
EFFECT OF CRYSTALLOGRAPHIC ORIENTATION ON THE KINETICS OF REACTION OF ALUMINIUM SINGLE CRYSTAL IN AQUEOUS SOLUTION OF SODIUM HYDROXIDE

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The effect of the concentration of OH^- ions, oxygen pressure, and temperature on the rate of reaction of aluminium in aqueous solution of sodium hydroxide was studied for surface planes corresponding to the (100), (110), and (111) crystallographic planes. Kinetic anisotropy was observed: the reaction rate increased and the apparent activation energy decreased in order (100)—(110)—(111). The kinetic parameters were related to some physical characteristics of the surface.

The chemical reactivity of metals is increasingly studied on single crystals with oriented surface planes because in this way a physically defined surface is obtained.

The majority of papers dealing with the chemical behaviour of single crystals of aluminium are concerned with the reactivity of the metal in gases such as oxygen, carbon monoxide or water vapours¹⁻⁵. In these papers the formation of the oxide film has been examined for particular surface planes, and changes in the work function caused by the action of the reaction medium have been studied. In ref.⁶ the kinetics of growth and the kinetics of formation of the anodic oxide film have been observed to be also dependent on the sample orientation. The kinetic behaviour of aluminium single crystals in alkaline solutions has not been so far investigated.

The aim of the present work was to examine whether (and if, then to what extent) the kinetic behaviour of aluminium during its reaction with aqueous solution of sodium hydroxide depends on its crystallographic orientation.

EXPERIMENTAL

The kinetic measurements were carried out in a 1 dm³ thermostatted glass vessel stirred at 950 r.p.m.; the temperature was held constant to within $\pm 0.1^\circ\text{C}$ over the region of 15–45°C, the oxygen pressure was 0.02–0.1 MPa, sodium hydroxide concentration 0.7–7.25 mol dm⁻³.

The aluminium single crystals were grown by the secondary recrystallization technique. The oriented sections corresponded to the (100), (110), and (111) crystallographic planes to within $\pm 2^\circ$. The density of dislocations on the three surface planes was of the same order of magnitude, viz. 10^{-6} cm^{-2} . Always one surface plane was exposed to the reaction medium while the remaining surfaces were coated with epoxide resin. The surface plane of interest was degreased, rinsed with

distilled water, allowed to activate for 3–5 min in 20% NaOH, rinsed again with distilled water, and submerged in the reaction solution at a constant distance from the stirrer blades.

For the reaction rate evaluation, the increment of dissolved aluminium in the reaction medium was monitored spectrophotometrically with aluminon, a reagent which forms chelates exhibiting an absorption maximum in the 545 nm range in weakly acid medium.⁷

The chemicals used were of reagent grade purity; sodium hydroxide was prepared from saturated solution. The reproducibility of measurement was 5–7%.

RESULTS AND DISCUSSION

Time Course of Aluminium Dissolution in Sodium Hydroxide

The reaction rate was evaluated from the plot of the time dependence of the amount of dissolved aluminium. The reaction was monitored for 1.5–2 h, and linear plots were obtained (Fig. 1); the uniform, time-independent dissolution was observed on the three planes, the linearity was preserved over the entire concentration region, at different partial pressures of oxygen and at all temperatures used. From this it can be inferred that within the reaction period followed, no layer of solid $\text{Al}(\text{OH})_3$ that would cause a diffusion retardation of the reactants forms on the surface, or if it forms, it dissolves immediately in the excess NaOH to give rise to complex equilibria from $[\text{Al}(\text{OH})_4]^-$ as far as $[\text{Al}(\text{OH})_6]^{3-}$ in concentrated hydroxide⁸.

Dependence of Aluminium Dissolution Rate on Hydroxide Concentration

The effect of NaOH concentration was examined over the region of $c_{\text{NaOH}} = 0.5$ to 7.25 mol dm^{-3} at oxygen pressure of 0.1 MPa and temperature of 25°C. For the three planes, the concentration dependence of the reaction rate exhibits a maximum. It should be noted that a qualitatively similar dependence has also been observed for the reaction of polycrystalline aluminium in electrolytes^{8,9}. Both the height and the position of the maximum, however, depend on the crystallographic orientation (Fig. 2). It is clear that the position of the maximum relates to the rate of the process; if the reaction rate is higher, the maximum will appear at higher NaOH concentrations. Explanation of this concentration dependence may be sought in physical changes occurring in the solution with increasing concentration of hydroxide (changes in the viscosity, electric conductivity, concentration of dissolved oxygen). Actually, the factors would play a role in transport-controlled reactions. The apparent activation energy values (see later), however, suggest that the process is controlled by the surface reaction, so that it is rather changes in the surface quality that are responsible for the concentration dependence of the reaction rate. Proceeding from the double-centre concept, the descending branch in Fig. 2 can be explained so that when a high fraction of the surface is occupied by the attacking OH^- particles, the concentration of the free centres, involved in the activated complex formation, is very low and the reaction rate starts to decrease with increasing NaOH concentration.

The reaction rates measured at different concentrations of hydroxide were subjected to logarithmic analysis to obtain the apparent reaction order with respect to OH^- ions. The value obtained both for the (100) and (111) planes was $n = 0.3$, that for the (110) plane was $n = 0.2$. (These values refer to the ascending branches of the concentration dependences.)

