

Studies of the interaction of copper with atomic and molecular oxygen

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Oxidation of copper by atomic oxygen was found to differ significantly from oxidation by ordinary molecular oxygen. Firstly, a strong enhancement of oxidation was observed, particularly at the initial stages of oxidation (up to 10^6 times compared to molecular oxygen). The reaction probability of atomic oxygen is between 0.01 and 0.5 for the temperature range 400 to 1100 K. Secondly, while only parabolic oxidation was observed in molecular oxygen under all experimental conditions studies, oxidation in atomic oxygen shows an initial linear stage (20 to 80 min in duration) for oxidation temperatures above 873 K, followed by parabolic stage. At about 1000 K, the parabolic rate constant depends only slightly on temperature and then decreases at above 1073 K. Thirdly, the oxide films formed in atomic oxygen were found to consist of Cu_2O only for all the temperature range studied, whereas in the case of molecular oxygen they contain 5 to 25% of CuO depending on oxidation temperature. The last two observations may be qualitatively explained by the “counter oxidation” reactions (thermodynamically allowed for the Cu/O system) which reduce oxides to the metal or a lower oxide.

1. Introduction

The exceptional electrical and thermal properties of copper make it an attractive material for space applications and thus encourage investigations of its interactions with atomic oxygen, which makes up about 90% of the residual atmosphere at low Earth orbit (LEO).

Copper specimens participated in a number of NASA materials stability experiments, in which materials were exposed to LEO environment on board spacecraft.^{1,2} The experiments demonstrated fast oxidation due to atomic oxygen. A laboratory study of the interaction of copper with thermal atomic oxygen using Rutherford back-scattering spectroscopy has also been reported.³ The experiments were performed with an atomic oxygen flux of 1.4×10^{17} atoms cm^{-2} s^{-1} and in the temperature range 140 to 200 °C. Parabolic time dependencies were observed at the conditions studied, i.e., the reaction rate was controlled by diffusion through the oxide layer, similarly to molecular oxidation. Strong enhancement of oxidation was found as compared with molecular oxygen, but activation energies were comparable. Oxide films formed consisted of cuprous oxide, Cu_2O .

In the present work, oxidation of copper by molecular and atomic oxygen was studied over wide temperature (473 to 1073 K) and pressure ranges.

2. Experimental

Experiments were carried out in a high-vacuum machine, described in more detail in refs. 4 and 5. Atomic oxygen was produced by 2450 MHz microwave discharge in oxygen–argon or oxygen–nitrogen gas mixtures.^{6,7} The degree of oxygen dissociation could be varied between 5 and 50%. The flux of atomic oxygen was measured using chemiluminescent titration by NO_2 .

The kinetics of copper interaction with oxygen were studied by monitoring electrical resistance of the specimens during oxidation experiments. Specimens were copper ribbons 50×1500 μm in cross-section and had two welded copper contacts to measure the potential drop across the central part of the specimen. The ribbons were heated resistively; temperature was maintained constant and measured using a thermocouple welded to the center of a specimen. The solubility of oxygen in copper is negligible at the temperatures studied in this work⁸ and the electrical conductivity of copper oxides is negligible compared with that of copper metal. Consequently, an increase in specimen electrical resistance in the course of oxidation reflects a decrease in the thickness of the metal core of a ribbon as oxide grows on the surface. Resistance data are presented in this work as R/R_0 , i.e., normalized by the resistance before the beginning of oxidation (at $t = 0$) to avoid possible errors due to some unavoidable uncertainty in the distance between the potential contacts. R/R_0 is thus the ratio of the initial specimen thickness (h_0) to current thickness of the metallic core during oxidation. Assuming that the oxide phase formed is Cu_2O , the electrical resistance can be converted into mass increase of a specimen (due to incorporation of oxygen) using the following equation:

$$m_{\text{O}_2} = \frac{M_{\text{O}_2} d_{\text{Cu}} h_0}{8M_{\text{Cu}}} \times \left(1 - \frac{1}{R/R_0}\right) \quad (1)$$

where m_{O_2} is the specific mass increase (g cm^{-2}); M_{O_2} and M_{Cu} are the molecular masses of oxygen and copper, respectively; d_{Cu} is the density of copper (g cm^{-3}); h_0 is the initial thickness of a specimen (before oxidation).

