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HIGH TEMPERATURE OXIDATION OF COPPER IN NITROGEN OXIDE OBEYING A LINEAR LAW

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The oxidation of copper in nitrogen oxide(700 - 820°C, 3.5 - 14 Torr) has been found not only to obey a linear oxidation law, but also to be a first order reaction. The apparent activation energy was 113 KJ/mol. According to the x-ray diffractometry, x-ray photoelectron spectroscopy and ion microanalysis, only Cu_2O was found in the oxide layers. The rate determining step was a reaction between nitrogen oxide and the surface of Cu_2O and it was shown by an equation: $2NO \longrightarrow N_2 + 2 \cdot O^{2-} + 4 \cdot \oplus$.

The oxidation of copper in nitrogen oxide has been found not only to obey a linear oxidation law, but also to be a first order reaction. Although many studies have been made of the high temperature oxidation of metals in oxygen or in the other corrosive gases, few investigators have considered reactions in nitrogen oxide.[1,2] It has been reported that the oxidation rate of nickel in nitrogen oxide was very rapid and it obeyed a linear rate law and the oxide layer formed on nickel(NiO) was very coarse.[2,3] On the other hand, few examples have been found of oxide formation reactions which obeyed the linear oxidation law[4] in the temperature region below 800°C.

Figur 1 shows the oxidation curves of copper(poly-crystal and single crystal) in 10 Torr of nitrogen oxide or oxygen at various temperatures that were measured with a Gulbransen-type microbalance set in a conventional high vacuum system. The poly-crystal specimens(99.999% Cu) were 10 x 5 mm^2 in area and had a thickness of 0.5 mm, while the single crystal specimen(99.999% Cu, Cu(100)) was 6 x 6 mm^2 in area and had a thickness of 0.6 mm. They were annealed in vacuum at 700°C for 2 hr, electropolished, and heated in hydrogen atomosphere at 700°C for 1 hr prior to the oxidation measurements. Nitrogen oxide of a high purity in a glass cylinder from the Takachiho Co. was used without further purification. Oxygen and argon were purified through bulb-to-bulb distillation with liguid nitrogen coolant. As is obvious from Fig. 1, the oxidation of copper, both the poly-crystal and (100) plane of Cu single crystal in nitrogen, oxide obeyed a linear law under these conditions, while that in oxygen obeyed a palabolic law.[5] The depth of the oxide layer on (100) plane of Cu single crystal was calculated about 3.0 μm on the oxidation in nitrogen oxide at 700°C for 60 min, with assumption that oxidation proceeded uniformly into the bulk of the crystal. The apparent activation energy of the oxidation of copper in nitrogen

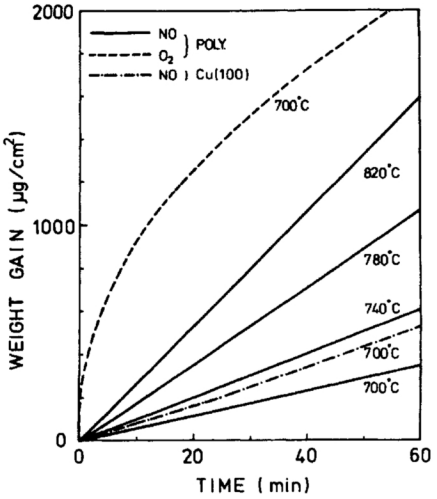

Fig. 1. Oxidation curves of copper in 10 Torr of nitrogen oxide or oxygen at various temperatures.

oxide was 113 KJ/mol.

The oxide layers formed in nitrogen oxide on these specimens were first examined by x-ray diffractometry. The diffraction patterns were only of Cu_2O besides to metallic copper. As shown in Fig. 2, the x-ray photoelectron spectra of $Cu2p_{1/2}$ either from the oxidized surfaces or from the argon ion etched surfaces of them gave no satellite peak around 965 eV(B.E.),[7] so that no CuO seems to be contained on the thin surface of the oxide. Moreover, IMA(ion microanalysis) spectra[8] of them gave no evidence for the existence of nitrogen in the oxide layers. These findings signify that only Cu_2O was formed on copper in the oxidation. This result is worth remarkable, because it has been reported[5] that CuO as well as Cu_2O has been found in the scale which was formed in an oxygen atmosphere at high temperatures. According to the optical metallogrphy, neither crack nor swelling was found on the oxide layers in this study. These findings correspond to the results that the oxidation of the copper single crystal and polycrystal obeyed a linear law and they gave almost equal values of the oxidation constant.

