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EFFECTS OF AMINES ON COPPER ETCHING WITH H_2SO_4-H_2O_2 SYSTEMS

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Abstract

The corrosion of copper in H_2SO_4-H_2O_2 etching solutions with amines was investigated at various flow rates (v). Amine additives give a retardation of H_2O_2 decompositions, increases in both corrosion rates and etch factor, and a protection of etched copper surfaces. However *n*-alkylamine additives acted as corrosion inhibitors at $v < 10$cm/s, those acted as corrosion accelerators at v of 10-220cm/s. The maximum corrosion rate was obtained with about 0.1 molal concentration of additives. Steric effects of substituted groups suppressed the acceleration of copper corrosion. The increases in both corrosion rates and flow rates gave the increase in etch factor. Corrosion rates with n-alkylamine increased in the order of ethylamine < *n*-propylamine < *n*-butylamine, those with butylamine isomers *tert*- < *sec*- < *iso*- < *n*-butylamine, and those with amine additives of different number of substituted groups *tri*- < *di*- < *mono*-*n*-propylamine, respectively.

Key words : *etching, copper, corrosion, hydrogen peroxide, amine*

1. INTRODUCTION

The copper etching solutions with sulfuric acid and hydrogen peroxide[1)-3)] have several advantages : 1) low cost, 2) no problem for the fume emission, 3) easy recovering of copper and sulfuric acid from spend etching solutions, and 4) easy control of etching solutions due to high capacity for copper and constant corrosion rate, etc. However, this etching system has the demerits : 1) hydrogen peroxide is unstable under a presence of metal ions in etching solutions under a high temperature, and 2) low etch factor, etc. The authors have found that amine additives are very useful for H_2SO_4-H_2O_2 copper etching solutions[4)]. The actions of amine additives changed from the inhibition at low flow rates to the acceleration at high flow rates, and both the corrosion rates and the etch factor depended on flow rates of etching solutions.

Amine additives acted as stabilizers against the decomposition of H_2O_2.

2. EXPERIMENTAL

Two kinds of specimens were cut of copper sheets (purity : 99.96%, thickness : 0.5㎜). The specimens with an exposed active area of 60㎜ ×20㎜ and with those of 6㎜×6㎜ were used for static and flowing corrosion measurements, respectively. After degreased, cleaned by acid and water, and dried, those were stored in a desicator or in benzene until required. A specimen was weighed just before corrosion measurements, was covered with quickly dried paint or adhesive tape except exposed areas, and then was mounted in a corrosion equipment. After corrosion for 3 minutes, a specimen was quickly washed with water, was free from paint, was dried in a disicator, and then was weighed. The bath temperature of a static bath of 1 L beaker was kept at (50±1)℃ by heat-exchanging with a circulator. The equipment for flowing corrosion experiments is shown in Fig. 1. The volume of an etching solution in the tank A was 9 L and the bath temperature was kept at (50 ±0.5)℃. The flow rates of etching solutions were calculated from the equation(1),

$$v = (v_0^2 + 2gh)^{1/2} \quad (1)$$

where v is the velocity at copper surface S, v_0 the velocity at the nozzle N, g the gravitational acceleration, and h the distance between N and S, respectively. The value of h was 5.5cm at high flow rate experiments, while h was 2㎜ at low flow rate experiments.

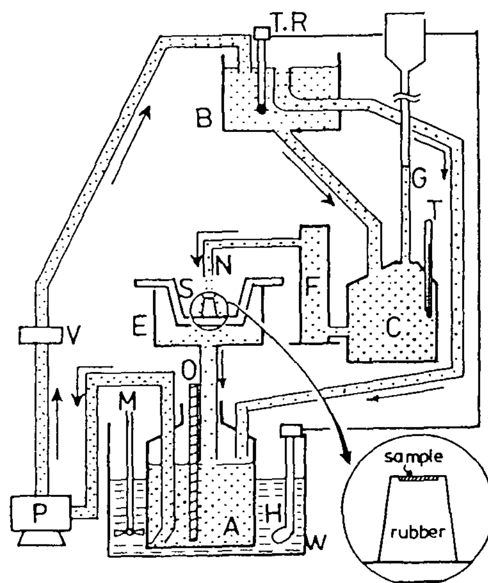

Fig. 1 Etching equipment
A : storage tank, B : tank for constant presure, C : tank for removing bubbles and measuring flow rates, E : etching tank, F : flow meter, G : glass tube for measuring flow rates, H : hrater, M : mixer, N : etching nozzle, O : obstructive board, P : chemical pump, S : sample holder, T : thermometer, T.R : thermoregulator, V : flow control valve, and W : water bath