Knowing m_{O_2} as a function of time, one may calculate the rate at which oxygen is absorbed by a specimen surface, Z_{abs} , and, consequently, the reaction probability of oxygen with the copper surface, S . The latter is defined as the ratio of the absorption rate to total incident flux: $S = Z_{\text{abs}}/Z$.

To check the reliability of the described method, a series of experiments has been made in which specimens were heated in a furnace and the oxidation was monitored gravimetrically using microbalances, both for molecular and atomic oxygen.

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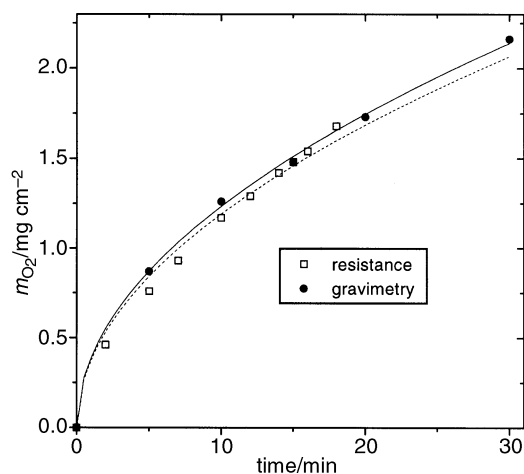


Fig. 1 Kinetic curves for oxidation of copper in air at 973 K, obtained by both gravimetry and by specimen resistance measurements.

Fig. 1 shows the kinetic curves obtained by the two methods. It is clear that the two methods give the same results for these conditions. The time dependence is parabolic; curves were fitted using eqn. (2).

$$m_{O_2} = \sqrt{k_p(t - t_0)} \quad (2)$$

Table 1 gives the values of the parabolic rate constant, k_p , for some oxidation conditions. Again, data obtained by resistance measurements and gravimetry agree fairly well.

3. Results and discussion

3.1. Oxidation in molecular oxygen

Oxidation of copper by molecular oxygen was investigated in the temperature range 723–1073 K and at oxygen pressures of 0.2 to 2.13×10^4 Pa. A parabolic time dependence was observed at all the studied conditions, indicating that diffusion is the rate-limiting step. Fig. 2 shows the linear dependencies of the square of mass increase on oxidation time for an oxygen pressure of 2.13×10^4 Pa.

X-Ray diffraction studies showed that the oxide layers formed at temperatures above 873 K were mostly Cu_2O with 7 to 10% of CuO . More CuO was found for lower temperatures—20–25%. To simplify comparison with the results of previous studies, electrical resistance data were converted into mass increase in this work. This was made assuming that the oxide phase is only Cu_2O . This assumption introduces a small systematic deviation in the results, but does not affect the kinetic regularities derived. Besides, the systematic error is almost within the reproducibility of experiments as follows from gravimetry results (Table 1 and Fig. 1).

Temperature dependencies of the parabolic rate constant are presented in Fig. 3 for two oxygen pressures. They show two temperature intervals with different effective activation energies. This change of activation energy occurs at about 873 K, in good agreement with data reported in the literature.⁸

Table 1 Parabolic rate constants for oxidation of copper in air ($P_{O_2} = 2.13 \times 10^4$ Pa) in the temperature range 773–973 K, determined by measuring electrical resistance (k_{res}) and gravimetrically (k_{grav})

T/K	$k_{res}/g^2 \text{ cm}^{-4} \text{ min}^{-1}$	$k_{grav}/g^2 \text{ cm}^{-4} \text{ min}^{-1}$
773	$6.14 \pm 1.03 \times 10^{-9}$	$8.88 \pm 0.31 \times 10^{-9}$
873	$2.58 \pm 0.24 \times 10^{-8}$	$2.88 \pm 0.04 \times 10^{-8}$
973	$1.53 \pm 0.03 \times 10^{-7}$	$1.46 \pm 0.03 \times 10^{-7}$

