
STUDY OF POTENTIAL OSCILLATIONS DURING REACTION OF AN ALUMINIUM SINGLE CRYSTAL WITH AN AQUEOUS KOH SOLUTION

Ivan HALAŠA and Milica MIADOKOVÁ

Department of Physical Chemistry, Comenius University, 842 15 Bratislava

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The authors investigated periodic potential changes measured on oriented sections of Al single crystals during spontaneous dissolution in dilute aqueous solutions of KOH, with the aim to find optimum conditions for the formation of potential oscillations. It was found that this phenomenon is related with the kinetics of the reaction investigated, whose rate also changed periodically. The mechanism of the oscillations is discussed in view of the experimental findings.

Aluminium is a perspective anodic material to be used in alkaline cells¹⁻⁴. Its corrosion behaviour in dilute aqueous solutions of alkali hydroxides has been investigated by many authors, however their views about the dissolution mechanism are not unified. Centnerszwer^{5,6} measured volumetrically the dissolution rate of Al in NaOH and NH₄OH; he assumed that the reaction is accompanied by an interaction between the metal and the OH⁻ ions. Schikorr⁷ observed during dissolution of Al in NaOH an induction period during which no hydrogen was evolved and which increased on adding Na₂SiO₃ into the solution. He obtained similar results with KOH and Ba(OH)₂; the rate of dissolution depended on the purity of the material and sample dimensions in all cases. Streicher^{8,9} studied the influence of NaOH concentration and temperature on the dissolution rate of Al and on its electrode potential. He observed an incubation period during which no hydrogen was evolved, an induction period during which a surface oxide film was dissolved, and a reaction period during which the reaction rate was not influenced by the film. The potential was equilibrated after 2 hours and its stationary value depended on both the temperature and concentration of the solution. Balezin and Klimov¹⁰ found in their systematic study that the nonlinear course of the concentration dependence of the dissolution rate of Al in solutions of alkali hydroxides is related with changes of the viscosity, conductance, and oxygen solubility. Loshkarev¹¹, Milička¹², and Macdonald⁴ found that the open-circuit potential of Al changes monotonically with the time during dissolution, attaining a steady value after 20 to 60 min according to the reaction conditions. Sysoeva¹³ considers the potential to be more suitable for following the dissolution rate than kinetic measurements

proper. Most authors studied polycrystalline Al of varying composition, which makes a comparison of their results problematical.

Oscillations of the electrode potential were first observed by Ostwald¹⁴ during dissolution of Cr in HCl. Periodic potential changes were also observed on steel in a solution of H₂SO₄ with a period of up to 25 h and they were attributed to alternate passivation and activation processes¹⁵. Potential oscillations of an Al electrode were first observed during anodic dissolution in 1M-NaOH¹⁶; a recent study¹⁷ showed that such oscillations occur also during spontaneous dissolution of an oriented Al single crystal on the {110} surface in 2–8M-NaOH. The oscillations were most distinct in 4M-NaOH, their induction period was 90 min, period 30 min, and amplitude about 20 mV, they were sensitive against convection and the measurements were done in the presence of air.

The aim of the present work was to exclude any influence of the air oxygen and to find optimum conditions for the potential oscillations of Al, to study in more detail their mechanism and the eventual relation with the kinetics of Al dissolution.

EXPERIMENTAL

Experiments were made in a laboratory flask of 1 dm³ holding capacity, placed in an ultra-thermostat; the temperature was kept at 25 ± 0.1°C. The solution was stirred with an electromagnetic stirrer at 1 000 rpm.

Oriented sections of an Al single crystal were used as in ref.¹⁸; the samples were activated 5 min in 20% NaOH, washed in redistilled water, dried, and immersed into the reaction solution at a distance of 1 cm from the stirrer.

The potential of Al was recorded as in ref.¹⁷ in parallel to the kinetic measurements. The reaction rate was measured as the volume of hydrogen evolved per unit time (in dm³ m⁻² min⁻¹). To this end we used the volumetric method after Akimov¹⁵. All solutions were deaerated with hydrogen by 10 min bubbling before the reaction and they were kept in a hydrogen atmosphere during the measurements.

Chemicals were of reagent grade, solutions were prepared from redistilled water. The accuracy of the potential measurements was ±0.5 mV and their reproducibility ±5 mV. The results of kinetic measurements are average from 3 experiments and are reproducible to within 3–5%.

