Influence of alkali metal hydroxides on the reaction of aluminium monocrystals

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Dedicated to Professor Ľ. Treindl, DrSc., in honour of his 60th birthday

The influence of alkaline medium on kinetic behaviour and potential of aluminium monocrystal was investigated in consideration of surface orientation of the aluminium samples. It has been found that the cation present in the hydroxide solution plays the decisive part in aggressiveness of the used hydroxide. In the medium of NaOH and KOH the kinetic and electrochemical anisotropy of the basal oriented sections {100}, {110}, and {111} of the monocrystal was observed. The different reactivity of individual samples is considered to be due to different electron affinity as well as to different density of surface atoms.

Изучено влияние щелочной среды на кинетическое поведение и потенциал монокристалла алюминия в зависимости от поверхностной ориентации образцов алюминия. Обнаружено, что агрессивность использованной гидроокиси в решающей мере зависит от катиона, находящегося в ее растворе. В среде NaOH и KOH наблюдалась кинетическая и электрохимическая анизотропия основных ориентированных слоев {100}, {110} и {111} монокристалла. Различная реакционноспособность отдельных образцов сопоставляется с различной электронной работой выхода, а также с различной плотностью поверхностных атомов.

The monocrystals with oriented sections are more and more frequently used as experimental material for revealing the essence of chemical reactivity of metals. That results from the fact that their surface is physically better defined when compared with polycrystalline materials.

Most papers on chemical behaviour of the monocrystals of aluminium deal with the reactivity of these monocrystals in gaseous medium. The chemical and electrochemical behaviour of aluminium monocrystal in the medium of NaOH was, to a certain extent, described in papers {1, 2]. The rate of aluminium dissolution in alkali metal hydroxides and in NH₄OH has hitherto systematically been investigated only by *Balezin* and *Klimov* [3] for polycrystalline materials.

The aim of this study has been more profoundly to investigate the effect of alkali metal hydroxides on kinetic and electrochemical behaviour of the mono-

crystal of aluminium with regard to its surface orientation and to disclose whether the observed changes in potential bear upon the kinetics of the reaction.

Experimental

The experiments were carried out in a flask of 1 dm^3 volume dipped in an ultrathermostat at the regulated temperature of $(25 \pm 0.1)\,°C$. The reaction medium was uniformly stirred by means of an electromagnetic stirrer working with constant number of revolutions 1000 min^{-1}.

The chemicals used were anal. grade reagents and redistilled water was employed for the preparation of solutions. The precision of potential measurements was ± 0.5 mV and the reproducibility varied within the interval ± 5 mV. The results of kinetic measurements are arithmetic means of three experiments and the reproducibility varies within the range 3—5 %.

Oriented sections of a monocrystal of aluminium were used as experimental material [1]. Before use the samples were activated in 20 % NaOH for 5 min. In order to provide equal hydrodynamic conditions for individual experiments, the samples were washed with distilled water, dried and dipped into the solution at the constant distance of 1 cm from the stirrer.

The potential of aluminium was taken by means of a recorder simultaneously with kinetic measurements according to the mode described in paper [2]. The reaction rate v referred to 1 m^2 of surface (expressed in dm^3 m^{-2} h^{-1}) was given by the slope of the relationship between the volume of generated hydrogen reduced to standard conditions [4] and time determined for the interval of 30—90 min. The instantaneous reaction rate v_0 (expressed in dm^3 m^{-2} min^{-1}) was determined from the volume increase caused by the hydrogen generated in one minute. The volumetric method according to *Akimov* [5] was used for determining this increase. All solutions were bubbled with hydrogen for 10 min before the reaction and the experiments were carried out in hydrogen atmosphere.
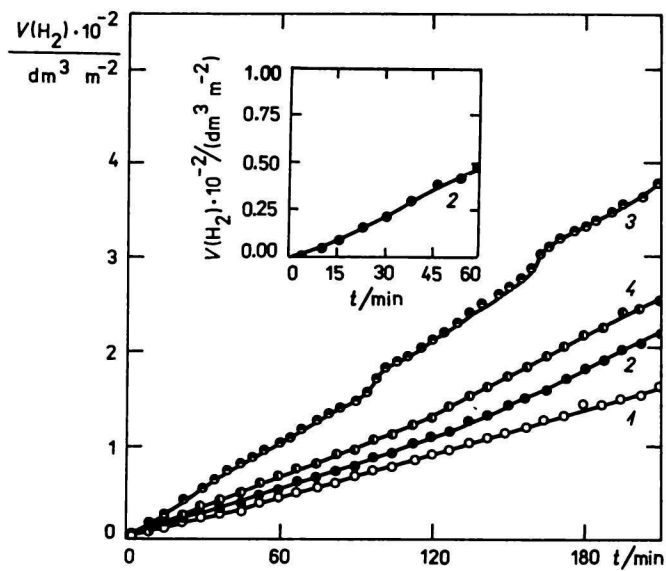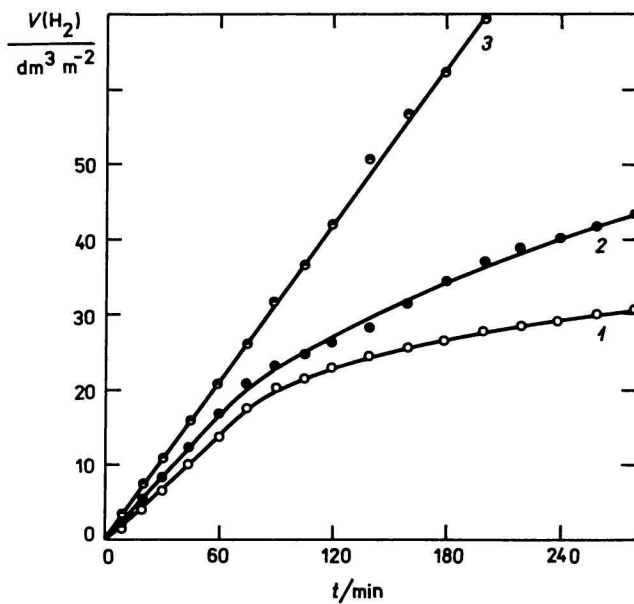
Results and discussion