Figure 3 shows the relation between the pressure of nitrogen oxide and the linear rate constants. The oxidation of copper in nitrogen oxide was a first order reaction, and the reaction rate was not influenced by a diffusion process of copper ion in the oxide layer. The experimental results show that the behavior of nitrogen oxide was very different from that of oxygen in oxidation of copper, though the equilibrium constant of reaction(1) is about 1.0×10^8 at 740°C.

$$2NO \rightleftharpoons N_2 + O_2 \qquad (1).$$

The rate determining step should be a reaction between nitrogen oxide and the surface of Cu_2O with defect structure and its reaction would be shown by equation (2)

$$2NO \longrightarrow N_2 + 2\cdot O^{2-} + 4\cdot\oplus \qquad (2).$$

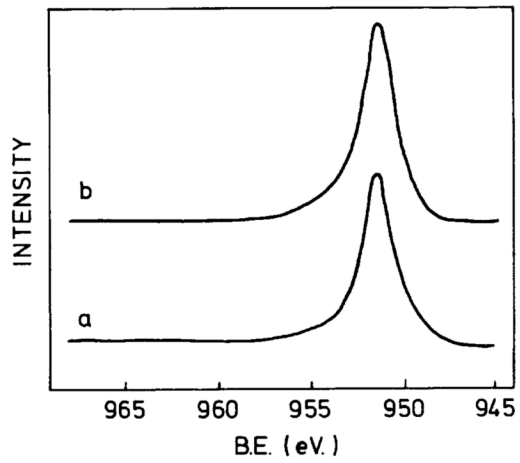

Fig. 2. Examples of x-ray photoelectron spectra of $Cu2p_{1/2}$ from the oxide layers formed on copper in 10 Torr of nitrogen oxide at 700°C for 1 h. (a: surface, b: argon ion etched surface--Ar^+ : 2kV, 65 $\mu A/cm^2$, 5 min)

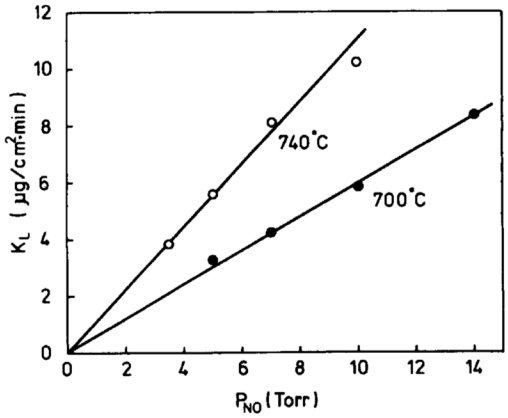

Fig. 3. The relation between the pressure of nitrogen oxide and the linear oxidation constants of copper.

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References

1). M.Farber, A.J.Darnell, and D.M.Ehrenberg, J.Electrochem.Soc., 102, 446(1955).
2). Y.Takasu, Y.Matsuda, S.Maru, and N.Hayashi, Nature, 255, 544(1975).
3). Y.Takasu, S.Maru, and Y.Matsuda, Bull.Chem.Soc.Japan, 49, 3349(1976).
4). K.Hauffe and H.Pfeiffer, Z.Metallk., 44, 27(1953).
5). K.Fueke, Kogyo Kagaku Zasshi, 63, 717(1960).
6). ESCA/AES Electron Spectrometer PHI Model 584 (MgK_{α}) was used.
7) The satellite peak is the shake-up peak of $Cu2p_{1/2}$ which is the characteristics of CuO.
8). Hitachi IMA-S(Ion-Micro-Analyzer) was used. Ar^{+} : 7-13 KV, Surface current: $0.6\mu A/0.8mm^{2}$.

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