# INFLUENCE OF CRYSTALLOGRAPHIC ORIENTATION ON THE POTENTIAL OF ALUMINIUM DURING REACTION WITH AQUEOUS NaOH SOLUTION

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In addition to kinetic measurements, the authors followed the potential of three oriented sections of Al monocrystal during its reaction with aqueous NaOH solution. The time dependences showed a shift of the potential to more positive values; the difference between the stationary, $E_{st}$, and initial, $E_0$, values was dependent on the orientation of the section and was related to its reactivity. Potential oscillations were observed on the (110) crystal face in the concentration region from 2 to 8 mol dm$^{-3}$ NaOH, and their period and amplitude were measured. The stationary potential was a parabolic function of the reaction rate at concentrations of NaOH from 0 to 5 mol dm$^{-3}$.

Changes of the potential of a metal during its chemical dissolution in a corrosive medium reflect the situation at the metal/solution interface and can supplement the kinetic studies of the reaction. This idea has been utilized only rarely; *e.g.* Butler *et al.*[1] measured the potential of base metals in solutions of NaHCO$_3$ + NaCl saturated with oxygen up to 150°C. With increasing concentration of oxygen the potential was shifted to more positive values the more the less electropositive metal was used. Vijh[2] assumes that the potential of the metal is controlled by a parallel cathodic reduction of oxygen and can be expressed as function of both cathodic and anodic reaction rates. We measured the potential of polycrystalline[3] and monocrystalline[4] Cu during dissolution in aqueous NaOH: the potential was only slightly influenced by changing oxygen concentration, but significantly depended on the activity of NaOH. With monocrystalline Cu, the potential was determined by the quantity of products formed. The present work deals with the potential of Al during spontaneous reaction with aqueous NaOH to supplement the earlier experimental findings[5].

## EXPERIMENTAL

The potential of Al was followed in parallel with the kinetic measurements; the apparatus, metal samples, and their standardization before the measurement are described elsewhere[5].

The electrode potential of Al single crystals was determined by measuring the electromotive force of the cell.

$$\text{Hg} | \text{Hg}_2\text{Cl}_2(s) | \text{KCl(sat} \| 2\text{M-NaOH} \| \text{NaOH}(c) | \text{Al}$$
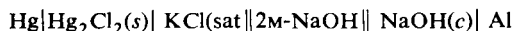
The diffusion potentials between the reference electrode (SCE) and the measured solution were determined by using another reference electrode (also SCE). The potential measurements were precise to within $\pm 0.5$ mV and reproducible to $\pm 5$ mV.

## RESULTS AND DISCUSSION

### Time Dependence of Potential During Dissolution of Al in NaOH

Figure 1 shows the course of the open-circuit potential of Al in 1M-NaOH at 25°C ($vs$ SHE) for the (100), (110), and (111) crystal faces. During the reaction, the potential is shifted in each case toward positive values to attain a stationary value, $E_{st}$, after $0.5-2$ hours. Obviously there is an electrochemical anisotropy: the absolute value of the stationary potential increases in the order

$$\left| E_{st}(111) \right| < \left| E_{st}(110) \right| < \left| E_{st}(100) \right| ,$$

whereas the initial potential (extrapolated to $t = 0$) decreases

$$\left| E_0(111) \right| > \left| E_0(110) \right| > \left| E_0(100) \right|$$

and so does the Al dissolution rate

$$v(111) > v(110) > v(100) .$$

Thus, the (111) face is most reactive, its initial potential $E_0$ being most negative in accord with expectation, but its stationary potential $E_{st}$ is most positive; and the differences between the final and initial potentials, $E_{st} - E_0 = \Delta E$, follow the same sequence as the reaction rates

$$\Delta E(111) > \Delta E(110) > \Delta E(100) .$$

Since the measured potential reflects the situation at the metal/solution interface, we assume that its changes are related with the structure and composition of the electric double layer. Kinetic measurements referring to changes in the volume concentration of $Al^{3+}$ ions, on the assumption that transport of reactants and products is sufficiently rapid, cannot express the changes in the interface; the kinetic curves[5] show the stationary state of the process nearly from the beginning.

Since no formation of an oxide layer can be assumed in the given medium[6], we must consider the intermediate products, namely $Al(OH)^{2+}$ and $Al(OH)_2^+$. Logically,

the highest value of $\Delta E$ should correspond to the most reactive face, which is in accord with Fig. 1. Although the initial potential values are subject to a larger error than the $E_{st}$ values (cf. Experimental), they express the sequence with respect to the crystallographic orientation.

### Influence of NaOH Concentration on the Potential of Al

The influence of the concentration or activity of NaOH on the $E_{st}$ value is shown in Fig. 2 for all three crystal faces. The sequence of $E_{st}$ values found from the time dependences is valid not only for 1M-NaOH but for the whole concentration interval under study.

