NOTES

BULLETIN OF THE CHEIMCAL SOCIETY OF JAPAN, VOL. 51 (4), 1225—1226 (1978)

The Oxidation Mechanism of Copper in Nitrogen Oxide

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(Received August 22, 1977)

Synopsis. The rate-determining step of the oxidation of copper in nitrogen oxide was proposed to be the dissociation of the adsorbed nitrogen oxide on the surface of the oxide film.

Although many studies have been made of the high-temperature oxidation of metals, few investigations of reactions in nitrogen oxide are recorded.[1,2] The present authors have reported in an earlier paper[3] that the oxidation of copper in nitrogen oxide (700—820 °C, 3.5—14 Torr) followed a linear rate law, suggesting that the rate-determining step is the reaction at the gas/oxide interface. Moreover, the following total reaction was proposed for the reaction;

$$2Cu + NO(g) = Cu_2O + 1/2N_2(g),$$

with an apparent activation energy of $\approx$113 kJ/mol. In this study, the oxidation of copper in nitrogen oxide was examined at higher pressures (20 and 30 Torr). The oxidation mechanism is discussed in the light of the present results and those from earlier studies.[3]

The experimental procedure was the same as that described previously.[3] The oxidation process was followed in a conventional high-vacuum system. The polycrystalline specimens (99.999% Cu) were 10×5 mm in area and had a thickness of 0.5 mm. The samples were annealed in a vacuum at 700 °C for 2 h, electropolished, and then heated in a hydrogen atmosphere at 700 °C for 1 h prior to the oxidation measurements. High-purity nitrogen oxide in a glass cylinder (Takachiho Co.) was used without further purification.

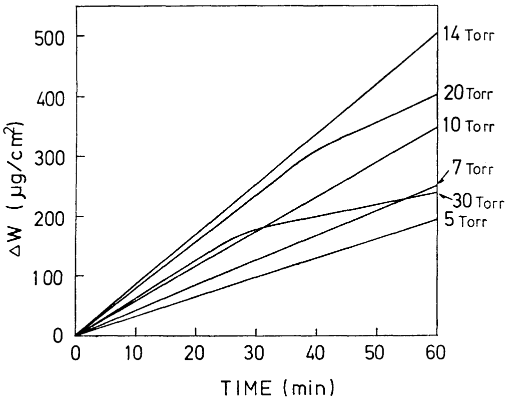

Fig. 1. Oxidation curves of copper in various pressures of nitrogen oxide at 700 °C.

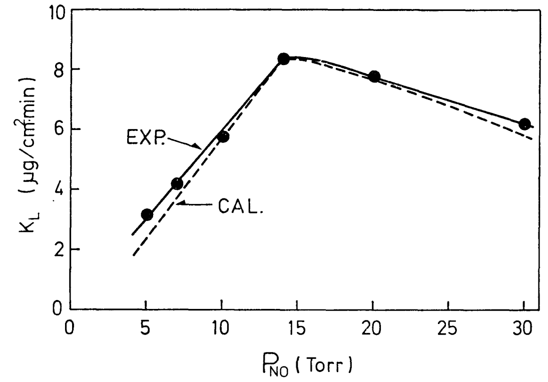

Fig. 2. The relation between the pressure of nitrogen oxide and the linear rate constant for the oxidation of copper at 700 °C. Dashed curve: theoretical result using Eq. 11 and normalized to maximum rate constant at p=14 Torr.

Figure 1 shows the oxidation curves for copper under various pressures of nitrogen oxide at 700 °C. The data obtained from this study at 20 and 30 Torr also obeyed the linear rate law in the early stage of the oxidation. The rate at these two pressures decreased later, however, showing evidence for two stages of oxide growth. The pressure dependence of the rate constant, K_L, in the early stage of the oxidation is shown in Fig. 2. At first the rate increased with the pressure, read a maximum around 14 Torr, and then decreased. This behaviour suggests that the rate-determining step of the oxidation is to be found in the dissociation of the absorbed nitrogen oxide on the surface of the oxide film. As has been discussed by Ritchie and Hunt[4] for the oxidation in oxygen, the surface reaction sequences for the NO–Cu system could be given as follows:

$$NO(g) + S = NO(a), \tag{1}$$

$$NO(a) + S = N(a) + O(a), \tag{2}$$

$$2N(a) = N_2(a) + S, \tag{3}$$

$$N_2(a) = N_2(g) + S, \tag{4}$$

$$O(a) = O^-(a) + \oplus, \tag{5}$$

$$O^-(a) = O^{2-}(a) + \oplus, \tag{6}$$

$$O^{2-}(a) = O^{2-}(\text{Lattice}) + S, \tag{7}$$

where (g) denotes the gaseous species; (a), the adsorbed species; S, the vacant adsorption site, and $\oplus$, the electron hole. If we consider Step 2 to be rate-determining, then

$$K_1 = \frac{[NO(a)]}{p[S]}, \tag{8}$$

$$r = k_2[S][NO(a)], \tag{9}$$

$$G = [S] + [NO(a)], \tag{10}$$

where K_1 denotes the equilibrium constant for Step 1; p, the pressure of nitrogen oxide; r, the oxidation rate; k_2, the rate constant for Step 2, and G, the total number of adsorption sites.

From Eqs. 8, 9, and 10 we obtain

$$r = \frac{k_2 K_1 G^2 p}{(1+K_1 p)^2}. \tag{11}$$

Equation 11 shows that r is proportional to the pressure of nitrogen oxide if $K_1 p \ll 1$, but that r is inversely proportional to the pressure if $K_1 p \gg 1$. The decrease in the reaction rate in the higher-pressure range can thus be attributed to a decrease in the number of vacant adsorption sites as a result of the adsorption of nitrogen oxide. The calculated values for the rate constant at 700 °C based on Eq. 11 are also plotted in Fig. 2, whereby the curve is normalized to the maximum rate constant at $p = 14$ Torr.

The authors are grateful to Dr. A. M. Bradshaw of the Fritz-Haber-Institut, Berlin, for helpful discussion and critical reading of the manuscript.

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