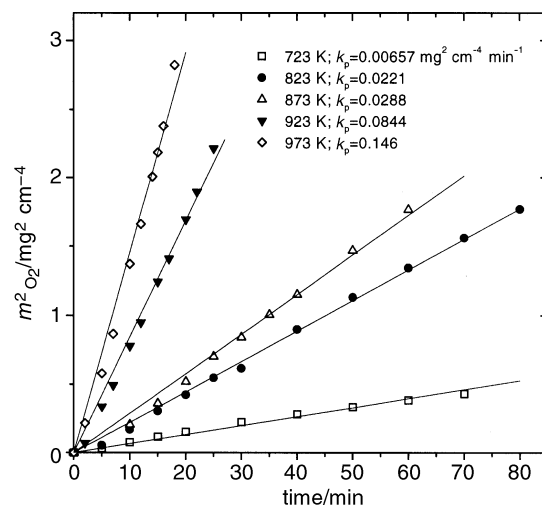


Fig. 2 Time dependence of square of the mass of absorbed oxygen for oxidation of copper in air at 1 atm. ($P_{O_2} = 2.13 \times 10^4$ Pa) in the temperature range 723–973 K.

Values obtained for oxidation in air at 0.1 atm, namely 112 ± 4 and 169 ± 11 kJ mol⁻¹ for the low and high temperature interval, respectively, agree well with previously reported data of 85 and 158 kJ mol⁻¹.⁸ Lower activation energies were observed for 1 atm, probably because very fast oxidation results in an oxide layer that has many grain boundaries, defects and possibly cracks, providing easier diffusion paths. One may expect cracking in the oxide films formed on copper as far as the molar volume of Cu_2O is about 1.7 times more than that of copper. Besides, CuO (monoclinic) forms in oxide layer too, which may result in substantial stresses on CuO/Cu_2O phase boundaries.

The decrease of activation energy at temperatures below 773–873 K (Fig. 3) was similarly attributed to the formation of porous and brittle oxide film at lower temperature.⁸ We also note that the quantitative composition of oxide layers changes at approximately the same temperature, namely, more CuO forms at lower temperatures, as mentioned above. This may increase both the porosity and the number of defects in the oxide layer, making diffusion easier.

A series of experiments were conducted at various pressures of molecular oxygen. It was found that at 973 K the pressure dependence of the parabolic rate constant is $k_p \propto (P_{O_2})^{1/5}$. Oxidation was too slow in molecular oxygen at 10^{-2} Pa (corresponding flux is about 2.7×10^{16} atoms cm⁻² s⁻¹,

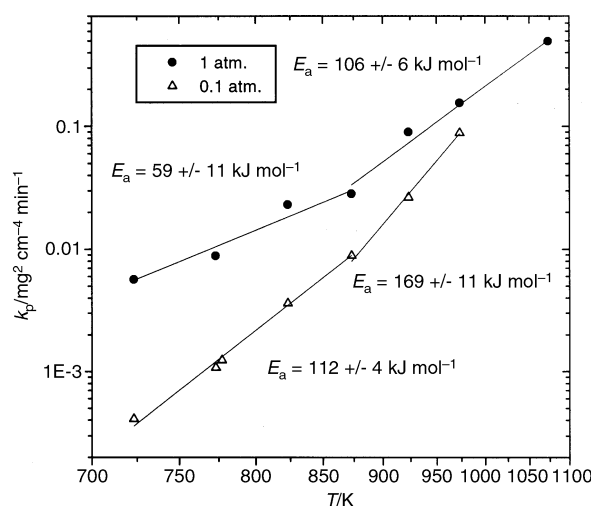


Fig. 3 Arrhenius plots of the parabolic rate constant for the oxidation of copper in air at 1 atm and at 0.1 atm.

similar to fluxes used in experiments with atomic oxygen) to be detected by resistance measurements in experiments as long as 3 h. X-Ray diffraction and metallography also showed very little or no oxide formation. This negligible oxidation in low-pressure molecular oxygen simplifies studies using dissociated oxygen (dissociation degree was in most cases 27%), because all the observed reaction rate may be attributed to atomic oxygen.

Sublimation of copper was observed at temperatures above 1173 K, leading to an increase of a specimen's electrical resistance even when no oxygen was introduced to the vacuum chamber. This set the upper temperature limit to our experiments.

