A KINETIC STUDY OF THE INHIBITING EFFECT OF BENZOTRIAZOLE ON THE REACTION OF COPPER SINGLE CRYSTAL IN SODIUM HYDROXIDE AQUEOUS SOLUTION*

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Received September 20th, 1982

The effect of benzotriazole on the reaction of copper single crystal in aqueous solution of NaOH has been studied by kinetic methods. The mechanism of the inhibiting effect is interpreted in terms of adsorption of benzotriazole anions on the pure metal as well as on its oxides, Cu_2O and CuO. The efficiency of inhibition depends on the crystallographic orientation, increasing in the order $I_{100} < I_{110} < I_{111}$.

In contrast to the inhibition of the corrosion of copper in acid and neutral solutions, this inhibition in alkaline solutions has attracted little attention[1-4].

Benzotriazole (BTA) as inhibitor for copper single crystals in sulphuric acid solutions has been studied by Mayanna and Setly[5], who have found that the inhibition depends on the crystallographic orientation and that at low concentrations BTA acts as an anodic inhibitor while at higher concentrations it operates as a cathodic inhibitor.

The inhibiting effect of BTA in the corrosion of copper in aqueous solutions of NaCl has been investigated[6,7] particularly with respect to the structure of the surface films formed, making up a barrier to the cathodic reaction.

A complex study of the effect of triazole and its derivatives on the corrosion of polycrystalline copper in various media has been carried out by Walker[3,4], who observed that whereas in acid and neutral solutions the degree of inhibition is about 50–90%, in weakly ammoniacal solutions it amounts to 10% only and in low concentrations BTA has even a stimulating effect.

In the present work the kinetics is studied of the reaction of the basic crystallographic planes of a copper single crystal in aqueous sodium hydroxide using benzotriazole as inhibitor.

* Part V in the series Study of the Reaction of Copper Single Crystal in Alkaline Medium; Part IV: This Journal *48*, 957 (1983).

EXPERIMENTAL

The kinetics of the reaction was investigated by monitoring the time increase in the concentration of Cu^{2+} ions in solution, employing the techniques described previously[8]. The reaction conditions were as follows: temperature 12·5 to 40°C (accuracy ±0·1°), partial pressure of oxygen 0·02 to 0·1 MPA, concentration of NaOH 0·1—4 mol l^{-1}, concentration of BTA 0·25—10 mmol l^{-1}, stirring velocity 1 200 rpm. Oriented sections of a copper single crystal were prepared and used as described previously[8,9].

The Cu^{2+} ions in solution were determined by the carbamate method with a mean error of 5—10%. The reaction rate was expressed in kg s^{-1} m^{-2} units. The measurements were performed under oxygen at a pressure of 0·1 MPa. For examining the pressure dependence, the partial pressure of oxygen was controlled by mixing it with nitrogen using a UPLS-3 flow meter. The surface morphology was observed on a JXA 2A microanalyzer (Jeol).

The chemicals used were reagent grade preparations, the solutions were made up using saturated solution of NaOH in distilled water from which carbonate had been removed by filtration.

The inhibiting effect was expressed as

$$I = (1 - \Delta m/\Delta m_0) \,.\, 100)\,, \qquad (1)$$

where Δm and Δm_0 are the amounts of copper (kg m^{-2}) dissolved within a preselected time interval (0·5 to 4 h) in the presence and in the absence of BTA, respectively. (The per cent values of I are given.)

Another quantity used for expressing the effect of BTA was the mean degree of coverage function $\bar{\theta}$, which for a time interval from τ_1 (= 0.1 h) to τ_2 (= 4 h) is

$$\bar{\theta} = \int_{\tau_1}^{\tau_2} (1/\tau)\, \theta \, \mathrm{d}\tau\,, \qquad (2)$$

where $\theta = (1 - v/v_0) \,.\, 100$, v and v_0 being the rates of dissolution in time τ in the presence and in the absence of inhibitor, respectively. (Again, the per cent values are used throughout this work.) The error in the determination of I and $\bar{\theta}$ was 5%.

RESULTS AND DISCUSSION

Effect of the presence of benzotriazole. The curves of dissolution of copper in NaOH in various conditions are shown in Figs 1 and 2 for the (111) and (110) planes, respectively. On the (100) plane the reaction can be completely suppressed by BTA in higher concentrations, as documented by Fig. 3.

The time dependences of the degree of coverage of the (111) plane for various concentrations of BTA are shown in Fig. 4. Their mean values were obtained by graphical integration. The dependences of $\bar{\theta}$ and I on the analytical concentration of BTA for the (111) and (110) planes are plotted in Fig. 5, the numerical data are given in Table I.