For a given crystal face, it can be seen from Fig. 2 that an increase in the activity of $OH^-$ ions results in a shift toward more negative values of $E_{st}$. In contrast to the dependence of the rate of dissolution on the concentration of NaOH, which passes through a maximum, the dependence $E_{st} = f(a_{OH^-})$ decreases in the whole concentration interval according to the equation

$$E_{st} = k_1 a_{OH^-}/(1 + k_2 a_{OH^-}) \tag{1}$$

which holds with a sufficient accuracy. This was verified by plotting $a_{OH^-}/E_{st}$ against $a_{OH^-}$; the regression coefficient $r$ and the values of the constants $k_1$ and $k_2$ are given in Table I.
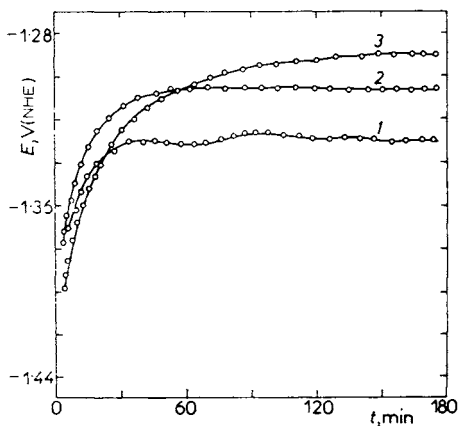


FIG. 1

Time course of the potential of Al in 1M--NaOH at 25°C corresponding to the crystal faces: 1 (100), 2 (110), 3 (111)
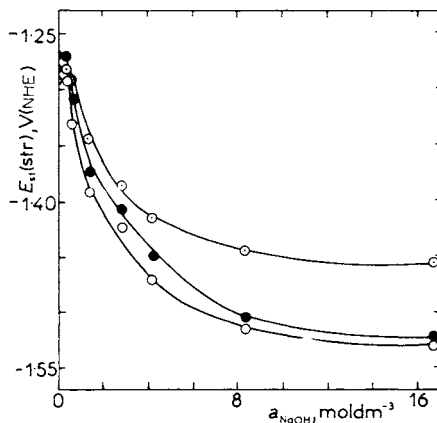


FIG. 2

Dependence of the stationary potential of Al on the activity of $OH^-$ ions at 25°C for crystal faces: ○ (100), ● (110), ⊙ (111)

Equation $(1)$, resembling an adsorption isotherm, can be considered as evidence for the fact that no surface oxide layer is present in alkaline medium, interaction of adatoms with $OH^-$ ions being one of the first steps of the anodic reaction:

$$(Al^{3+}.3\,e^-) + OH^- \rightarrow Al(OH)^{2+} + 3\,e^- . \qquad (A)$$

The intermediate $Al(OH)^{2+}$ ions undergo follow-up reactions

$$Al(OH)^{2+} + OH^- \rightleftarrows Al(OH)_2^+ \qquad (B)$$

$$Al(OH)_2^+ + OH^- \rightleftarrows Al(OH)_3 \qquad (C)$$
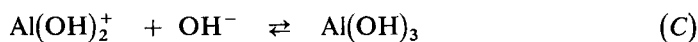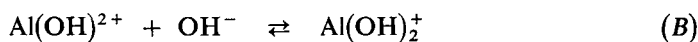
TABLE I

Values of regression coefficient $r$ and coefficients $k_1$ and $k_2$ in Eq. $(1)$

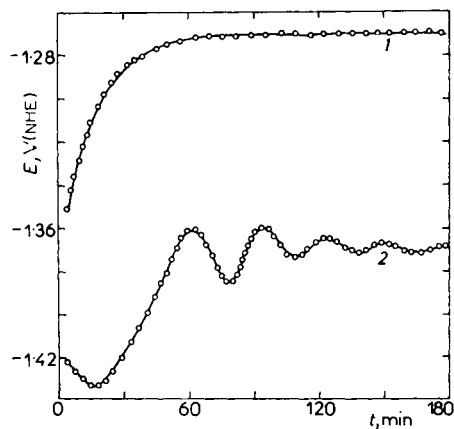| Crystal face | $r$ | $k_1$ | $k_2$ |
|---|---|---|---|
| (100) | 0·999874 | −0·0790 | −0·6503 |
| (110) | 0·999829 | −0·0853 | −0·6513 |
| (111) | 0·999935 | −0·0634 | −0·6844 |



FIG. 3

Damped oscillations of the potential of Al corresponding to the (110) crystal face. *1* 0·5M-NaOH; *2* 2·0M-NaOH; 25°C
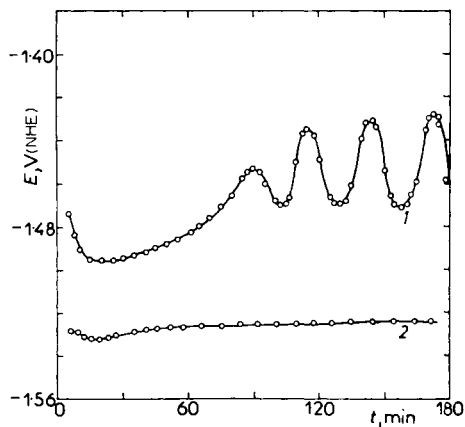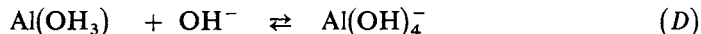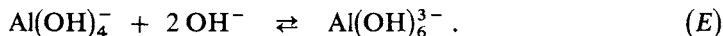


