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Oxidation of Copper in Nitrogen Dioxide

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Synopsis. Thermal microgravimetry, mass spectrometry, and X-ray diffractometry were used to investigate the ability of NO_2 to oxidize copper. NO_2 oxidizes a copper plate with formation of oxide film consisting of Cu_2O (predominant) and CuO. The oxidation obeys a cubic law, and proceeds faster than in oxygen. An oxidation mechanism is presented on the basis of kinetic and structural data.

Although many studies have been made on high temperature oxidation of metals in oxygen, only a few have adopted NO_x as oxidizing agent.[1-3] We previously reported that copper could be oxidized in NO around 973 K but that the oxidation rate was much lower than that in oxygen.[4,5] The present investigation examined corrosive characteristics of nitrogen dioxide NO_2 for oxidation of copper by means of thermal microgravimetry, mass spectrometry, and X-ray diffractometry, mainly with a view elucidating the oxidation mechanism for this system.

Experimental

A poly-crystalline copper plate (99.99%Cu, 0.5 mm in thickness) was annealed *in vacuo* at 1073 K for 2 h, and then cut to the size 10×10 mm². After being abraded with an emery paper, the specimen was electropolished in an acid solution (H_2SO_4:H_3PO_4:H_2O=170:540:308 in volume), and rinsed in water and acetone. Highly pure NO_2, NO, and N_2O each in a glass cylinder (Takachiho Chemical Co., Ltd.) were used without further purification. The oxygen and argon were purified by bulb-to-bulb distillation with liquid nitrogen coolant. The oxidation process was followed by a Gulbransen-type microbalance contained in a conventional high-vacuum apparatus which could be evacuated to 2×10^{-5} Torr (1 Torr=133.3 N m^{-2}). Before use for the oxidation experiment, the test specimen was reduced in 20 Torr of hydrogen at 973 K for 1 h. Argon was used to determine the zero point of the microbalance. Oxide species were identified by an X-ray diffraction analysis (Cu $K\alpha$, 0.9 kW), in which the oxide film formed on each specimen was analyzed as it was. A mass spectrometer (JOEL, JMS–D-100) was used to determine the composition of the gas phase. Gas samplers for mass spectrometry were attached to the reaction tube of the microbalance equipment.

Results and Discussion

Figure 1 shows oxidation curves for copper plates placed at 673 K in 10 Torr of each of the corrosive gases NO_2, NO, N_2O, and O_2. Oxidation rate of copper in NO_2 was the highest and that in NO was the lowest. As indicated in Fig. 2, the oxidation of copper in NO_2 obeyed a cubic rate law $(\Delta W)^3=k_c\cdot t$, where ΔW signifies weight gain, k_c the cubic rate constant, and t oxidation time. According to

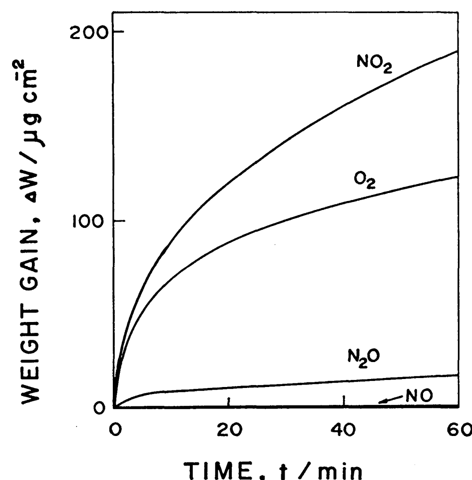


Fig. 1. Oxidation curves of copper plates in 10 Torr of NO_2, NO, N_2O, or O_2 at 673 K.

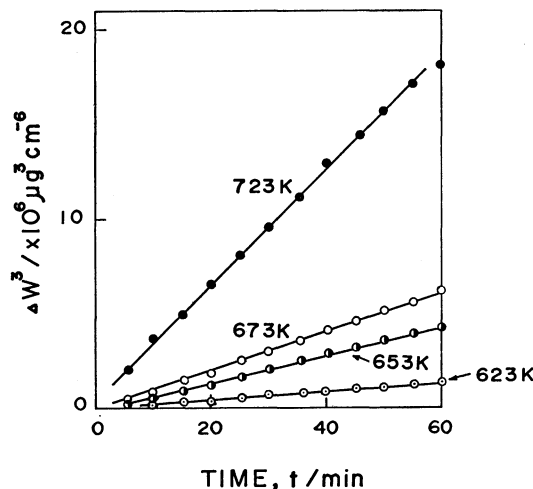


Fig. 2. Cubic plots of the oxidation curves of copper at various temperatures in 10 Torr of NO_2.

