Anodic Polarization of Copper Single Crystal Planes in Sulphuric Acid

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Anodic polarization of copper single crystal (110), (100) and (111) planes in 0·1N sulphuric acid is studied. During polarization the overpotentials on single crystal planes change with time and attain steady values. The change in overpotential is attributed to the change in overall activity of the surface. At a given current density, the value of steady overpotential is low on the (110) plane and high on the (111) plane. The mechanism of dissolution of copper single crystal planes is discussed using current-potential plots. The exchange current densities on different crystal planes are in the order $i_o(110) > i_o(100) > i_o(111)$. The change in surface topography during polarization have no effect on the electrochemical kinetic parameters. From the values of overpotentials and exchange current densities the stabilities of the crystal planes are found to be in the order: $(111) > (100) > (110)$.

METAL dissolution has been studied using polycrystalline[1] and single crystals of copper[2-7] by means of either short time transients or by the long time polarization in which topography of the dissolved surface and overvoltages have been analysed. All these investigations were concerned with the acid copper sulphate solution and the current density ranges well below i_0 value. It has shown[8] that copper ion in solution affects the kinetics of dissolution of copper. In the present communication the results of the investigations on the effect of crystal orientation on the anodic polarization of copper in sulphuric acid are presented.

Materials and Methods

Solutions were prepared from freshly distilled and pre-electrolysed sulphuric acid (AR) using conductivity water. Copper (99·999% purity) single crystal (110), (100), (111) planes with dislocation density of the order of $10^5/cm^2$ were fixed in Tygon tubing, exposing only the desired planes. The crystal planes were mechanically polished on 4/0 emery paper using ethyl alcohol as lubricant and electropolished in 1:1 orthophosphoric acid[9] at a cell potential of 1·2 V for 30 min. The polarization was carried out in deaerated stirred 0·1N sulphuric acid between current densities 0·2 and 5 mA/cm² at $30° \pm 0·1°$. The detailed experimental procedures have been given elsewhere[7].

Results

At all current densities, during anodic polarization of copper single crystal planes in sulphuric acid, the overpotentials were recorded at regular intervals until the metal removed from the surface was equivalent to a thickness of 5 c/cm² (c, the thickness in coulomb).

On the (110) *plane* — Fig. 1 shows the variation of overpotential with thickness during the dissolution of copper (110) plane. At 0·2 mA/cm², the overpotential increased gradually with time and

attained steady value during dissolution. The same trend in increasing and attaining a steady overpotential was observed at different current densities. However, the steady state attainment was observed at the same dissolution thickness (1 c/cm²).

On the (100) *plane* — At any given current density the overpotential increased with time and attained steady value similar to the (110) plane (Fig. 2). The steady state attainment of overpotential at all current densities was found to be a thickness equivalent to 2 c/cm².

On the (111) *plane* — The change of overpotential with thickness on the (111) plane was different than on the (110) and (100) planes. At all current densities, the overpotentials initially decreased and attained steady values at a thickness of 2·5 c/cm² (Fig. 3).

The extent of variation of overpotential with time was high on the (111) plane and least on the (110) plane. The time intervals required to attain steady overpotentials on different single crystal planes were in the order $(111) > (100) > (110)$. At any
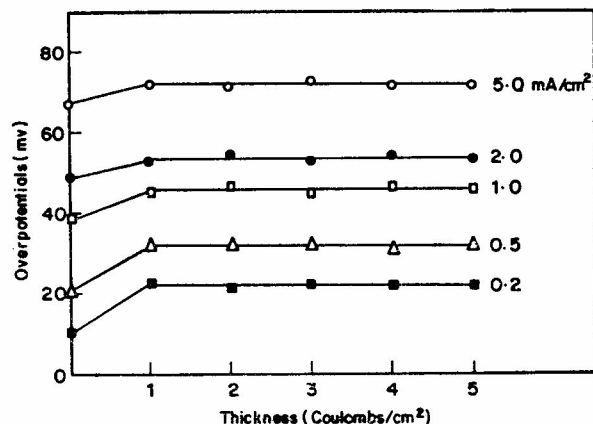

Fig. 1 — Overpotential-thickness curves at various current densities on copper (110) plane
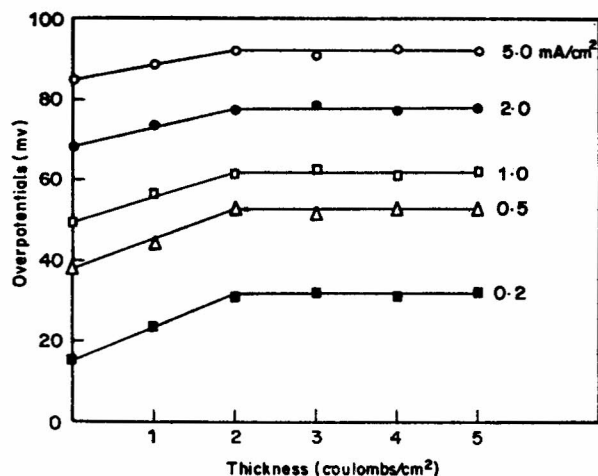
Fig. 2 — Overpotential-thickness curves at various current densities on copper (100) plane
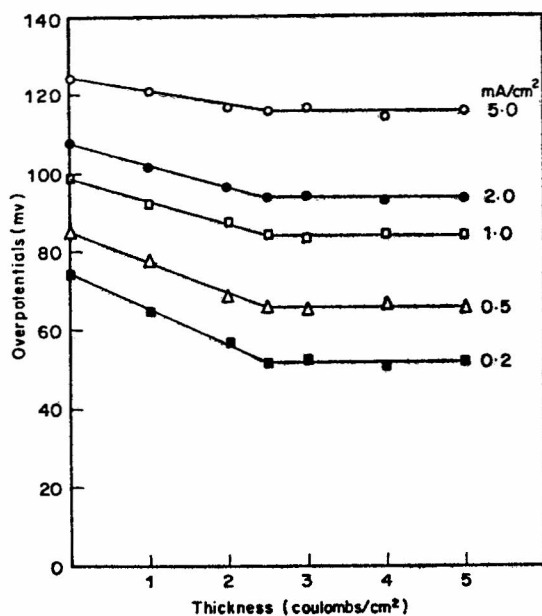

