LEGENDA:

On the oxidation of copper to CuO in air

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Abstract

A custom made thermo-balance was built to conduct oxidation tests of pure copper in air from 700 °C to 1000 °C. The copper was fully oxidized to CuO. During the whole experiments data was continuously recorded to a PC. It was found that in a first oxidation stage, the copper oxidizes to form Cu_2O. the kinetics of this oxide formation is described by the parabolic rate law. After Cu_2O was formed, this oxide further oxidized to CuO. In this case, Cu_2O oxidation followed the cubic rate law. The change in rate law indicates a distinct reaction mechanism. It is well known that Cu_2O is formed after a diffusive mechanism; however in the case of CuO formation still it is not clear which mechanism is responsible for this oxidation process. In describing this reaction, it is believed that as Cu_2O oxidizes to form CuO some changes in the defect structure of the former have to occur so instead of exhibiting a purely diffusion controlled reaction a combination of defects and ionic species migrating through an oxide layer must be responsible for the change in controlling mechanism.

Keywords: Copper, Cu_2O, CuO, defect structure, high temperature oxidation, kinetic law.

Resumen

Se oxidó de cobre en aire entre 700 y 1000°C. Las pruebas se realizaron en un dispositivo termogravimétrico que se construyó para estas pruebas. El cobre se oxidó por completo a CuO. Durante cada experimento, se registraron datos de temperatura y ganancia de peso en una PC. Se encontró que en una primer etapa, el cobre se oxidó a Cu_2O. La cinética de oxidación sigue la Ley Parabólica lo que indica que este proceso se controla por difusión en la capa de óxido. En una segunda etapa, el Cu_2O se oxidó a CuO; en este caso la cinética de oxidación cambió de parabólica a cúbica, lo que indica que el mecanismo de oxidación difiere del difusivo. En este caso, la concentración y naturaleza de defectos estructurales en el óxido debe ser el mecanismo controlante de este proceso de oxidación.

Palabras clave: Cobre, Cu_2O, CuO, defectos estructurales, oxidación a altas temperaturas, ley cinética.

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Background

High temperature oxidation of copper has been vastly studied. It is well known that copper oxidizes following the parabolic rate law, and diffusion of copper ions through the oxide scale is the rate limiting step.

The kinetics of high temperature oxidation can be described by the general expression:

$$y^n = kt \tag{1}$$

Where y is the mass gained per unit area (mg/cm^2), t is the time (s), k is a rate constant ($mg/cm^2/s$) and n is an exponent that determines the nature of the rate limiting step. It has been found that oxidation is diffusion controlled when n =2, thus in such case equation (1) is termed as the parabolic rate law. The implication of this law is that the oxide layer formed on the metal surface becomes protective, decreasing the rate of subsequent oxidation.

However, the value of n may vary depending on the metal or alloy being oxidized, if n tends to 1, then, the tarnish product no longer is protective since it flakes off the material and the metal may be fully oxidized at a faster rate. On the other hand, if n gets a value larger than 2, the oxidation product may or may not become protective and the corrosion mechanism may differ from that of diffusion control.

On the other hand, little is known about the oxidation to CuO. It has been found that oxidation to CuO deviates from the parabolic law; furthermore there is no agreement on the oxidation mechanism responsible for the oxidation to CuO. In view of this shortage of information, it was decided to study the continuous oxidation of copper metal to CuO in air between 700 and 1000 °C.