the mass spectrometry, the gas phase after a 1 h oxidation of copper at 673 K in 10 Torr of NO_2 consisted of about 97 per cent of NO_2 and a few per cent of NO and N_2O. Since the dissociation of nitrogen dioxide is not negrigible above 753 K, oxidation measurements were performed below 723 K. The oxide film formed in NO_2 was rather coarse and consisted of both Cu_2O (predominant) and CuO, while the one formed in O_2 was dense and consisted only of CuO. In Table 1, the oxidation law, rate constant, apparent activation energy, and kinds of the oxides formed were listed for comparison between oxidation behaviors of copper in NO_2 and O_2. According to

Table 1. Comparison between characteristics of NO_2 and O_2 for the oxidation of copper plates

Gas	Oxidation law	k_c[a)] $\mu g^3\ cm^{-6}\ min^{-1}$	E_a[b)] $kJ\ mol^{-1}$	Oxides
NO_2	Cubic	11×10^4	84	Cu_2O, CuO
O_2	Cubic	3.8×10^4	88	CuO

a) k_c is the rate constant at 673 K. b) E_a is apparent activation energy.

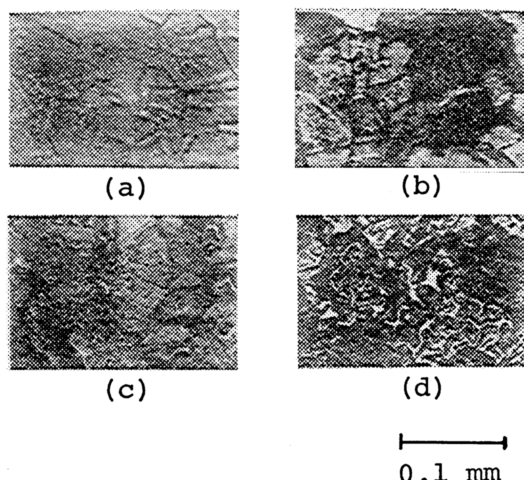


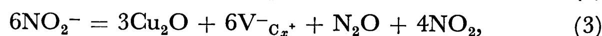
Fig. 3. Optical metallographs of the surfaces of Cu specimens oxidized in 10 Torr of O_2 or NO_2 at 673 K. (a): Non-oxidized (electropolished), (b): oxidized in 10 Torr of O_2 for 1 h, (c) and (d): oxidized in 10 Torr of NO_2 for 5 min and 1 h, respectively.

the Mott theory,[6–8] the rate determining process in the oxidation which obeys cubic rate law is the transfer of ions through the oxide layer under an electronic field formed between the adsorbed layer of gas and the oxide-metal interface. The reason for the higher rate of oxidation of copper in NO_2 than in O_2 is possibly in relation to the formation of a coarse oxide film as shown in Fig. 3. Such a coarse oxide film might result from formation of two different oxides Cu_2O and CuO. On the basis of the above results, the following oxidation mechanism is proposed in which only Cu_2O is considered as metal oxide species because it is predominant in the oxide layer.

Gas-oxide interface

$$NO_2 + e_x^- = NO_2^-, \tag{1}$$

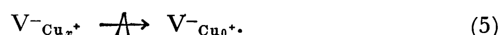
$$2NO_2^- = Cu_2O + 2V^-_{Cu_x^+} + NO + NO_2, \tag{2}$$



$$6NO_2^- = 3Cu_2O + 6V^-_{C_x^+} + N_2O + 4NO_2, \tag{3}$$

In oxide

$$e_0^- \longrightarrow e_x^-, \tag{4}$$



$$V^-_{Cu_x^+} \nrightarrow V^-_{Cu_0^+}. \tag{5}$$

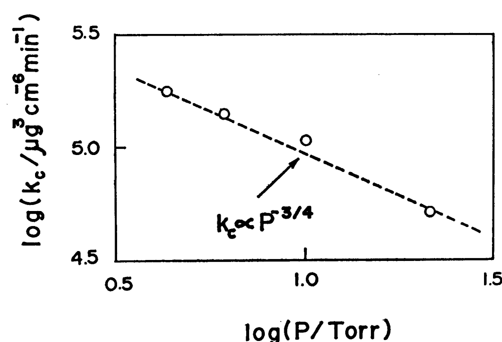


Fig. 4. The relation between the pressure of NO_2 and rate constant for the oxidation of copper at 673 K.

Oxide-metal interface

$$V^-_{Cu_0^+} + Cu = e_0^-, \tag{6}$$

where $V^-_{Cu_x^+}$, $V^-_{Cu_0^+}$, e_x^-, and e_0^- signify the cation vacancy at the gas-oxide interface, that at the oxide-metal interface, the electron at the gas-oxide interface, and the one at the oxide-metal interface, respectively. Considering the theory presented by Mott,[6–8] the cubic rate constant at a constant temperature can be given by $k_c \propto P^n_{NO_2}$, where $n=-1/2$ (in the case of Reaction 2) or $n=-3/2$ (in the case of Reaction 3).[9] The pressure dependence of oxidation constant obtained from this experiment is $-3/4$ as shown in Fig. 4. This value is within the region for the theoretical values given above, suggesting that both Reactions 2 and 3 are occurring in the oxidation process.

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