The specimen for measurement of etch factor had an exposed area of 10㎜×20㎜, in the center of which Pb-Sn alloy of 2㎜×20㎜ was deposited. After specimens were etched, those were molded in a epoxy resin and then were cut. The sections of etched copper plate were polished and were observed by a metallograph. The etch factor is calculated by (a depth of corrosion at surface)/(a depth of corrosion at side). The concentrations of H_2O_2 in an etching solution were maintained by the addition of H_2O_2 during experiments. The errors of measurements were lower than 5%.

3. RESULTS AND DISCUSSION

3. 1 Fundamental etching solutions

As shown in Fig. 2a, the corrosion rates were linear with respect to concentrations of H_2O_2, and at high flow region (120-220cm/s), the slopes was almost constant, $(10\pm0.2)\times10^{-6}$ (m/min)/(mol/L). When the concentration of H_2O_2 was zero, the corrosion rate was $(0.3\pm0.2\text{-}1)\times10^{-6}$m/min[5),6)]. As shown in Fig. 2b, the corrosion rates depended on concentrations of sulfuric acid and copper sulfate though those approached to constant values at high concentration region. At the flow rate of 180cm/s, the activation energy calculated from corrosion rates measured at (20-60)℃ was 55kJ/mol. The value seems to be much larger than that in

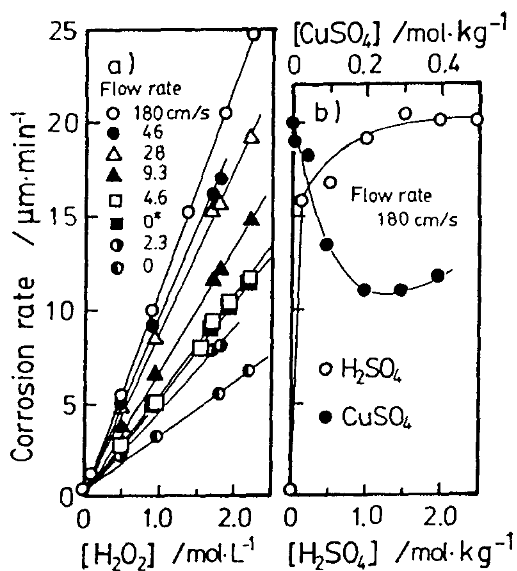

Fig. 2 Relations between corrosion tates and concentrations of a)H_2O_2 in a 2mol/kg H_2SO_4 solution b) H_2SO_4 in a 2mol/ kg H_2O_2 solution, and $CuSO_4$ in the basic etching solution. Bath temperature : 50℃. Corrosion time : 3min. 0* : values obtained from the static experiments.

the case of a diffusion-controlled reaction. The composition of the fundamental copper etching solution was determined as 2 mol H_2SO_4+2mol H_2O_2+1kgH_2O and the corrosion rate was 20×10^{-6} m/min at 50℃ at 160cm/s. The decomposition of H_2O_2 in an etching solution was increased with concentrations of Cu^{2+} ion, but was markedly supressed by the addition of *n*-butylamine as shown in Fig. 3.

