to Wagner's parabolic law. Plots of the square of the variation of the sample weight as a function of time show a good linear correlation and allow the rate constant to be determined. Experiments at various temperatures confirm that the system exhibits an Arrhenius behaviour and the frequency factor as well as the activation energy have been calculated.

RESUMO

A cinética de oxidação do cobre ao ar foi estudada a varias temperaturas na faixa de 500 °C a 924 °C por termogravimetria. Nesta faixa de temperaturas a oxidação conduz à formação de óxido de cobre I e o sistema apresenta uma cinética controlada por difusão de acordo com a lei parabólica de Wagner. Gráficos do quadrado da variação do peso da amostra em função do tempo apresentam uma boa correlação linear e permitem a determinação da constante de velocidade. Determinações a várias temperaturas confirmam que o sistema exhibe um comportamento de Arrhenius e o fator de frequência, bem como a energia de ativação, foram calculados.

Key words: Oxidation Kinetics, Thermogravimetry

INTRODUCTION

Solid state chemistry has been of increasing interest in recent times because of its technological importance as well as the possibility of mathematical modeling for the description of the kinetic behaviour of systems.

Heterogeneous kinetics implies in phase transfer of substances during the chemical reaction. Thus, the reaction rate for an heterogeneous reaction may depend not only on the chemical step but also on other steps involving diffusion, adsorption, desorption etc. The system behaviour under such

conditions depends of factors like: viscosity of the medium, surface characteristics, amount of products formed and others that may affect the reaction rate.

Metal oxidation kinetics is an example of a solid-gas heterogeneous reaction. Reactions occurring on metallic surfaces are frequently controlled by diffusion and the presence of defects in the product layer plays an important role in the kinetics.

In the present work the oxidation kinetics of copper has been studied in order to establish the mechanism and to analyze the factors that determine the reaction rate. When copper reacts with oxygen two oxides, with different stabilities may be formed. While copper I oxide (Cu_2O) can be formed in a large temperature range, copper II oxide (CuO) has its existence limited to a restricted temperature interval.

The copper oxidation kinetics was studied by Ebisuzaki and Sanborn¹, in the temperature range of 687 °C to 1000 °C. They confirmed the validity of Wagner's parabolic law^{2,3} and calculated the Arrhenius parameters. A detailed study, including isothermal and non-isothermal assays, was presented by Garnaud⁴. The isothermal assays allowed the determination of the forming conditions for the copper II oxide and copper I oxide as well as the influence of the apparent activation energy of the system.

Copper II oxide can only be formed when the relation between the number of copper ions and the number of oxygen ions, present in the external surface of the film, is less than a certain critical value⁵. The critical value is not achieved while the metallic surface is not completely covered by a layer of oxide. The temperature is a paramount factor for the formation of copper II oxide and, at 1000 °C, when copper is oxidized in air, only copper I oxide is formed. The CuO is inexistent bellow 150 °C, reaches a maximum between 300 °C and 500 °C decreases again at higher temperatures becoming minimum above 900 °C.

EXPERIMENTAL

High purity metallic copper samples (99.92%, determined by electrogravimetry), in the form of square plates 0.5 mm thick and with a total area between 0.14 cm² and 0.16 cm², were used in all measurements. The

samples were treated, for 30 seconds, with HNO₃ 1:1, rinsed in distilled water, ethanol and dried in an hot air stream. After treatment, each sample was weighted in a thermobalance (Perkin-Elmer, TGS-2, System DSC-4) at room temperature. The thermobalance was programmed to operate at constant temperature and the variation of the sample weight registered as a function of time for about 150 minutes. All measurements have been carried out with the samples in air.

OXIDATION KINETICS

Kinetic processes governed by diffusion comprise two fundamental steps⁶; the chemical reaction itself and mass transport to the reaction region. The latter step may be the slowest, and constitutes the rate determining step.

When diffusion occurs monodimensionally, as in the present experiment, the nuclear growing can be described by a parameter **h**, representing the thickness of the layer which has not reacted⁷ in a time **t**. Fick's first law for the diffusion of fluids in solids allows to write:

$$\frac{d\alpha}{dt} = -D.A \left(\frac{dx}{dh} \right) \quad (I)$$

where **A** represents the diffusion area; **x** is the concentration of the species which diffuses into the layer; **D** is the diffusion coefficient and $d\alpha/dt$ represents the thickness variation of the formed oxide layer with time.