3.2. Oxidation in atomic oxygen

Studies of copper interaction with atomic oxygen were carried out with an incident flux of 2×10^{16} atoms $\text{cm}^{-2} \text{s}^{-1}$ (about 5×10^{-3} Pa). The temperature range studied can be divided into two intervals for which different activation energies and some differences in kinetics were observed: 473 to 823 K and 873 to 1073 K. In contrast to molecular oxygen, oxide layers formed during oxidation in dissociated oxygen consisted of Cu_2O only.

In the temperature interval 473–773 K, kinetic curves followed a parabolic law from the very beginning of oxidation, similarly to molecular oxygen. The obtained time dependencies are presented in Fig. 4.

More interesting behavior occurs at 873–1073 K. Linear oxidation was observed for the first 20–80 min (Fig. 5), followed by a parabolic time dependence. This initial linear time dependence indicates rate-limitation by chemical reactions on phase boundaries rather than by diffusion. It probably means that, because of the high oxidation rate (see Fig. 6 below), oxide formed at the initial stage of the oxidation is porous and non-protecting. As the oxide thickness increases, diffusion becomes the rate-limiting step. The duration of the linear stage increases with temperature while the reaction rate slightly decreases. For this temperature range, parabolic rate constants were determined by fitting the kinetic curves starting from about 90 min, when the time dependence was actually parabolic.

Fig. 6 shows the difference between reaction probabilities, S , of atomic and molecular oxygen with copper for initial stages of oxidation. The probability is several orders of magnitude larger in the case of atomic oxygen, approaching 0.4 at higher temperatures.

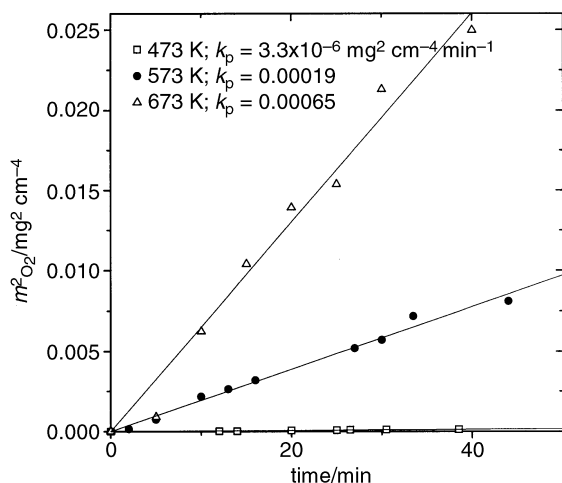


Fig. 4 Square of mass increase as a function of oxidation time for the reaction of copper with atomic oxygen at an incident flux of 2×10^{16} atoms $\text{cm}^{-2} \text{s}^{-1}$ and temperatures below 773 K.

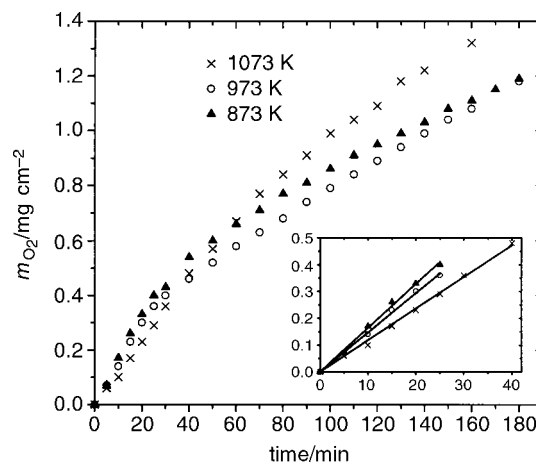


Fig. 5 Kinetic curves for oxidation of copper by atomic oxygen ($Z = 2 \times 10^{16}$ atoms $\text{cm}^{-2} \text{s}^{-1}$) in the temperature range 873–1073 K; inset shows the initial linear sections.