The inhibition efficiency for the (111) plane is found to obey the relation

$$I = k_1 c^{k_2}\,; \qquad (3)$$

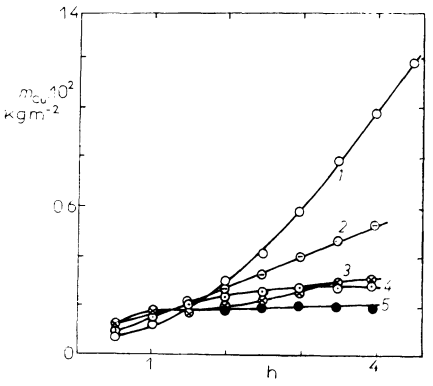

FIG. 1

Time course of dissolution of $Cu_{(111)}$ in 0·5M-NaOH in various conditions: *1* t = = 15°C, P = 0·1 MPa; *2* t = 30°C, P = = 0·1 MPa, c_{BTA} = 1 mmol l^{-1}; *3* t = = 15°C, P = 0·05 MPa, c_{BTA} = 1 mmol. .l^{-1}; *4* t = 15°C, P = 0·1 MPa, c_{BTA} = = 1 mmol l^{-1}; *5* t = 15°C, P = 0·1 MPa, c_{BTA} = 10 mmol l^{-1}

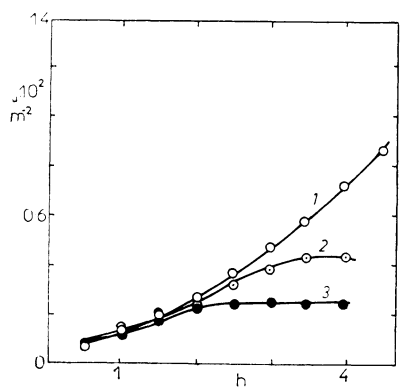

FIG. 2

Time course of dissolution of $Cu_{(110)}$ in 0·6M-NaOH at 15°C and P = 0·1 MPa. Concentration of BTA (mmol l^{-1}): *1* 0, *2* 1, *3* 10

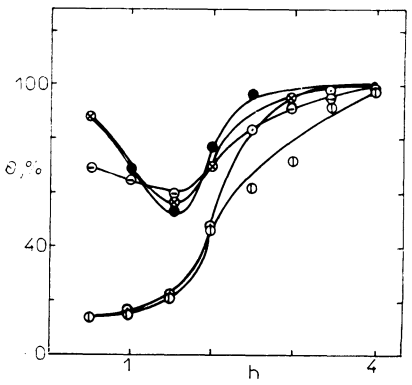

FIG. 3

Time course of dissolution of $Cu_{(100)}$ in 0·5M-NaOH at P_{O_2} = 0·1 MPa. Temperature (°C) and concentration of BTA (mmol l^{-1}): *1* 30, 1; *2* 15, 0; *3* 15, 1; *4* 10, 10

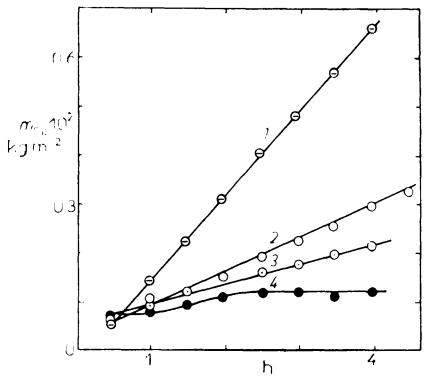

FIG. 4

Effect of BTA concentration on the time course of the degree of coverage of $Cu_{(111)}$ in 0·5M-NaOH at P_{O_2} = 0·1 MPa, t = 15°C. c_{BTA} (mmol l^{-1}): *1* 0·5, *2* 1, *3* 5, *4* 7·5, *5* 10

the constants, as found from a lienar plot of log I *vs* log c, are $k_1 = 142{\cdot}8\ \mathrm{l\ mol^{-1}}$ and $k_2 = 0{\cdot}10$.

The mean degree of surface coverage for the (111) and (110) planes can be approximated by a relation analogous to Frumkin's adsorption isotherm,

$$bc = [\bar{\theta}/(1 - \bar{\theta})] \exp(-2a\bar{\theta}), \qquad (4)$$

the linear form of which gave the constants values $a = -2{\cdot}245$, $b = 25{\cdot}073\ \mathrm{l\ mmol^{-1}}$ for the (111) plane and $a = -1{\cdot}21$, $b = 2{\cdot}967\ \mathrm{l\ mmol^{-1}}$ for the (110) plane.