Fig. 3 — Overpotential-thickness curves at various current densities on copper (111) plane

TABLE 1 — TAFEL SLOPES AND EXCHANGE CURRENT DENSITIES (i_0) FOR THE DISSOLUTION OF COPPER SINGLE CRYSTAL PLANES IN $0.1N$ SULPHURIC ACID AT 30°C

Crystal plane	$d\eta/d \log i$ (mv)	$10^{-5} \times i_0$ (A/cm²)
(110)	38.0	6
(100)	42.0	3
(111)	45.0	1

TABLE 2 — CHARACTERISTIC ETCH PITS AT DIFFERENT CURRENT DENSITIES DURING ANODIC POLARIZATION OF COPPER SINGLE CRYSTAL PLANES IN SULPHURIC ACID

Current density (mA/cm²)	Type of etch pits		
	(110)	(100)	(111)
0.2	Fine ridges	Layers with irregular edges	Layers
0.5	do	Layers with occasional square layers	do
1.0	Thick ridges	Big pyramids and spirals	do
2.0	do	Pyramids with spiral turns at the apex	do
5.0	do	Pyramids and spirals at the edges	Triangular pits and layers

Anodic dissolution produced layers and triangular pyramidal pits on the (111) plane, spirals and square pyramids on the (100) plane, and ridges on the (110) plane.

Discussion

Damjanovic *et al.*[10] have proposed an empirical equation

$$i = [(1-A)i_{0/111/}+A i_{0/hkl}] \exp(-\alpha\eta F/RT) \qquad ...(1)$$

to explain the change of overpotential with time during deposition of copper on copper (111) plane. In Eq. (1) A is the fraction of the electrode covered by new (hkl) faces with their exchange current density $i_{0/hkl/}$. Initially $A{\to}0$ and $(1/A){\approx}1$. Hence Eq. (1) becomes

$$i \approx [i_{0/111/}+A i_{0/hkl/}] \exp(-\alpha\eta F/RT) \qquad ...(2)$$

The dissolution is an exact reciprocal of deposition under the current density ranges both below[11] and above[7] i_0 value. Hence, one can make use of the above equation to account for the change in overpotential with time during dissolution of copper (111) plane.

The observed variation of overpotential with time is due to the formation of new crystal faces of different activity. Which face and how fast they will form depends on the conditions of anodic dissolution, viz. the current density, temperature, and in particular, purity of the solution. In the case of single crystal substrate, the activity of the electrode surface is measured in terms of i_0. Exchange current densities on the three major crystal

given current density, both initial and final overpotential values on different single crystal planes were in the order.

$$\eta(111) > \eta(100) > \eta(110)$$

In order to evaluate the electrochemical kinetic parameters, for the anodic dissolution of copper single crystal planes, Tafel plots were made employing steady state anodic polarization values. The values of Tafel slopes and exchange current densities for the (110), (100) and (111) planes, given in Table 1, show that the exchange current densities on different single crystal planes are in the order: $i_{0(110)} > i_{0(100)} > i_{0(111)}$. Tafel slope was found to be 40 ± 5 mV.

During dissolution of copper single crystal planes between current densities 0.2 and 5 mA/cm², characteristic etch pits were obtained (Table 2).

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planes of copper are found to be in the order[7,10]:

$$i_{0(111)} < i_{0(100)} < i_{0(110)}.$$

The side faces of the pyramidal etch pits on (111) plane are aligned along [100] direction. This indicates that the new faces i.e. (hkl) planes formed on the (111) plane are of higher activity than the original (111) plane. Hence, $i_{0(hkl)} > i_{0(111)}$ plane, and A increases during dissolution, resulting in increase of i_0 and decrease of overpotential (Fig. 3). It has been known[10,12] that the pyramidal faces formed on the (100) plane and side faces formed on the (110) plane are aligned along [111] and [100] directions respectively. Hence, during dissolution the more active surface is replaced by less active planes. From this, one perhaps could expect an increase in overpotential with time on the (110) and (100) planes (Figs. 1 and 2).

The characteristic etch pits observed during dissolution of copper single crystal planes can be explained by making use of earlier theories[12-15]. Topographical changes observed during dissolution are found to have no effect on the electrochemical parameters. Mattson et al.[1] and Sheshadri et al.[7] have proposed the following mechanism for anodic dissolution of copper and copper single crystal planes in acidic copper sulphate solution,

$$Cu \longrightarrow Cu^+ + e$$
$$Cu^+ \underset{rds}{\longrightarrow} Cu^{2+} + e$$
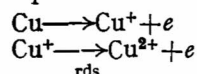
with the Tafel slope of $2 \cdot 303RT/2F$, i.e. 29 mV per logarithmic rate unit at 20°, which corresponds to second electron transfer as the rate controlling step. In the present system, the Tafel lines constructed from the potential-current density data have a slope close to $2 \cdot 303RT/2F$ (Table 1). Hence, the same mechanism holds good for all single crystal faces of copper. From the values of exchange current densities and overpotentials, one can conclude that the (111) plane is the least active and the (110) plane is more active. This is in accordance with the fact that the (111) plane is a close packed plane with large work function[16] and is more resistant to dissolution[17] than the other two planes.

Acknowledgement

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