RESULTS AND DISCUSSION

Influence of OH⁻ Concentration on the Potential of Al

We expected, by analogy to ref.¹⁷, periodic potential changes in the medium of NaOH in hydrogen atmosphere on all faces of the Al crystal, however this was the case only with the {110} face and not with {100} and {111}. In 2–3M-NaOH, damped oscillations occurred after an induction period of 90 min. In 3.5M-NaOH the oscillations were undamped with an induction period of 120 min, and in 4M-NaOH the induction period was 480 min. At concentrations of NaOH equal to or higher than

5 mol dm^{-3} no periodic potential changes were observed during the experimental time interval (10 to 15 h). The oscillation period was prolonged up to 180 min compared to the same system in the presence of air, and the maximum potential excursion attained 150 mV. In the medium of KOH periodic potential changes were observed even on the $\{100\}$ crystal face and the induction period was 170 min in 4M-KOH, but we preferred to study the oscillations on the $\{110\}$ face, where the induction period was shorter (to save time).

The influence of KOH concentration on the time course of the potential of Al $\{110\}$ face is shown in Figs 1 and 2. Damped oscillations with an induction period of about 1 h appeared in 2M-KOH, but in 3.5M-KOH they became undamped with an induction period of 90 min. Their amplitude attained up to 120 mV. At concentrations of KOH higher than 4.5 mol dm^{-3} no periodic potential changes were observed. With the damped oscillations, the potential attained a steady value corresponding about to the peak of the first wave after 5 h of reaction. The amplitude decreased considerably with the time, in contrast to the period, which was constant.

With undamped oscillations, the maximum potential excursion and the length of the period were constant. The transition from damped to non-damped oscillations occurred in the interval from 3 to 3.5M-KOH; the highest concentration at which the oscillations could be observed was $4.5\text{--}5 \text{ mol dm}^{-3}$ and the lowest was 1.5 to 2 mol dm^{-3} . These limits were determined by adding water or concentrated KOH into the solution, whose volume changed negligibly. The determination of the upper concentration limit is illustrated in Fig. 3. A similar dependence was observed in following the transition from damped to non-damped oscillations and in determining the lower concentration limit of the damped oscillations.

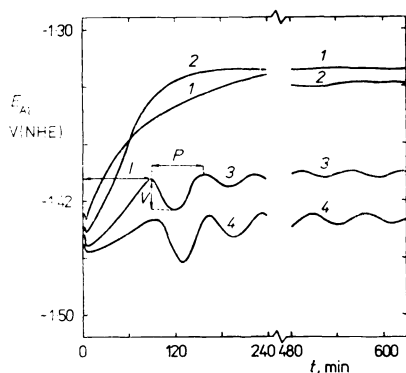


FIG. 1

Influence of KOH on the time course of the potential of Al $\{110\}$. Concentration of KOH, mol dm^{-3} : 1 0.5; 2 1; 3 2; 4 3

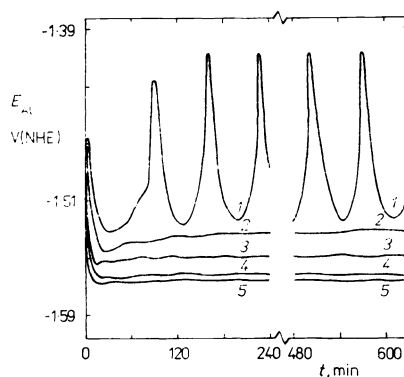


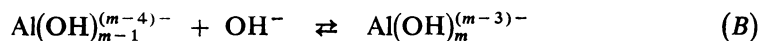
FIG. 2

Influence of KOH on the time course of the potential of Al $\{110\}$. Concentration of KOH, mol dm^{-3} : 1 4; 2 5; 3 6; 4 8; 5 12

According to our knowledge, no theory exists which would explain such regular potential changes. The reaction



is in alkaline medium connected with the formation of various hydroxo complexes of aluminium¹¹:



with $m = 1-6$.

The rapid specific adsorption of OH^- ions and their interaction with surface Al atoms causes instantaneous formation of a high concentration of intermediate products, such as $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_2^+$, which are only stable in weakly acidic medium^{19,20} and change rapidly to $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$, or $\text{Al}(\text{OH})_6^{3-}$. This leads probably to some steady state characterized by adsorption of the products on the electrode surface connected with the evolution of hydrogen, whereby the initial increase of the potential can be elucidated. Partial lowering of the OH^- concentration at the electrode surface probably causes the reaction to pass into the second stage, in which the rate of dissolution of the products is comparable to the rate of their formation²¹, and this leads to a potential decrease ("denudation" of the metal surface takes place). In this way the specific adsorption of OH^- ions is enhanced and the mentioned steady state is formed, i.e. the potential is shifted to more anodic values. If the considered products are desorbed into the solution, the steady state is disturbed, which leads to a rapid shift of the potential to more cathodic values, the conditions for the specific adsorption of OH^- ions are restored and again the steady state is formed. These concepts are in accord with those about stationary and non-stationary diffusion of OH^- ions to the metal surface¹¹. The different magnitudes of the amplitude and period of the oscillations and the fact that they are damped