Integration of Equation (I), under constant temperature, gives for **x** the value:

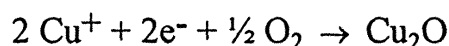
$$x = \frac{h_0 \alpha}{A.D} \left(\frac{d\alpha}{dt} \right) \quad (II)$$

where **h₀** represents the thickness of the layer which has not reacted in the time **t=0**. Making $k = A.D/h_0$ and considering that **x** is time independent⁸, integration of Equation (II) leads to:

$$\alpha^2 = 2kt \quad (III)$$

Equation (III) is the well known Wagner's parabolic law⁹ which describes the behaviour of diffusion controlled kinetic systems.

The oxidation of copper in the temperature range of the present experiment can be represented by:



When a sample of metallic copper is submitted isothermally to an oxidizing atmosphere a weight increase results due to the incorporation of an oxygen atoms per molecule of Cu_2O formed. The system obeys the parabolic law and the weight increase, measured as a function of time, allows the rate constant to be determined. The use of a thermobalance makes it possible to carry out the reaction with very small copper samples without loss of precision. Once the weight increase of the system, Δm , has been measured the amount of Cu_2O formed can be calculated from the stoichiometry by:

$$M_{\text{Cu}_2\text{O}} = \frac{\Delta m \cdot \bar{M}_{\text{Cu}_2\text{O}}}{\bar{M}_{\text{O}}} \quad (\text{IV})$$

where $M_{\text{Cu}_2\text{O}}$ is the weight of copper I oxide formed in the reaction, $\bar{M}_{\text{Cu}_2\text{O}}$ is the molecular weight of copper I oxide and \bar{M}_{O} , represents the atomic weight of oxygen.

The value of $M_{\text{Cu}_2\text{O}}$, obtained from Equation (IV), allows the thickness of the oxide layer to be calculated once the density of copper I oxide and the area are known. Supposing that the oxide layer grows uniformly, its area must coincide with that of the metallic sample subject to oxidation. Representing by ρ the copper I oxide density and by A the surface area of the sample being oxidized, one may write:

$$\alpha = \frac{\Delta m \cdot \bar{M}_{\text{Cu}_2\text{O}}}{\bar{M}_{\text{O}} \cdot \rho \cdot A} \quad (\text{V})$$

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Substituting the layer thickness, given by Equation (V), in the parabolic law (3), results:

$$\frac{\Delta m^2 \cdot \bar{M}_{\text{Cu}_2\text{O}}^2}{\bar{M}_\text{O}^2 \cdot \rho^2 \cdot A^2} = 2kt \quad (\text{vi})$$

Equation (6) shows that if the system obeys the parabolic law, a linear relation should be obtained when the square of the mass change is plotted against time. The slope of the linear fit allows the reaction rate to be determined.

RESULTS AND DISCUSSION

A total of eleven determinations at varying temperatures, in the range 500 °C to 924 °C, have been performed as described in the experimental section. Figure 1 shows typical values of Δm as a function of time for the temperature of 712 °C. A graph relating Δm^2 as a function of time at 712 °C is presented in Figure 2. The good linear fit observed in the latter indicates that the proposed model (equation 6) describes adequately the system behaviour. The slope of the straight line allows the rate constant for copper oxidation to be determined.

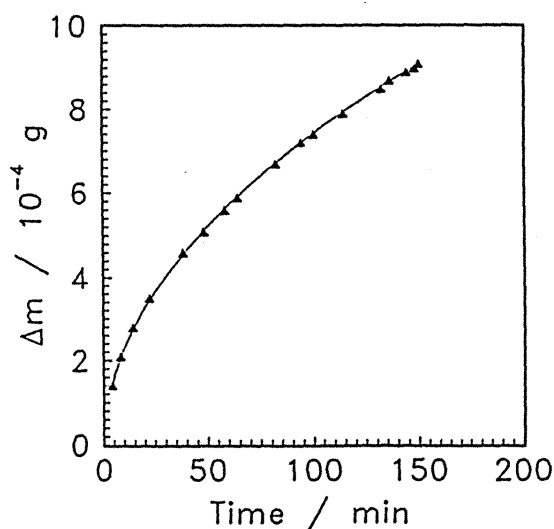


Figure 1 - Mass increase of copper as a function of time (reaction temperature = 712 °C)

Values of rate constants determined by this procedure were plotted in an Arrhenius graph (Figure 3), $\ln(k) \times 1/T$, in order to allow the Arrhenius parameters for the system to be calculated.