3. 2 Addition of n-alkylamine and corrosion rates

The effects of *n*-alkylamines on corrosion rates were dependent on the chain length of aliphatic groups of amines, the concentration of amines, and the flow rates v of an etching solution. In general under the conditions of laminar flow with large Reynolds number toward a fixed plate, the thickness of a boundary layer is homogeneous to a fixed plate and is proportional to $v^{-1/2}$. Hence, the corrosion rate is proportional to $v^{1/2}$ in the diffusion-controlled reaction. Fig. 4 and Fig. 5 show the effects of methyla-

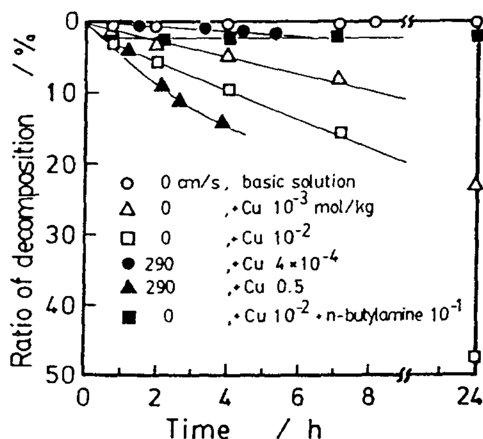

Fig. 3 Effects of $CuSO_4$ and n-butylamine on decompositions of H_2O_2 in the basic etching solution at 50℃

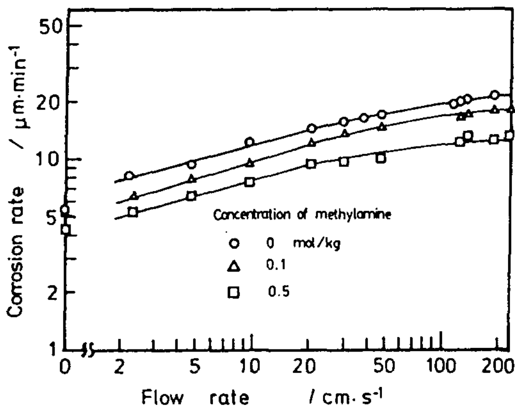

Fig. 4 Effects of methylamine on corrosion rates

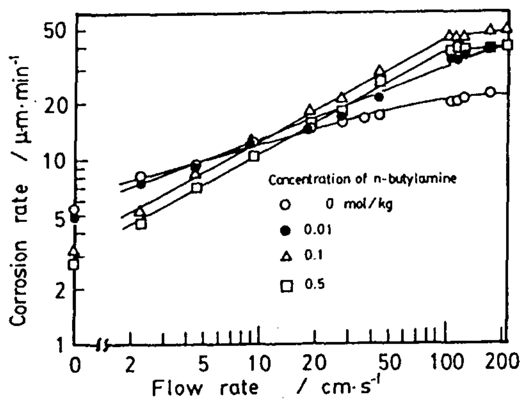

Fig. 5 Effects of n-butylamine on corrosion rates

mine and n-butylamine on corrosion rates, respectively. The corrosion rates increased with the increase of v. At flow rates higher than 120cm/s, the corrosion rates were independent of v and those may be chemically controlled. The slopes of log (corrosion rate) vs. log (v) plots increased with the increase in concentrations of n-butylamine. At concentrations 5×10^{-2} molal, the value of slopes was 1/2 and the corrosion reaction was diffusion-controlled. The increase in concentrations of methylamine lowered the corrosion rates and methylamine acted as an inhibitor. However, n-butylamine acted as an inhibitor at flow rates lower than 10cm/s and it acted as an accelerator at flow rates higher than 10cm/s. The effects of n-propylamine on corrosion were similar to those of n-butylamine, and those of ethylamine showed intermediate corrosion behavior between methylamine and n-propylamine as shown in Fig. 6. At high flow rates, the corrosion rates increased with the increase of concentrations and reached to the maximum in the vicinity of 0.1 molal.

3. 3 Polarization measurements

The anode and cathode polarization curves were shown in Fig. 7. In a sulfuric acid solution, the cathode polarization is large and the corrosion of copper is controlled by the reduction of H_2O_2 dissolved in a solution. In the fundamental etching solution, the cathode polarization decreased largely due to the reduction of O_2 and the corrosion potential shifted by 70mV toward positive potential. When 0.1molal n-butylamine