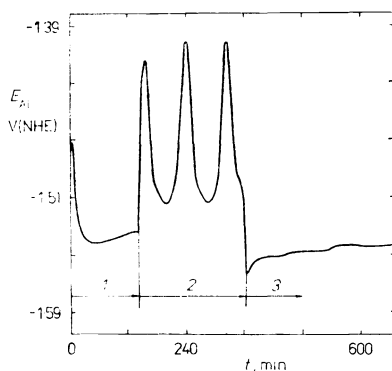


FIG. 3
Time dependence of the potential of Al {110} during changing concentration of KOH, mol dm⁻³: 1 5; 2 4.5; 3 6

or non-damped according to the KOH concentration may be related with the solubility of the particular reaction products involved in the scheme (B). It follows that a certain critical concentration of the hydroxide is necessary for the oscillations to be formed and perhaps also to vanish. It can be seen from Fig. 4 that the maximum excursion of the potential of Al{110} tends, in contrast to the period, to a limiting value with increasing concentration. Therefore, it can be assumed that at high KOH concentrations (more than 5 mol dm^{-3}) potential oscillations could also be formed after some time with a very long induction period and period.

The different behaviour of the crystal faces {110}, {100}, and {111} in alkaline solutions and the potential oscillations may be connected with semiconducting properties of the surface layers. For this reason, it would be premature to consider a derivation of an equation for the potential of a second-order electrode, unless further experiments are made.

Influence of Stirring on the Potential of Al

This effect was followed during dissolution of Al{110} in 4M-KOH. This was found as the optimum concentration for the oscillations. It turned out that the potential oscillations were undamped under these conditions regardless of the convection, which was not necessary. It can be seen from Fig. 5 that the rotation rate influences only the amplitude of the oscillations and not their period, evidence for the formation of a steady state at the metal surface. At 800 rpm, the amplitude acquired its maximum value which did not increase further with the rotation rate. Thus, the chosen rate¹⁸

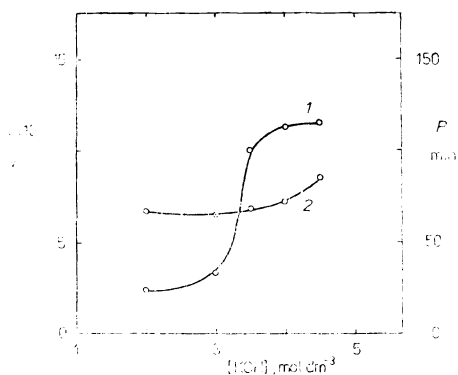


FIG. 4

Dependence of the maximum excursion, V (curve 1) and of the period, P (curve 2) of the potential oscillations of Al{110} on KOH concentration

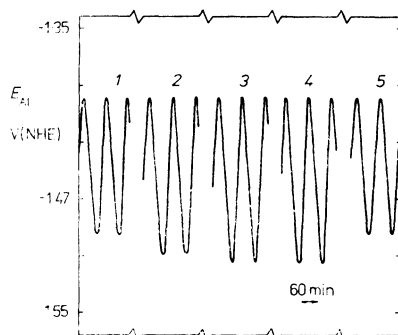


FIG. 5

Time dependence of the potential of Al{110} in 4M-KOH at various stirring rates, min^{-1} : 1 0; 2 300; 3 800; 4 1 000; 5 0

of 1 000 rpm was sufficient to ensure suitable hydrodynamic conditions at the electrode surface. After stopping the convection, the potential amplitude attained its initial value, hence no time effect took place.

Since the character of the potential oscillations of $\text{Al}\{110\}$ did not change during the reaction, it can, in accord with the literature²², be assumed that the periodic changes are related with the rate of surface reactions rather than with physical processes such as diffusion or convection. This was substantiated by an experiment in which an Al electrode was rapidly transferred during the reaction into a solution which did not contain dissolved Al. The potential course remained unchanged (Fig. 6a). Hence, the reaction was not influenced by the metal ions dissolved during the reaction. Similarly, we checked the assumption about "denudation" of the metal surface and formation of a steady state by adsorption of the reaction products on the Al surface. If the reaction was interrupted by rinsing with water at the maximum of the potential-time dependence, the potential course was after immersion into the electrolyte similar to that at the beginning of the reaction (after activation of the sample) with the same induction period (Figs 6b and 2). If the reaction was interrupted by rinsing at the minimum of the potential-time dependence, the potential showed oscillations without the induction period (Fig. 6c).