FIG. 4

Non-damped oscillations of the potential of Al corresponding to the (110) crystal face. *1* 4·0M-NaOH; *2* 8·0M-NaOH; 25°C

$$Al(OH)_3 \quad + \quad OH^- \quad \rightleftarrows \quad Al(OH)_4^- \qquad (D)$$

and in concentrated NaOH solutions even

$$Al(OH)_4^- + 2\,OH^- \quad \rightleftarrows \quad Al(OH)_6^{3-} \,. \qquad (E)$$

*Potential Oscillations of Aluminium in* NaOH *Solutions*

Potential oscillations were observed after the reaction had proceeded for some time on the (110) face in the concentration interval from 2 to 8M-NaOH. This is shown in Fig. 3 (damped oscillations in 2M-NaOH) and in Fig. 4 (non-damped oscillations in 4M-NaOH); the induction period in the latter case was about 90 min, period of oscillations 30 min and amplitude 20 mV.

Increasing concentration of the hydroxide caused shortening of the induction period and diminishing of the amplitude of the oscillations, which disappeared at a concentration of $8\ \text{mol dm}^{-3}$.

Convection of the solution favours non-damped oscillations; when the stirring is stopped, the oscillations are damped. In the latter case the potential acquired a mean value; in both cases the quantity $E_{st}$ was set equal to the mean value of the potential.

We did not study the periodic phenomenon in more detail. Based on the mentioned experimental facts, it can be assumed[7-9] that rapid specific adsorption of $OH^-$ ions (at higher NaOH concentrations) and their interaction with the electrode surface according to the step $(A)$ results in a higher surface concentration of intermediate products, which cause a shift of the potential toward positive values. Further re-action with $OH^-$ ions, which are present at the interface at a high concentration, in the steps $(B) - (E)$ leads to the final products $Al(OH)_3$ and, eventually, $Al(OH)_6^{3-}$ ions passing into the solution, whereby the conditions for specific adsorption of $OH^-$ ions on the surface are reestablished. This process is assumed to have the character of a parallel reaction, which is supported by suitable hydrodynamic con-ditions caused by stirring.

In the kinetic study of the reaction of aluminium with a solution of NaOH no oscillations of the reaction rate were observed. If the intermediate products $Al(OH)^{2+}$ and $Al(OH)_2^+$ form a monolayer at the interface, their quantity formed during one period of the potential is so small that it cannot be detected by our kinetic method using informations from the bulk of the solution.

When the hydroxide concentration increases further, the oscillations come to their end, which is related with the solubility of the products of the subsequent reaction steps (the rate at which the complex formation equilibria are established) and with the nature of the final product. It is probable that similar potential oscilla-tions could be observed on other crystal faces at suitable reaction conditions.

*Relation Between Kinetic and Electrochemical Behaviour of* Al *in* NaOH
*Solutions*

The results of the kinetic study of the reaction of Al single crystals with aqueous
sodium hydroxide[5] can be correlated with the values of the stationary potential $E_{st}$,
eventually $\Delta E$, obtained from potential measurements during the reaction (Fig. 5).
The dependence of $v$ on $E_{st}$ in the concentration interval from 0 to 5 mol dm$^{-3}$ sat-
isfies the equation

$$v^2 = K(E_{st} - E_{v_0}) = \Delta E , \qquad (2)$$

where $E_{v_0}$ denotes stationary potential extrapolated to zero rate of the reaction
and $K$ is a constant, given in Table II together with the corresponding regression
coefficients.

TABLE II
Values of regression coefficient $r$ and coefficient $K$ in Eq. (2)

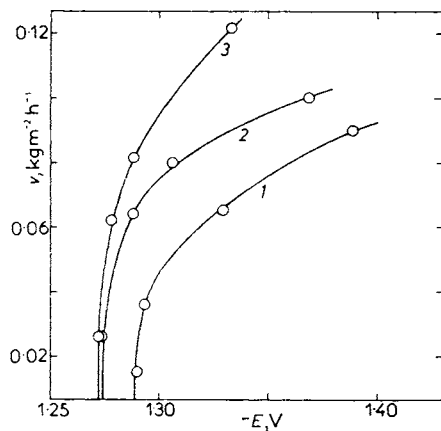| Crystal face | $r$ | $K^a$ |
|:---:|:---:|:---:|
| (100) | 0·9861 | 0·7628 |
| (110) | 0·8929 | 0·8894 |
| (111) | 0·9641 | 2·1222 |

$^a$ kg$^2$ m$^{-4}$ h$^{-2}$ V$^{-1}$.



FIG. 5

Relation between kinetic and electrochemical
behaviour of Al in NaOH solution for crystal
faces: *1* (100), *2* (110), *3* (111)

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