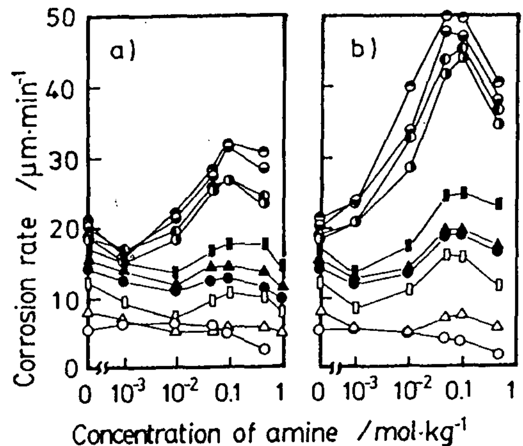

Fig. 6 Effects of a)ethylamine and b)n-propylamine on corrosion rates Flow rates are ○ : 0, △ : 2.3, □ : 9.3, ● : 19, ▲ : 28, ■ : 46, ◑ : 120, ◐ : 130, ◒ : 180, and ◓ : 220cm/s

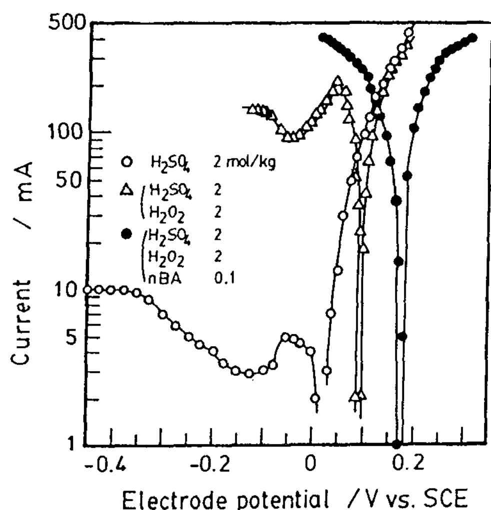

Fig. 7 Polarization curves of copper electrode in the static corrosion solutions at 50℃. The counter electrode is Pt wire and nBA is n-butylamine.

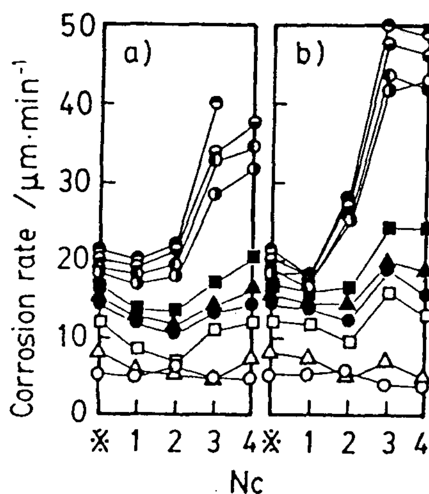

Fig. 8 Relation between corrosion rates and Nc, number of carbon of alkyl substituents of a-mines. Concentrations of amines are a)10^{-2} and b)0.05 mol/kg. Flow rates are given in Fig. 6.
※ No addtivite.

was added in the fundamental etching solution, the anode polarization increased and the cathode polarization decreased, and the corrosion potential shifted further positively by 75mV.

3. 4 Effects of the chain length of aliphatic groups in *n*-alkylamine

Fig. 8 shows the relations between corrosion rates and Nc(the number of carbon of alkyl groups of amines). The longer chain of alkyl groups of *n*-alkylamines gave rise to the more effective inhibition of copper corrosions at low flow conditions and the more effective acceleration at high flow conditions. *N*-butylamine (K_a $=14.1\times10^{-11}$ at 50℃[7]) presents as a cation in a strong acid solution. The potential of zero charge of copper is about -0.2 V *vs*. SCE[8]. It is estimated that the copper surface is charged positively at the corrosion potential (about 0.17 V) and *n*-butylamine cation adsorbs not electrostatically but chemically on the copper surface. Perhaps, at anode surfaces, *n*-butylamine cations cover copper surfaces by the chemical adsorption, increase an anode polarization and give rise to the inhibition of corrosion at low flow conditions. On the other hand, at cathode surfaces, both the decrease in a cathode polarization (Fig. 7) and the increase in the slope of corrosion rates to flow rates with the increase in n-butylamine concentrations (Fig. 5) are estimated to be produced by the acceleration of H_2O_2 reduction due to *n*-butylamine adsorbed strongly at cathode surfaces. The power of a chemical adsorption increases with the increase in the electron density on nitrogen atom of amine. As the adsorption quantity of amine which is caused by both the long chain of aliphatic groups and the high concentration of a-mines became the more, both the inhibitions at