TABLE I

Values of the mean degree of surface coverage $\bar{\theta}$ for the $Cu_{(111)}$, $Cu_{(110)}$ and $Cu_{(100)}$ planes and of the inhibition efficiency I, for various concentrations of benzotriazole

c_{BTA} / mmol l^{-1}	I, %			$\bar{\theta}$, %		
	111	110	100	111	110	100
0·25	—	35·8	—	—	20·5	—
0·5	66·3	—	22·6	52·5	—	22·6
1·0	73·4	54·5	46·0	60·7	39·8	46·0
2·5	78·3	63·2	65·1	72·2	55·9	65·1
5·0	82·6	68·5	70·2	79·4	66·4	68·5
7·5	87·5	—	—	82·0	—	—
10·0	90·8	75·4	71·7	84·4	73·1	70·0

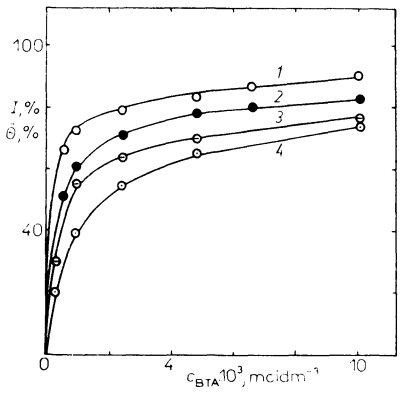

FIG. 5

Dependences of the inhibiting effect (I) and the mean degree of coverage ($\bar{\theta}$) of Cu in 0·5M-NaOH on the concentration of BTA at 15°C, $P_{O_2} = 0{\cdot}1$ MPa. *1* I, *2* $\bar{\theta}$ for $Cu_{(111)}$; *3* I, *4* $\bar{\theta}$ for $Cu_{(110)}$

For the (100) plane the I and $\bar{\theta}$ functions depended on the concentration of BTA in a manner analogous to the Langmuir adsorption isotherm,

$$\bar{\theta} = c/k_0 + k_c \qquad (5$$

with the constants $k_0 = 1{\cdot}174 \,.\, 10^{-3}$ mol $.\, l^{-1}$ and $k_c = 1{\cdot}26$.

Effect of temperature. The inhibiting effect of BTA on the reaction in dependence on temperature is shown in Fig. 6. It is clear that the effect is associated with the formation of oxides, which at different temperatures are present in various proportions on the dissolving surface. At lower temperatures (below 20°C for the (111) plane) Cu_2O is predominantly formed, whereas at higher temperatures (above 20°C) CuO appears; a layer of the latter has a passivating effect and in NaOH prevents the reaction altogether[8]. In the presence of inhibitor a competitive adsorption of OH^- and BTA^- ions takes place, resulting in an ihibition to the formation of Cu_2O at lower temperatures; the linear shape of the time dependences indicates that the steady state, with identical rates of formation and of consecutive dissolution of Cu_2O, remains preserved. The passivating layer of CuO, occurring at higher temperatures (as confirmed by electron microanalysis and visual observations) is disturbed by BTA, and as a result, I acquires negative values.

The temperature dependences (Fig. 7) of the rate of dissolution were linearized to give the apparent activation energies (Table II).

Effect of pressure of oxygen. The reaction of copper dissolution in NaOH has been found[8] to depend on the oxygen pressure over the range examined, *viz.* 0·02 to 0·1 MPa. For the (111) plane the dependence in the presence of BTA agrees qualitatively with that established previously.

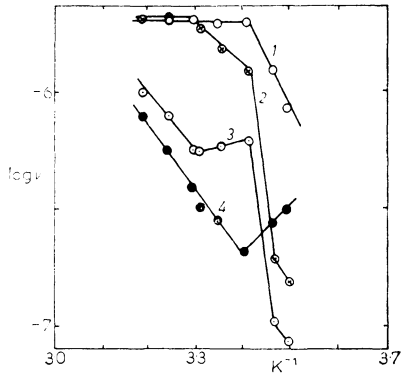

FIG. 6

Effect of temperature ($10^3/T$, T in K) on the rate of dissolution of $Cu_{(111)}$ (*1*, *4*) and $Cu_{(100)}$ (*2*, *3*) in 0·5M-NaOH at P_{O_2} = = 0·1 MPa. *1*, *2* in the absence of BTA, *4*, *3* in the presence of BTA (1 mmol l^{-1})

Effect of concentration of sodium hydroxide. Similarly as in the absence of BTA (ref.[8]), in its presence the dependence of the rate of dissolution on the concentration of NaOH exhibits a maximum. The inhibiting effect of BTA appears at NaOH concentrations of 0·25–1 mol l^{-1}; at higher concentrations the effect is negligible. Fig. 8 shows the effect of the OH^- concentration on the temperature quotient, expressed *via* the v_{20}/v_{15} rate ratio for the (111) plane. At low NaOH concentrations

TABLE II

Values of the apparent activation energy E^* in the absence of benzotriazole (*A*) and in the presence of benzotriazole in a concentration of 1 mmol l^{-1} (*B*)