Effect of Oxygen Pressure

The pressure dependence was examined in 1M-NaOH at 25°C over the oxygen pressure region of 0.02–0.1 MPa. The oxygen-to-nitrogen ratio in the gas mixture fed above the solution level was controlled with flow meters. No appreciable effect of the oxygen pressure on the course of dissolution was observed in the conditions used; the differences between the reaction rates were within the limits of experimental error.

Effect of Temperature

The measurements were performed at 15–45°C and $c_{\text{NaOH}} = 1 \text{ mol dm}^{-3}$. Fig. 3 demonstrates that for the three planes the temperature dependence obeys the Arrhenius law over the entire temperature region followed. The values of the apparent activation energy and temperature coefficients of the reaction rate (Table I) suggest that the process occurs within the kinetic region, *i.e.*, it is controlled by some step of the phase reaction.

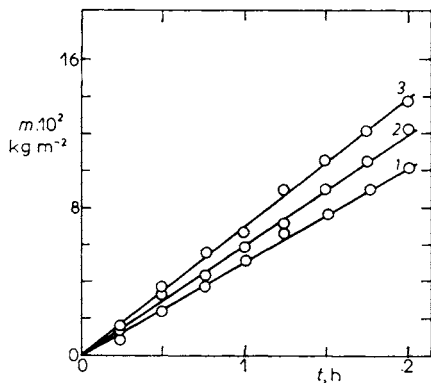


FIG. 1

Time course of dissolution of aluminium single crystal in 1M-NaOH at 25°C and $P_{\text{O}_2} = 0.1 \text{ MPa}$. Plane: 1 (100), 2 (110), 3 (111)

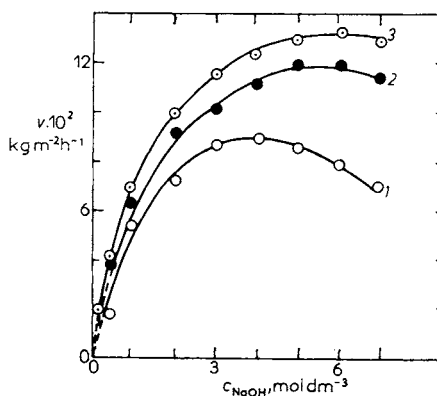


FIG. 2

Effect of concentration of NaOH on the rate of dissolution of aluminium single crystal at 25°C and $P_{\text{O}_2} = 0.1 \text{ MPa}$. Plane: 1 (100), 2 (110), 3 (111)

The apparent activation energy can be correlated with the reaction rate in 1M-NaOH (Table II) or with physical characteristics of the solid phase surface such as the electron work function^{10,11} or the atomic density of the surface.

TABLE I

Apparent activation energy E^* and temperature coefficients of dissolution rate $\alpha = v_{t+10}/v_t$ at $c_{\text{NaOH}} = 1 \text{ mol dm}^{-3}$

Plane	E^* kJ mol^{-1}	α		
		15–25°C	25–35°C	35–45°C
(100)	57.9	2.2	2.0	1.8
(110)	48.9	1.7	1.8	1.9
(111)	43.5	1.9	1.7	1.9

TABLE II

Rate of aluminium dissolution v and electron work function W in 1M-NaOH at 25°C

Plane	$v \cdot 10^2$ $\text{kg m}^{-2} \text{ h}^{-1}$	W^a eV
(100)	5.5	4.2
(110)	6.3	3.65
(111)	6.9	4.05

^a Ref.¹⁰.

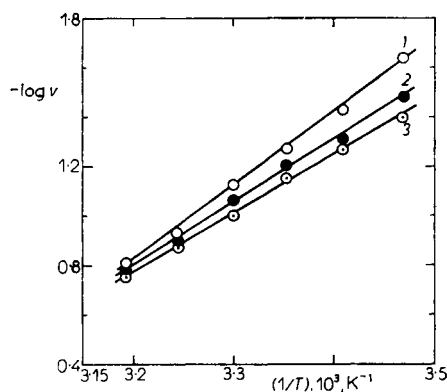


FIG. 3
Temperature dependence of rate of dissolution of aluminium single crystal in 1M-NaOH at $P_{\text{O}_2} = 0.1 \text{ MPa}$. Plane: ○ (100), ● (110), ○ (111)

The apparent activation energies of aluminium in 1M-NaOH increase in order

$$E_{111}^* < E_{110}^* < E_{100}^*$$

and the dissolution rates increase in the reverse order,

$$v_{100} < v_{110} < v_{111}.$$

This is consistent with what we expect based on the chemical kinetics concept.

Of physical characteristics that may relate appreciably to the reactivity of the crystallographic planes, the electron work function and atomic density can be considered. As to the former, available data are not unique. The values by Lang and Kohn¹⁰ (Table II) increase in order

$$W_{110} < W_{111} < W_{100}$$

while the atomic densities increase in order

$$\rho_{110} < \rho_{100} < \rho_{111}.$$

Thus, the only fact to be deduced from the comparison of the kinetic parameters with the physical characteristics of the surface is that the slowest dissolving plane, with the highest apparent activation energy, is that exhibiting the highest electron work function, whereas the most reactive plane, with the lowest apparent activation energy, is that possessing the highest atomic density.

The results suggest that the mechanism of reaction of aluminium single crystals in aqueous solution of NaOH is the same as for polycrystalline aluminium, as has been discussed in detail previously⁸.

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