low flow rates and the accelerations at high flow rates were considered to become the more strongly. The further adsorption of amines produces both the acceleration of cathodic reactions and the depression of diffusion, so that the corrosion process approaches to the diffusion-controlled reaction. The appearance of the maximum in the vicinity at 0.1molal amine concentration can be considered to be not due to the increase of viscosity but due to the depression of diffusion. The increase in the thickness of diffusion layer[9], which is proportional to (kinematic viscosity)$^{1/6}$, is calculated as 1.01 times and is negligible. On the other hand, the saturation of n-alkylamine adsorption is reported to occur at about 0.1 molal[10),11)]. It is estimated that the number of active sites which accelerates cathodic reactions is constant above concentrations of the saturated adsorption. The further addition of amines causes only the depression of diffusion without further acceleration of cathodic reaction, so that the corrosion rate are considered to decrease at amine concentrations over 0.1 molal.

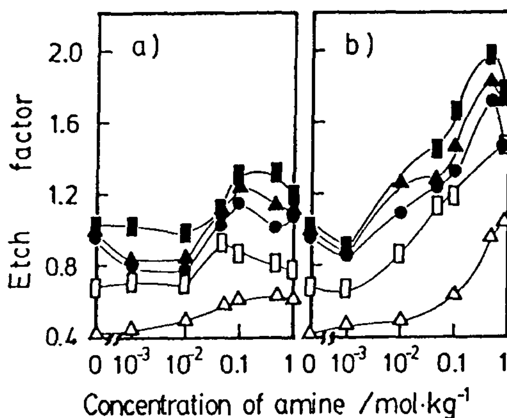

Fig. 9 Effects of a) ethylamine and b)n-butylamine on etch factor. Flow rates are given in Fig. 6.

3. 5 Effects of amines on etch factor

The effects of ethylamine and *n*-butylamine on etch factor were shown in Fig. 9a and Fig. 9b, respectively. The effects of amines on etch factor shown resemble those on corrosion rates shown in Fig. 6. The etch factor increased with the increase in both concentrations of amines and flow rates. At low flow rate region, the etch factor was lower than 1. In general, the side etching is accelerated by the formation of a local cell and it is pronounced at low flow rate region. According to the increase of flow rate, the etch factor became large and was about 2 at 46cm/s with 0.5 molal of n-butylamine. The flow rate at the side of copper being etched under Pb-Sn resist is lower than that at the copper surface being etched. The higher the flow rates, the differences of flow rates between on the surface and on the side expand the more largely, leading to the expansion of differences of corrosion rates. Consequently, the etch factor increases.

3. 6 Steric effects of substituted groups

The relationships between corrosion rates and steric effects of amine additives were examined. Fig. 10 shows the effects of *n*-butylamine isomers on corrosion rates and etch factor at high flow rate of 160cm/s. The addition of butylamine isomers accelerated the corrosion rates at all concentrations and corrosion rates had the maximum in the vicinity of 0.1 molal concentrations butylamine isomers. The corrosion rates increased in the order of *tert*-buthylamine < *sec*-butylamine < *iso*-butylamine < *n*-butylamine. The effects of the number of substituted groups on corrosion rates are shown in Fig. 11.

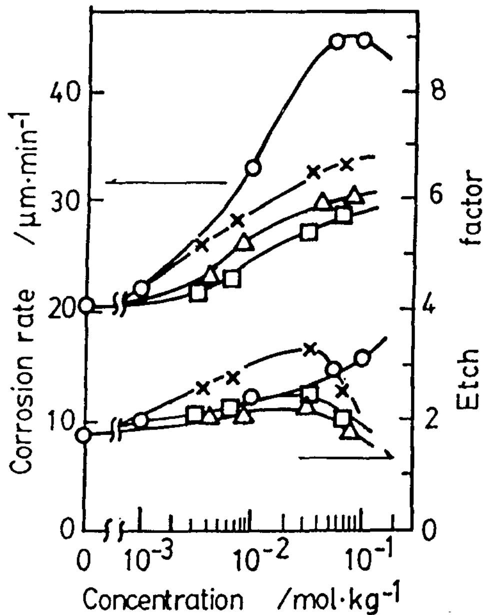

Fig. 10 Effects of butylamine isomers on corrosion rates and the etch factor.
50℃, v=160cm/s
○ : n-butylamine, △ : iso-butylamine,
□ : sec-butylamine, × : tern-butylamine,