Pllne	Temperature region °C	E^*, kJ mol^{-1}	
		A	*B*
$Cu_{(111)}$	12·5–20·0	76·7	−53·6
	20·0–40·0	0	38·3
$Cu_{(100)}$	12·5–15·0	70·2	70·2
	15·0–20·0	258·4	258·4
	20·0–30·0	34·5	−7·7
	30·0–40·0	0	49·8

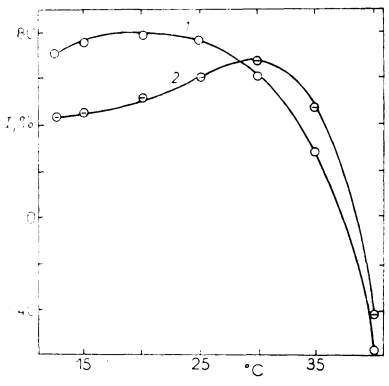

FIG. 7

Temperature dependence of the inhibiting effect of BTA on the dissolution of $Cu_{(111)}$ (*1*) and $Cu_{(100)}$ (*2*) in 0·5M-NaOH at P_{O_2} = = 0·1 MPa, c_{BTA} = 1 mmol l^{-1}

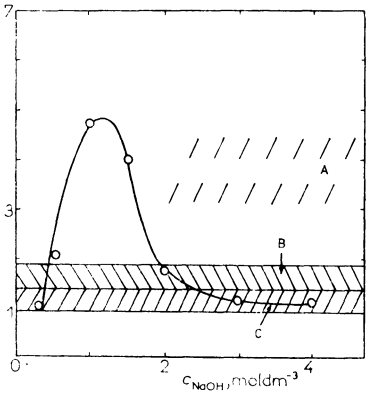

FIG. 8

Dependence of the v_{25}/v_{15} rate ratio on the concentration of NaOH at P_{O_2} = 0·1 MPa, c_{BTA} = 1 mmol l^{-1}

(below 0·5 mol l^{-1}) the process occurs in the transition and the diffusion regions (*B*, *C*), in the range of $c_{NaOH} = 0{\cdot}5 - 2$ mol l^{-1} the kinetic region is involved (*A*), and at $c_{NaOH} \geqq 2{\cdot}0$ mil l^{-1} the process is governed by diffusion (*C*). If compared with the data of ref.[10] the kinetic region is seen to be shifted by the presence of BTA to higher concentrations.

The nature of the inhibiting effect of BTA thus depends both on the reaction conditions and on the crystallographic plane concerned. Now, it must be taken into accout that BTA dissociates well in aqueous solutions to give the BTA^- anion,

$$BTA + H_2O \rightleftarrows BTA^- + H^+ ; \quad pK_a = 8{\cdot}2 \text{ (ref.[11])}$$

so in alkaline solutions the BTA^- ion species will be highly predominant ($c_{BTA} \approx \approx [BTA^-]$) – in 0·5M-NaOH the concentration ratio of the dissociated to he non-dissociated forms will be about $5 \cdot 10^{4{\cdot}8}$ (ref.[12]). In view of the mechanism of dissolution of copper single crystals in NaOH as formulated previously[8] in conjunction with the experimental data obtained, it can be inferred that BTA, occurring predominantly as BTA^- ions in the solutions under study, is adsorbed on the pure copper as well as on the forming copper(I) and copper(II) oxides. The adsorption on pure copper has a direct inhibiting effect on the formation of Cu_2O and an indirect inhibiting effect on the formation of CuO. Whereas the adsorption of BTA^- on the Cu_2O formed inhibits its consecutive dissolution, on the CuO layer the BTA^- ions exert a disturbing effect, accelerating its dissolution ($I < 0$).

The differences observed for the various crystallographic planes can be discussed in terms of the adsorption coefficient values in Eq. (*4*). These data point to a stronger bonding to the (111) plane surface than to the (110) plane, which is consistent with our previous conclusions[10] which show that having a higher positive charge, the former plane favours the adsorption of anions more than the latter. The negative values of the coefficients *a* indicate that the adsorbed BTA^- ions affect each other in a manner such that the adsorption is promoted; the effect consists probably in an interaction of the conjugated systems on the benzene ring or on the ring formed by the nitrogen atoms.

The inhibiting effect can be correlated with the changes in the chemical potential. The chemical potential changes associated with the dissolution of the metal in the presence and in the absence of inhibitor differ by

$$\Delta\mu = -RT \ln (\Delta m / \Delta m_0) , \qquad (6)$$

where Δm and Δm_0 are the amounts of metal dissolved in the two cases, respectively. This can be modified to give

$$\Delta\mu = -RT \ln (1 - I) , \qquad (7)$$

hence, the inhibiting effect is related with the difference in the chemical potentials as

$$I = 1 - \exp\left(-\Delta\mu/\boldsymbol{R}T\right). \qquad (8)$$

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Translated by P. Adámek.