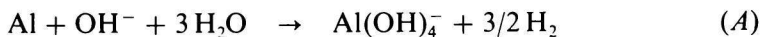*Influence of alkali metal hydroxides on the reaction kinetics*

The effect of LiOH, NaOH, and KOH on aluminium dissolution was examined on three basal faces of the monocrystal ({100}, {110}, {111}). The dependence

of the hydrogen evolved in reaction (A) on time is given for some experiments in Figs. 1 and 2.

$$Al + OH^- + 3\,H_2O \quad \rightarrow \quad Al(OH)_4^- + 3/2\,H_2 \qquad (A)$$

In the interval of 30—90 min the dissolution of aluminium proceeded uniformly in all cases, the surface of samples remained almost unchanged and the reaction rate v could be determined from the slope of the curve expressing the volume of the evolved hydrogen as a function of time. The initial uneven course of dissolution due to a short induction period gradually disappeared (Fig. 2). This fact gives evidence of constant relations at the metal—solution interface which did not change in this stage of reaction and thus the arising products of corrosion were evenly transported from the surface of samples into solution.

As far as LiOH is concerned, a deviation from linearity of the investigated relationships (Fig. 1) started to appear after 90 min at lower concentrations for all three examined surfaces. The determination of reaction rate with respect to individual crystal faces did not reveal any kinetic anisotropy. The variation of the rate of dissolution did not exceed the reproducibility of experiments (Table 1). The retardation of dissolution of aluminium in the presence of LiOH may be related with the formation of insoluble in water lithium aluminates or hydroxoaluminates the deposition of which on the surface was even visually observable. We may assume that a curvature of the investigated plots due to the formation of insoluble products should appear after a certain time in more concentrated LiOH solutions, too.

The dissolution of aluminium in solutions of NaOH has little linear course similarly as described in paper [1] for solutions with oxygen atmosphere. However, the reaction rate was lower when compared with the corresponding rates in the system with oxygen atmosphere. That is to be expected because oxygen plays the role of one of the depolarizers [6] in reaction (B).

$$Al + OH^- + 2\,H_2O + 1/2\,O_2 \quad \rightarrow \quad Al(OH)_4^- + 1/2\,H_2 \qquad (B)$$
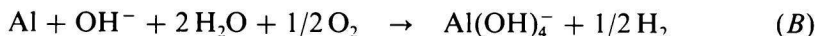
Nevertheless, the kinetic anisotropy remained preserved. The reaction rate with respect to crystal face used increased in the order: {100}, {110}, {111}. The face {111} with the highest atomic density was the most reactive while the face {100} with smaller atomic density and higher electron affinity was the least reactive [1, 7].

Analogous order of the dissolution rates with respect to the crystal face used was also observed for KOH solutions (Table 1). The moderate deviation from linearity of the relationship between volume of the evolved hydrogen and time (Fig. 2) may be related with the acceleration of the reaction due to an increase in real surface of samples caused by the failure in corrosive medium [8].

Table 1

Rate of aluminium dissolution ($v/(dm^3\ m^{-2}\ h^{-1})$) as a function of concentration or activity of MeOH for differently oriented samples

c(MeOH) mol dm⁻³	a(LiOH) mol dm⁻³	a(NaOH) mol dm⁻³	a(KOH) mol dm⁻³	LiOH			NaOH			KOH		
				{100}	{110}	{111}	{100}	{110}	{111}	{100}	{110}	{111}
0.5	0.29	0.34	0.36	12.9	14.0	12.9	42	48	51	40	46	45
1	0.52	0.68	0.74	14.0	15.2	16.4	45	51	65	46	52	66
2	0.97	1.42	1.73	14.8	15.2	17.0	75	75	91	73	72	89
3	1.40	2.35	3.15	18.1	17.0	19.1	87	92	100	88	90	98
3.5	1.61	2.92	4.13	18.4	19.3	—	91	93	—	90	90	—
4	1.82	3.61	5.26	18.8	20.5	18.9	88	94	113	88	92	110
4.5		4.43	6.71				87	97	—	88	95	—
5		5.39	8.35				88	97	116	87	96	112
6		7.79	12.8				87	96	116	84	94	110
8		16.0	29.3				80	92	112	80	85	108
10		32.2	60.5				81	81	110	78	80	102
12		62.2	122.4				77	79	100	72	80	89

