

## INFLUENCE OF HALIDES ON KINETICS OF COPPER DISSOLUTION IN SODIUM HYDROXIDE

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The influence of  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$  ions on the kinetics of dissolution of (100) and (111) faces of a copper single crystal in a sodium hydroxide solution in the presence of oxygen was investigated. The results are interpreted in terms of adsorbability of the anions. Differences between the crystal faces are attributed both to the potentials of zero charge and to the different kinetic behaviour of these faces in pure sodium hydroxide solutions.

The influence of halide ions on the corrosion of metals is generally known. The stimulating or inhibiting effect of these ions depends on the corrosion medium, on their concentration, and other reaction conditions, and the mechanism of their action has been investigated mainly in acidic medium.

In cases where the metal is chemically inert against halides, their inhibiting or stimulating effect has been elucidated mostly by their specific adsorption on the metal surface<sup>1-4</sup>; the stimulating effect in the presence of oxygen has been attributed to catalysis of oxygen reduction on the metal<sup>1</sup>, mainly with  $I^-$  and  $Br^-$  ions. If the halides react with the metal, their inhibiting effect is caused by the formation of sparingly soluble halides of the metal in question<sup>5-7</sup>.

Since the specific adsorption concerns mainly interaction between the ion and the metal, in the case of single crystals the effect of halides will depend on the crystallographic orientation of the metal surface. For example, the specific adsorption of  $Cl^-$  ions on a silver single crystal decreases in the order<sup>8</sup> (111) > (100) > (110) together with the negative standard Gibbs adsorption energy. An analogous result was obtained by Mayanna<sup>6</sup>, who calculated the heat of adsorption of  $I^-$  ions on the basic faces of Cu single crystal in the medium of sulphurous acid. Owing to the dependence of the specific adsorption on the orientation of the metal surface, the halides will hence influence differently the dissolution of the individual crystal faces, which was substantiated also by other authors<sup>5,7</sup>.

We investigated the effect of  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$  ions on the kinetics of dissolution of the (100) and (111) faces of Cu single crystals in solutions of NaOH in oxygen atmosphere, where the differences in the reaction kinetics in NaOH solutions without additions were reported earlier<sup>9,10</sup>.

## EXPERIMENTAL

The experimental arrangement and the method of measurement of the kinetics and potential were described earlier<sup>9,10</sup>. The temperature of measurement was 15°C. All reagents were of reagent grade, halides were in the form of sodium salts. The results are averages from three independent measurements, the mean relative error being 5–10%.

## RESULTS AND DISCUSSION

*Influence of fluorides.* Fluorides accelerate the dissolution of both faces of the copper crystal (Fig. 1): whereas the dissolution of the (111) face proceeds with a less pronounced maximum at NaF concentrations  $10^{-6}$ – $10^{-5}$  mol/dm<sup>3</sup>, with the (100) face there are sharp maximums at  $3 \cdot 10^{-4}$  and  $10^{-2}$  mol/dm<sup>3</sup> NaF. The surface of the sample at these concentrations was covered with a layer of Cu<sub>2</sub>O. At other concentrations of NaF, where the rate of dissolution is only slight ( $10^{-7}$ ,  $10^{-3}$ , and  $0.2$  mol/dm<sup>3</sup>), only traces of Cu<sub>2</sub>O were found on the surface.

The potential of copper in 0.5 mol/dm<sup>3</sup> NaOH in oxygen atmosphere at 15°C is  $E_{c(100)} = -0.030$  V,  $E_{c(111)} = -0.032$  V. The potential of the (111) face in the presence of F<sup>-</sup> ions is more positive and is essentially independent of their concentration, whereas the potential of the (100) face changes analogously as the rate of dissolution, its value being more positive at concentrations near to the maximums and more negative in the region of minimum rates, as compared with  $E_{c(100)}$  (Fig. 2).

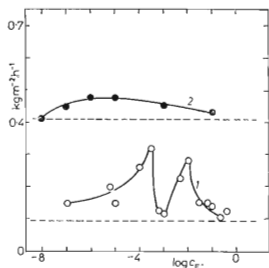


FIG. 1

Influence of fluoride ions on the rate of Cu dissolution in 0.5 mol/dm<sup>3</sup> NaOH at 15°C,  $P_{O_2} = 0.1$  MPa. 1 (100), 2 (111)

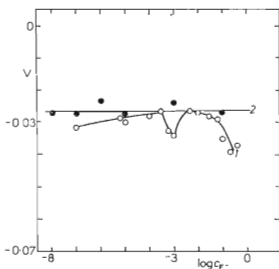


FIG. 2

Influence of F<sup>-</sup> ions on the potential of Cu. Conditions as in Fig. 1. 1 (100), 2 (111)

*Influence of chlorides.* Also chloride ions have an activating effect in the whole range under study (Fig. 3). The (100) face dissolves most rapidly at concentrations close to  $10^{-6}$  mol/dm<sup>3</sup>, whereas the effect of chloride ions on the (111) face becomes apparent only above  $10^{-3}$  mol/dm<sup>3</sup>. The potential does not change with the concentration and is on both faces more negative than  $E_c$  ( $E_{c(100)} = -0.050$  V,  $E_{c(111)} = -0.034$  V).