Influence of Temperature on the Potential of Al

The influence of the temperature on the potential of $\text{Al}\{110\}$ was followed in 4M-KOH at temperatures from 10 to 35°C. As with the concentration dependence, there was a lower temperature limit, namely 10°C, at and below which the potential ceased to oscillate and it attained a constant limiting value. When the temperature increased, non-damped oscillations appeared, whose maximum amplitude approached about 130 mV with increasing temperature and did not change with the time. The period behaved similarly and its growth with the temperature had an exponential character similar to the concentration dependence. The stationary or mean value

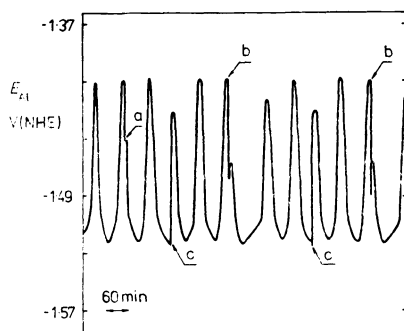


FIG. 6
Time dependence of the potential of $\text{Al}\{110\}$ during a replacement of the solution; b rinsing with water at the maximum potential; c rinsing with water at the minimum potential

of the potential was shifted to more negative values with increasing temperature or reaction rate. The maximum potential excursion, periods, and stationary or mean potential values at different temperatures are given in Table I. It can be assumed that a further temperature increase would cause the oscillation period as well as the induction period to attain such high values that they could not be measured during one experiment. Moreover, the Al electrodes would suffer a considerable weight loss at such conditions. Therefore, such experiments were not realized.

It is obvious that the solubility of the envisaged end products is controlled by the temperature changes, which accordingly influence the course of the electrode potential. It is also possible that at higher temperatures soluble complexes are formed that contain more than one central Al atom, namely $Al_x(OH)_y$, where $x = 2, 3, \dots, 14$ and $y = 2, 4, \dots, 34$ as suggested in the literature^{20,23}, causing more rapid "denudation" of the Al surface connected with a potential shift toward more negative values.

TABLE I

Influence of the temperature on the maximum excursion, period, and on the stationary or mean value of the potential of Al {110} during dissolution in 4M-KOH

t °C	V mV	P min	E_{st} V
10	—	—	-1.385
15	6	54	-1.398
20	76	54	-1.428
25	120	72	-1.466
30	130	81	-1.481
35	131	153	-1.492

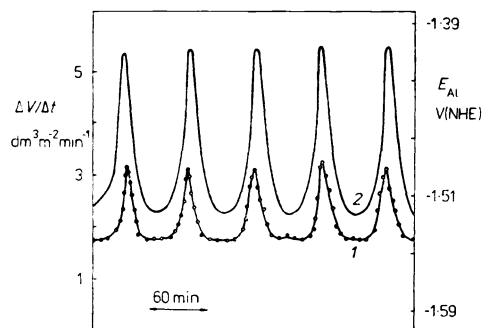


FIG. 7

Dependence of the rate of dissolution of Al {110} on the time (curve 1) and the potential-time dependence for the same electrode in 4M-KOH (curve 2)

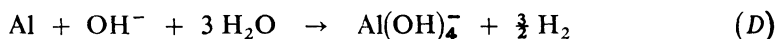
Kinetic Study of Al Dissolution

The reaction kinetics was followed in parallel to recording the potential changes during dissolution of Al{110} in KOH. We measured the volume of hydrogen formed during the reaction²⁴

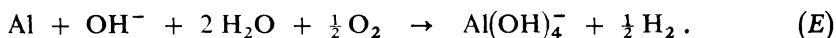


During a monotonic change of the potential the rate of H₂ evolution did not change, evidence for a rapid attainment of the steady state mentioned. This phenomenon is the result of constant conditions at the metal/electrolyte interface during the reaction; the corrosion products are transported uniformly from the Al surface into the solution or beyond it (H₂).

Together with the potential oscillations, we recorded periodic changes of the rate of H₂ evolution (Fig. 7). It turned out that there is a close relation between the two phenomena. The study of this relation was facilitated by the absence of oxygen in the reaction system, since its chemisorption on the Al surface could interfere with the reaction. The overall reaction⁴



together with reaction (B) corresponds to the dissolution of Al in the absence of oxygen as a depolarizer in contrast to the results obtained for spectrally pure polycrystalline Al in oxygen atmosphere²⁵:



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