Experimental

2.1 – Materials and devices

To conduct our tests, a thermogravimetric set up was specifically built. This set up consisted of a muffle furnace and an analytical balance with capacity of 300 g and resolution of 0.01 mg. A metallic structure was installed around the muffle so on top of it the balance was placed. From the bottom of the balance's plate a platinum wire (99.997% purity Alfa Aesar) with 0.5 mm in diameter was hung so the copper (99.999% Alfa Aesar) samples could be inserted into the muffle through an opening on the roof of the furnace. On the back end of the muffle, a stainless steel lance was placed next to each of the copper samples. Argon gas (grade 5.0) was blown at a rate of 50 mL/min to the sample so during heating to the testing temperature the copper sample was protected from oxidation. Additionally a k-type thermocouple was inserted into the muffle's hearth so it registered the temperature inside the furnace. Both the balance and the thermocouple were hooked to a data acquisition system (DAS) which in turn was connected to a PC. Weight gain and temperature readings were recorded at intervals of 30 seconds each. Figure 1 shows a picture of this thermogravimetric device.
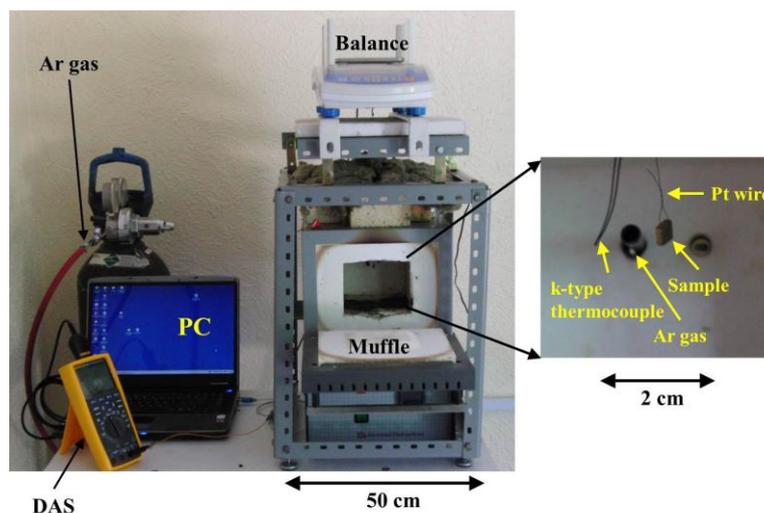
Figure 1. Experimental set up

2.2 – Procedure

The copper samples (4.5 mm × 4.5 mm × 1.0 mm) were cut and then rinsed in tap water and then ground with sand paper (Buehler) from grade 120 to grade 1000. After grinding, the samples were again rinsed in water and pickled in a nitric acid solution (0.2 M) to ensure proper surface cleaning. After pickling, the samples were rinsed again with water and dried with hot air. Upon cleansing completion, the samples were weighed and measured; after this, the samples were hung from the balance.

With the sample hanging inside the muffle, it was closed and then Argon gas was allowed into the furnace. At this point the muffle was turned on. During heating the balance remained idle. Once the test temperature was reached, the argon flow was switched off and the balance was started so the mass gain began to be collected. Each experiment was conducted for 24 hrs, and temperature and weight data was gathered and recorded every 30 s.

Results and discussion

Results from the experiments are shown in Figure 2. In this figure, it can be seen that the rate of oxidation of copper is slower at 700 °C. This rate increases considerably as the temperature increased to 1000 °C; surprisingly, there is no much difference in comparing the rate of oxidation at 800 and 900 °C, in some instances, it can be noticed in the figure that apparently copper oxidizes faster at 800 °C than at 900 °C.

It is also noticed in each of the plots in Figure 2 that after a rapid mass gain, the oxidation kinetics slows down describing a parabolic like behaviour. It is also noticed that after certain time, the plot show a slight change in slope. This change varies with temperature, for example at 1000 °C it happens after nearly 12.5 hrs of exposure, whereas at 700 °C the change occurs at approximately 21 hrs.