The variation of Δm as a function of time and Δm^2 as a function of time for all the experiments show curves of the same nature which indicates that the system obeys the same stoichiometry in the temperature range of the present study. The initial assumption that only one copper oxide (Cu_2O) is formed is then confirmed.

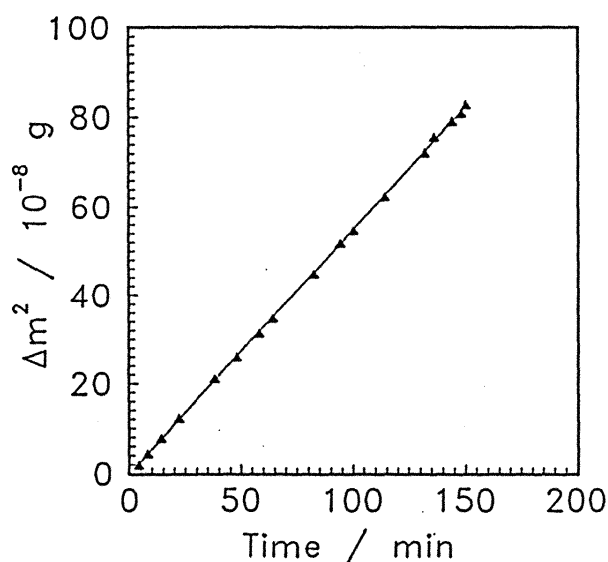


Figure 2 - Square of the mass increase of copper as a function of time. (reaction temperature = 712 °C)

The mass change of the samples as a function of time shows a marked increase at beginning of the reaction which corresponds to the formation of the oxide layer. After 15 minutes the system starts to shown a regular increase of Δm , which means that the oxide layer has been formed and the kinetic is diffusion controlled.

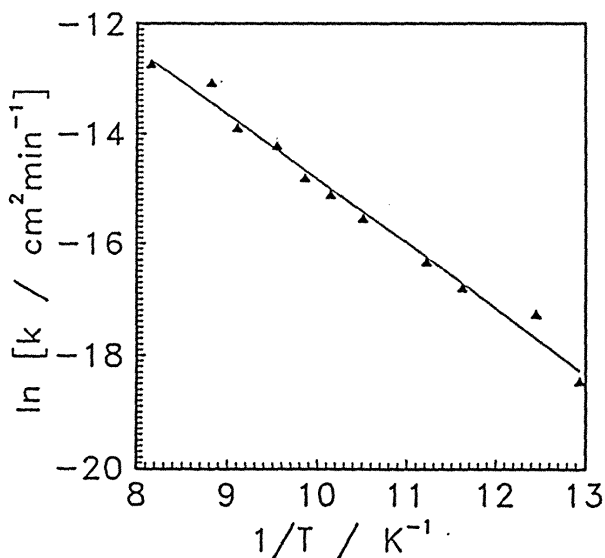
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Figure 3 - Arrhenius plot for the oxidation of copper by air

The rate constants are expressed as $\text{cm}^2\text{min}^{-1}$ showing that the reaction rate depends on the area available for reaction. The control of the sample area, which must remain constant during reaction, is necessary for the correct determination of the rate constants.

The graph presented in Figure 3 allows the determination of a frequency factor of $4.7 \times 10^{-2} \text{ cm}^2\text{min}^{-1}$ and an Arrhenius activation energy of $23.3 \pm 0.9 \text{ kcal.mol}^{-1}$ which gives for the rate constant an equation of the form:

$$k = 4.7 \times 10^{-2} \exp[-23.3 (\text{kcal.mol}^{-1})/RT] \text{ cm}^2\text{min}^{-1}$$

The fact that the system follows the parabolic law indicates kinetics which is controlled by the diffusion of oxygen through the oxide layer formed on the copper surface.

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