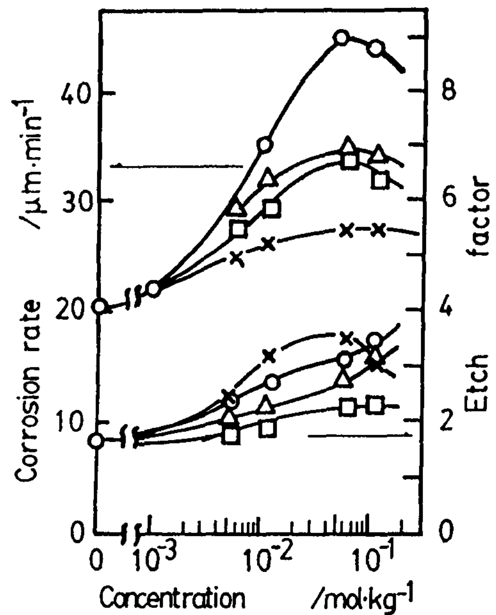

Fig. 11 Effects of the number of substituent group on corrosion rates and the etch factor
50℃, v=160cm/s
○ : n-butylamine, △ : di-n-propy1*amine,
□ : tri-n-propy1e × : di-n-butylamine

The corrosion rates increased with the addition of amine additives in all concentrations and increased in the order of *tri-* < *di-* < mono-*n*-propylamine. These suggest that the lowering of adsorption quantity by the steric hindrance is superior to the increase of the adsorption power by branching of the chain or the increase of substituted groups. The decrease in active sites of H_2O_2 reduction suppresses the lowering of the cathode polarization so that the increase in the corrosion rates will be lowered. The etch factor at high flow rate of 160cm/s was larger than about 2. The addition of amines caused the increase of etch factor. In the case of *n*-butylamine isomers, the etch factor increased in the order of sec-butylamine < *iso*-butylamine < *n*-butylamine < *tert*-butylamine. Shown in Fig. 11, the increase in the number of substituted groups lowered the etch factor. It appear that the decrease of corrosion rates with the decreases of both adsorption quantity and active sites by the steric hindrance lower the etch factor.

4. CONCLUSIONS

By the investigations on a copper etcing solution with sulfuric acid, hydrogen peroxide and amine additives under static and flow conditions, the following conclusions were obtained.

1) The fundamental composition of the copper etching solution was 2 mol H_2SO_4+2mol H_2O_2+1kg H_2O, and the most useful additive was (0.05-0.1) molal of n-butylamine or n-propyl-

amine. Amines inhibited the decomposition of H_2O_2 and improved the storage life of the etching solutions.

2) The additives of ethylamine, n-propylamine and n-butylamine acted as the inhibitors at low flow rates and acted as the accelerators at high flow rates, while methylamine acted as the inhibitor at all flow rates.

3) Both corrosion rates and etch factor had the maximums when the concentrations of amine additives were in the vicinity of 0.1 molal.

4) The addition of amines decreases a cathode polarization due to H_2O_2 reduction reaction and the steric effects of substituted groups suppressed the acceleration of copper corrosion by amine additives.

5) The increase in both corrosion rates and flow rates increased the etch factor.

6) The corrosion rates with n-alkylamine additives increased in the order of ethylamine < *n*-propylamine < *n*-butylamine, those with butylamine isomers increased in the order of *tert*- < *sec*- < *iso*- < *n*-butylamine, and those with amine additives of different number of substituted groups increased in the order of *tri*- < *di*- < *mono*-*n*-propylamine.

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