These changes in slope indicate that the oxidation process switched from oxidizing copper to form Cu_2O to oxidize Cu_2O to obtain CuO.
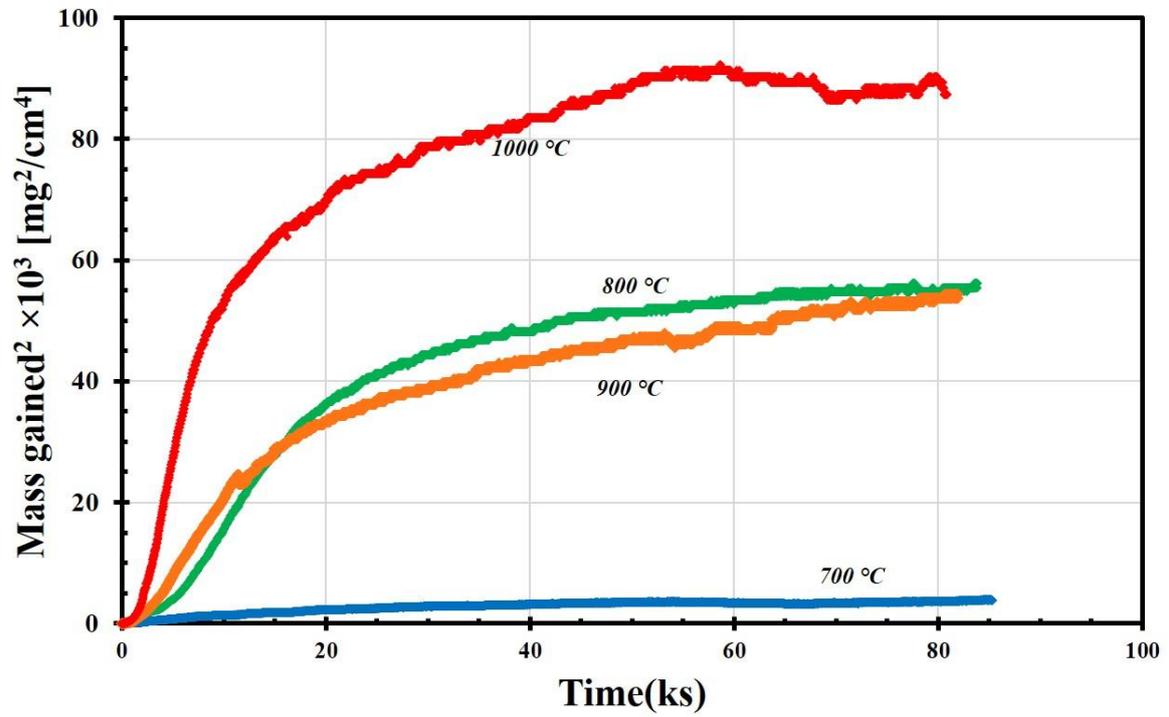
Figure 2. Mass gained per unit area as a function of time at different temperatures.
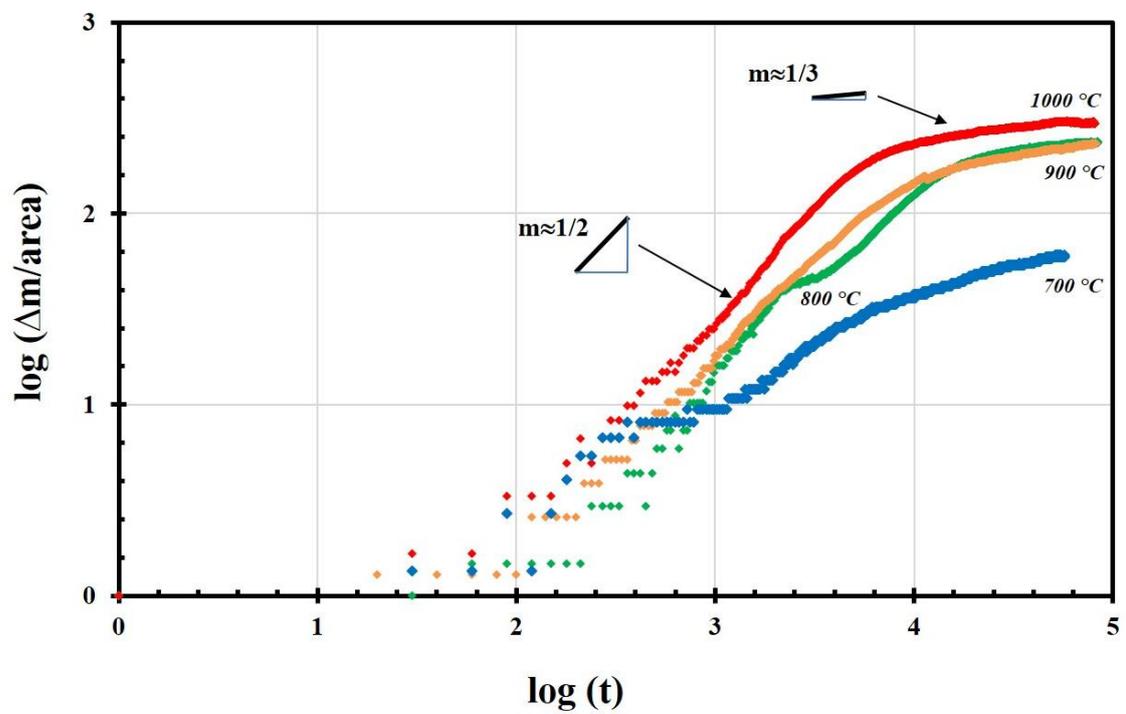
Figure 3. log (mass gained/area) vs log (t).