*Influence of bromides.* Whereas the Br<sup>-</sup> ions stimulate the reaction on the (100) face, their effect on the (111) face is different (Fig. 4): the rate of dissolution increases steeply with the concentration of Br<sup>-</sup> ions up to a maximum at  $10^{-6}$  mol/dm<sup>3</sup> and then decreases. At concentrations higher than 0.1 mol/dm<sup>3</sup>, the reaction is inhibited. The potential of the (100) face does not change appreciably and is negative with respect to  $E_{c(100)}$ . The potential of the (111) face is more negative than  $E_{c(111)}$  in the region where the reaction is inhibited, and becomes more positive with decreasing concentration of Br<sup>-</sup> ions (Fig. 5).

*Influence of iodides.* This is analogous as with Br<sup>-</sup> ions except that I<sup>-</sup> ions inhibit the dissolution of the (111) face already at concentrations higher than  $6 \cdot 10^{-4}$  mol/dm<sup>3</sup> (Fig. 6, 7). A thin layer of Cu<sub>2</sub>O, more or less compact, was observed on the surface, except for 0.1 mol/dm<sup>3</sup> NaI, where only slight traces of Cu<sub>2</sub>O were found after the reaction was finished.

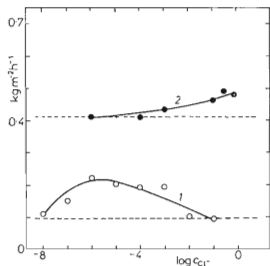


FIG. 3  
Influence of Cl<sup>-</sup> ions on the rate of Cu dissolution in 0.5 mol/dm<sup>3</sup> NaOH at 15°C,  $P_{O_2} = 0.1$  MPa. ----- Rate in the absence of salt, 1 (100), 2 (111)

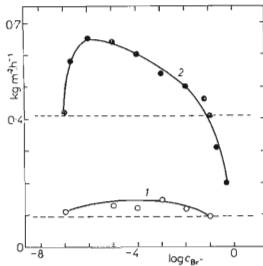


FIG. 4  
Influence of Br<sup>-</sup> ions on the rate of Cu dissolution in 0.5 mol/dm<sup>3</sup> NaOH at 15°C,  $P_{O_2} = 0.1$  MPa. ----- Rate in the absence of NaBr, 1 (100), 2 (111)

In the region  $0.1 > c > 6 \cdot 10^{-4}$  mol/dm<sup>3</sup>, where I<sup>-</sup> ions inhibit the reaction, their adsorption can be expressed (as in ref.<sup>6</sup>) by the Langmuir adsorption isotherm:

$$c/\Theta = 1/b + c, \quad (1)$$

where  $b$  is a constant for the given conditions,  $c$  volume concentration, and  $\Theta$  coverage given as<sup>11</sup>

$$\Theta = 1 - v/v_0, \quad (2)$$

where  $v_0$  is the dissolution rate in the absence of I<sup>-</sup> ions and  $v$  that in their presence. A plot of  $c/\Theta$  against  $c$  gives a straight line representing Eq. (1).

We took into consideration that the changes in the solubility of oxygen with the salt concentration up to 0.1 mol/dm<sup>3</sup> are so small that they do not influence the reaction rate. The conductivity of the solution has no essential influence on the reaction either<sup>12</sup>, so that its changes at concentrations of the salt lower than 0.1 mol/dm<sup>3</sup> can be neglected.

Our results show that halides stimulate the dissolution of the (100) face; the same applies for the (111) face except that Br<sup>-</sup> and I<sup>-</sup> ions inhibit the reaction at concentrations higher than 0.1 and  $6 \cdot 10^{-4}$  mol/dm<sup>3</sup>, respectively.