The values of the parabolic rate constant obtained for oxidation in atomic oxygen are presented in Fig. 7. It also shows good agreement with the data obtained in ref. 3 for a higher oxygen atom flux. The activation energy is 62 kJ mol^{-1} in the temperature range 473–823 K, but the temperature dependence becomes weaker at higher temperatures and the oxidation rate even decreases above 1073 K. A possible cause for

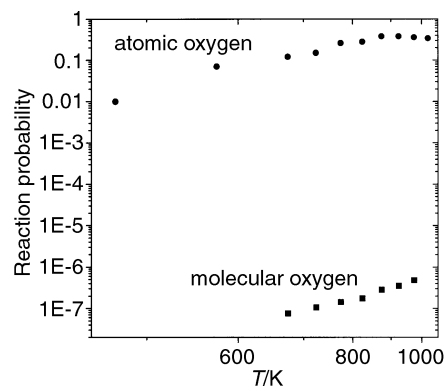


Fig. 6 Temperature dependence of the reaction probabilities of atomic and molecular oxygen at the initial stage of oxidation (20 min).

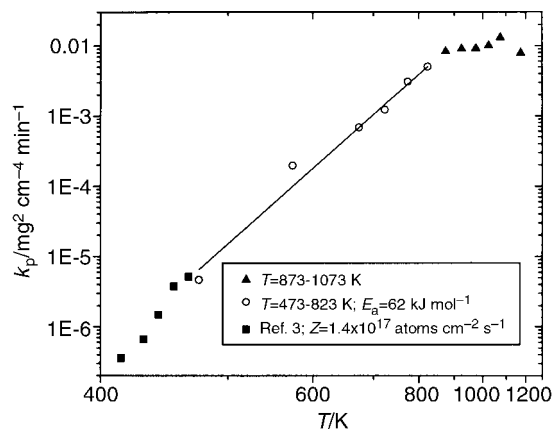


Fig. 7 Parabolic rate constant as a function of temperature for the oxidation of copper by atomic oxygen at a flux of 2×10^{16} atoms $\text{cm}^{-2} \text{s}^{-1}$.

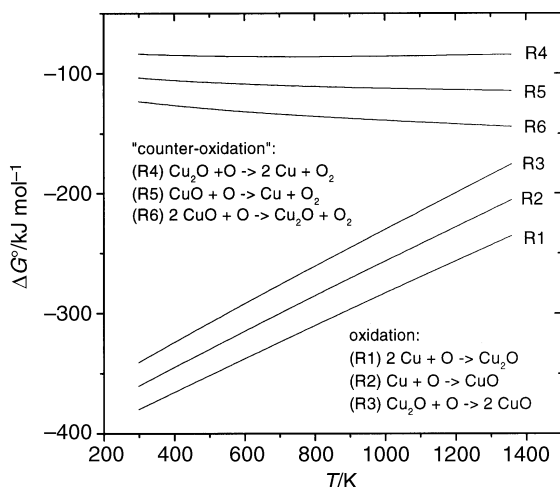
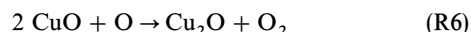
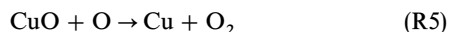
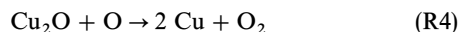


Fig. 8 Standard ΔG° for the oxidation [(R1)–(R3)] and “counter oxidation” [(R4)–(R6)] reactions as a function of temperature.

the weak temperature dependence is that besides the oxidation reactions, *i.e.*



“counter oxidation” reactions also take place:



These reactions are thermodynamically allowed under our experimental conditions and their ΔG° (negative) decreases further with temperature, unlike for oxidation reactions (Fig. 8). Besides, as far as reactions (R4)–(R6) involve breaking the Cu–O chemical bonds, one may expect that their activation energies are higher than for the oxidation reactions (R1)–(R3). So, the “counter oxidation” reactions (R4)–(R6) may be insignificant at low temperatures compared with (R1)–(R3), but become important and significantly reduce the overall oxidation rate at higher temperatures.

In addition to slowing down the oxidation at high temperatures, the “counter oxidation” reactions (R5) and (R6) are capable of explaining the fact that only Cu_2O forms in atomic oxygen in contrast to $\text{Cu}_2\text{O}/\text{CuO}$ mixed oxide in the case of molecular oxygen.

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