During the first oxidation process, it is well established that the rate controlling step is that of diffusion of copper ions through the oxide scale (1, 2). Data in figure 1 suggests that the initial oxidation process closely follows the parabolic rate law as expressed in equation (1).

However, with regard to the second oxidation process (Cu_2O to CuO), there is little information about the kinetics of oxidation of the cuprous oxide; furthermore, little has been discussed about the possible oxidation mechanism responsible for this process.

The data reported (3,4) agrees in that oxidation of Cu_2O is a slower process than the oxidation of Cu. It is also known that this oxidation process deviates from the parabolic rate law, thus diffusion itself is not solely responsible for the oxidation of the cuprous oxide. It is expected that as temperature increases, some structural defects such as vacancies or the presence of interstitials or even the motion of grain boundaries may contribute to the scale formation.

To figure out the possible oxidation mechanism, the data shown in Figure 2 is re-plotted by taking the logarithm of each axis. This is shown in Figure 3. In this figure is evident that there is a significant change of slope. The initial slope as shown in the figure is nearly 1/2, whereas towards the end of the curve, the slope in each data set decreases to about 1/3. This implies that after Cu_2O has been formed, the oxidation of this oxide to CuO follows the cubic rate law since the exponent n in equation (1) now has a value of 3.

By noting this change in slope, it is clear that the oxidation of Cu_2O is slower than that of copper metal. To determine the possible oxidation mechanism, it necessary to take a look at the nature of structural defects at the Cu_2O/CuO interface. Cu_2O is a p-type oxide which means it is metal deficient in its molecule; therefore to compensate for the extra negative charges, some copper vacancies should form at such interface, as seen in Figure 4. This also would create an electric field around these defects.

According to Cabrera and Mott's (5) classic theory, such electric field would help in the creation cationic valences as well as electronic holes. If defect concentration remains constant, then it is expected that oxidation reactions at Cu_2O/CuO and CuO/O_2 interfaces proceed quite rapidly. If that is the case, then transport through the CuO network should be the rate limiting step.

If defect concentration changes throughout the CuO network, concentration gradients may develop at the reaction interfaces. This is likely to happen due to the non-stoichiometry of CuO. As the cupric oxide is formed, a potential difference would be enabled and an associated electric field should establish. During oxidation, transport of Cu^{2+} ions is represented by:

$$j_{Cu^{2+}} = -u_0 \cdot n_0^t \cdot \frac{V}{\varepsilon}$$

(2)