The different effects of anions on different crystallographic faces can be expected from at least two points of view, namely with respect to the potential of zero charge,

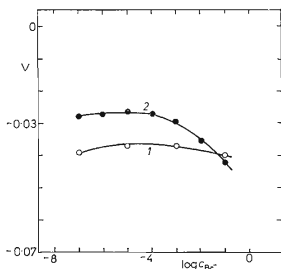


FIG. 5

Influence of Br<sup>-</sup> ions on the potential of Cu. Conditions as in Fig. 4. 1 (100), 2 (111)

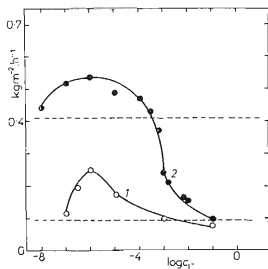


FIG. 6

Influence of I<sup>-</sup> ions on the reaction rate of Cu in 0.5 mol/dm<sup>3</sup> NaOH at 15°C,  $P_{O_2} = 0.1$  MPa. ----- Rate in the absence of NaI, 1 (100), 2 (111)

which is different on the (100) and (111) faces, and with respect to different kinetics and mechanism of the reaction in sodium hydroxide<sup>9</sup>.

The potential of zero charge is related<sup>13</sup> to the work function of electrons according to  $E_q = w_{e1} - 4.72$ , which holds for solutions with a small specific adsorption. Although this relation is only approximate and does not apply for all metals, we can assume that the potential of zero charge will be less positive on the (111) face than on (100), since the work function of electrons is much lower on the former than on the latter. It follows that the (111) face will be charged more positively than (100) and will thus be preferred in the adsorption of anions, as was experimentally found.

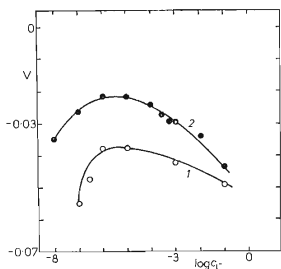


FIG. 7

Influence of  $I^-$  ions on the potential of Cu. Conditions as in Fig. 6. 1 (100), 2 (111)

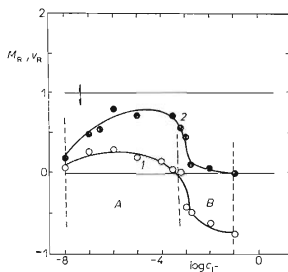


FIG. 8

Dependence of  $M_R$  2 and  $v_R$  1 on the concentration of  $I^-$  ions for the (111) face

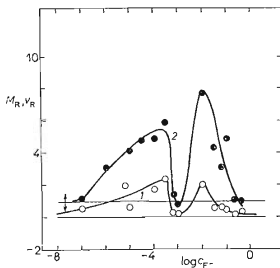


FIG. 9

Dependence of  $M_R$  2 and  $v_R$  1 on the concentration of  $F^-$  ions for the (100) face

Concerning the reaction kinetics, we stated previously<sup>9</sup> that the rate-limiting reaction step on the (100) face is the interaction of adsorbed dissociated oxygen molecules with electrons:



In stationary state, the rates of formation of  $\text{Cu}_2\text{O}$  and its dissolution are approximately equal and control the reaction rate on the (111) face.

The anions can presumably influence either of the two mentioned processes (formation and dissolution of  $\text{Cu}_2\text{O}$ ) or both at the same time. Their influence can be evaluated, for example, by comparing the ratio of the quantity of  $\text{Cu}_2\text{O}$  on the surface to the concentration of  $\text{Cu}^{2+}$  ions in solution,  $M_s$ , with the corresponding ratio in the pure system,  $M_0$ . To enable the comparison of systems with different values of  $M_0$ , we introduce the quantity  $M_R = M_s/M_0$ . If  $0 \leq M_R < 1$  we have  $M_s < M_0$ , i.e., the addition of the salt caused either more rapid dissolution of  $\text{Cu}_2\text{O}$  or its slower formation. Which of these two processes will be influenced by the anions to a larger extent, this will depend on the relative change of the velocity,  $v_R (= (v_s - v_0)/v_0)$ ;  $v_0$  rate in the absence of salt;  $v_s$  rate with salt.

The dependences of  $M_R$  on  $v_R$  at various iodide concentrations are for the (111) face shown in Fig. 8. In the region where  $v_R > 0$  (region A),  $\text{I}^-$  ions accelerate the dissolution of the oxide, and in the region where  $v_R < 0$  (region B) these ions are adsorbed on the metal surface to such an extent that they hinder the oxide formation. The influence of other halides on the (111) face can be explained similarly.

If  $M_R > 1$ , anions can accelerate the formation of the oxide or hinder its dissolution. Since  $v_R \geq 0$  for the influence of halides on the (100) face, we can infer that these anions act at the given conditions so as to stimulate the formation of  $\text{Cu}_2\text{O}$  (Fig. 9).  $\text{F}^-$  ions, which show the least specific adsorption, but are most hydrated, have the largest effect on the reaction on the (100) face. Therefore it seems worth-while to investigate the effect of cations on this surface, which will be the subject of further work.

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