u_0 represents the mobility of Cu^{2+} ions, n_0^t is the cationic concentration at the Cu_2O/CuO interface, V is the potential difference established by the electric field (V) and ε is the oxide film thickness.
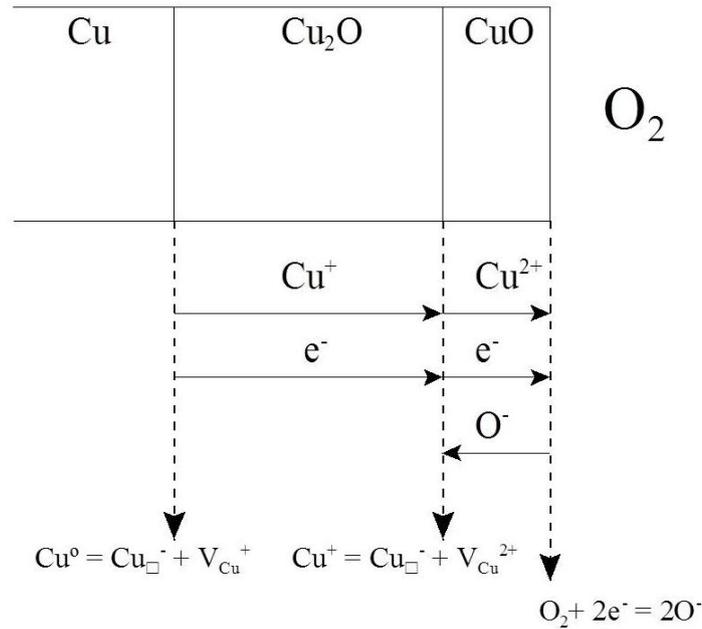
Figure 4. Defect formation during CuO formation.

By considering Fick's first law of diffusion, the molar flux of Cu^{2+} ions is:

$$j_{Cu^{2+}} = D\frac{dC}{dx} \tag{3}$$

Integration of equation (3) with the proper boundary conditions; yields a concentration profile which can be described as:

$$j_{Cu^{2+}} = \frac{k}{\varepsilon}\frac{d\varepsilon}{dt} \tag{4}$$

Combining equations (2) to (4):

$$\frac{d\varepsilon}{dt} = -u_0 \cdot n_0^t \cdot \frac{V}{\varepsilon} \tag{5}$$

In equation (5), the term n_0^t, it can be approximated by a simple relationship between the voltage drop and the oxide thickness:

$$n_0^t = A\frac{V}{\varepsilon} \tag{6}$$

Substitution of equation (6) into equation (5) yields:

$$\frac{d\varepsilon}{dt} = \frac{k_c}{\varepsilon^2} \qquad (7)$$

This equation represents the differential form of the cubic rate law, which upon integration and multiplication of the density of the oxide yields:

$$y^3 = k_c t \qquad (8)$$

y is the mass gained per unit area (mg/cm^2), kc is the cubic rate constant (mg^3/cm^6/s) and t is the time (s).

Plotting y^3 vs t, results in straight lines whose slopes represents the cubic rate constant. Values for this constant obtained with the data shown in Figure 2 are presented in Table 1 below.

**Table 1 - Cubic rate constant at
different temperatures**

T [°C]	kc [mg^3/cm^6/s]
700	4.29
800	12.73
900	27.02
1000	32.09

With the values in Table 1, it was found that the activation energy for the oxidation of Cu$_2$O is 8.57 kJ/mole. This value is in good agreement with data published elsewhere (4,6,7). Zhu et. al (4) calculated the activation energy for the formation of CuO as 3 kJ/mole; however they estimated this value by means of the logarithmic rate law. On the other hand, Hauffe and Kofstad (6) and latter Plascencia et. al (7) determined each that the cubic rate law has a better fit than the logarithmic rate law; and estimated the activation energy of CuO formation as 8 kJ/mole and 6 kJ/mole respectively.

Conclusions

The oxidation of Cu2O to CuO has been revisited and new data has been proposed. The oxidation of cuprous oxide in air between 700 and 1000 °C, is depicted by the cubic rate law and its activation energy was estimated at 8.57 kJ/mole. Structural defects within the oxide network are responsible for the oxidation mechanism.

Acknowledgements

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