Influence of aggressiveness of medium on the reaction kinetics

The investigation of the reaction kinetics at varying concentration of the used hydroxides has shown that the rate of metal dissolution gradually increased with increasing hydroxide concentration and after reaching an indistinct maximum (in concentration region 4—8 mol dm^{-3}) it decreased. At isomolar concentrations of the hydroxide the reaction rate was markedly the lowest when using LiOH and it was the highest in the cases of NaOH. The order of reaction rates found for NaOH and KOH and different crystal faces was preserved (Table 1). In order to eliminate unequal activity of isomolar hydroxides the reaction rate was also investigated as a function of hydroxide activity. The rate of the investigated reaction at isomolar activities of hydroxides irrespective of face orientation of monocrystals is much lower when LiOH is used than it is for NaOH or KOH.

Thus the aggressiveness of a given hydroxide is significantly affected by the cation present in the solution in spite of the fact that it does not directly participate in the reaction. The aluminium surface in aggressive medium contains a great abundance of water molecules as well as adsorbed rests of oxygen from solution and the effect of the cations evidently consists in influencing the arrangement of these molecules and the relations in interface by their solvation properties. The cations form ion associates and this ability increases with their inclination to adsorption and their ability to transfer a charge in the order from Li$^+$ to K$^+$ [9]. Since a cation with a larger radius which is less hydrated forms ion associates exhibiting smaller stability constants than firmly hydrated Li$^+$ and more easily undergoes desolvation, it ought to accelerate the reaction more than a cation with smaller radius. The anomalous behaviour of aluminium in KOH solution with respect to NaOH solution of equal concentration is obviously caused not only by unequal activity but also by the fact that the solubility of the arising potassium hydroxoaluminates is much lower than the solubility of sodium salts though, in contrast to LiOH, it did not manifest itself in the curvature of the relationship between time and amount of the evolved hydrogen.

The dependence of reaction rate on hydroxide concentration which exhibits a maximum is typical of metal dissolution [10, 11]. *Balezin* and *Klimov* [3] identify its course with the course of the conductivity depending on OH$^-$ concentration while the rate of aluminium dissolution is proportional to the conductivity of electrolyte. The authors of paper [12] connect the nonlinear course of this relation describing the dissolution of metals in alkaline media with a change in viscosity or solubility of oxygen in the medium as well as with the change in water activity depending on OH$^-$ concentration. It results from these facts that the character of the dependence of the rate of metal dissolution on

Table 2

Stationary potential of aluminium (E_{st}/V) as a function of concentration of MeOH for differently oriented samples

$c(MeOH)$ mol dm^{-3}	LiOH			NaOH			KOH		
	{100}	{110}	{111}	{100}	{110}	{111}	{100}	{110}	{111}
0.5	-1.573	-1.568	-1.582	-1.269	-1.286	-1.270	-1.378	-1.331	-1.293
1	-1.670	-1.676	-1.668	-1.330	-1.310	-1.302	-1.380	-1.335	-1.303
2	-1.758	-1.745	-1.750	-1.401	-1.379	-1.335	-1.409	-1.400	-1.360
3	-1.774	-1.769	-1.781	-1.429	-1.402	-1.374	-1.449	-1.436	-1.392
3.5	-1.806	-1.798	—	-1.447	-1.457	—	-1.452	-1.458	—
4	-1.823	-1.826	-1.830	-1.514	-1.460	-1.401	-1.481	-1.466	-1.435
4.5				-1.542	-1.546	—	-1.492	-1.470	—
5				-1.551	-1.552	-1.446	-1.544	-1.534	-1.450
6				-1.555	-1.558	-1.449	-1.562	-1.550	-1.473
8				-1.562	-1.558	-1.487	-1.563	-1.562	-1.498
10				-1.567	-1.560	-1.501	-1.569	-1.564	-1.529
12				-1.580	-1.566	-1.531	-1.582	-1.574	-1.558

hydroxide concentration cannot fully be generalized because it is, for the most part, given by the reaction mechanism and also depends on physical properties of the medium.

Effect of alkali metal hydroxides on electrode potential of aluminium

Simultaneously with kinetic measurements we also recorded the temporal changes in the electrode potential of aluminium the course of which depended on kind and concentration of the used hydroxide as well as on orientation of the aluminium samples.

As to LiOH, the dependence of potential on time exhibited monotonous character. After a rapid initial increase a flat local minimum came into existence and approximately after 30 min the potential was established at a certain stationary value E_{st} which shifted to more negative values with increasing hydroxide concentration. The electrochemical anisotropy of individual crystal faces was not observed (Table 2).

As far as NaOH is concerned, the anisotropic properties of the used samples appeared. At isomolar hydroxide concentrations the stationary potential grew to more positive values with increasing reaction rate (Table 2) in the order {100}, {110}, {111}.
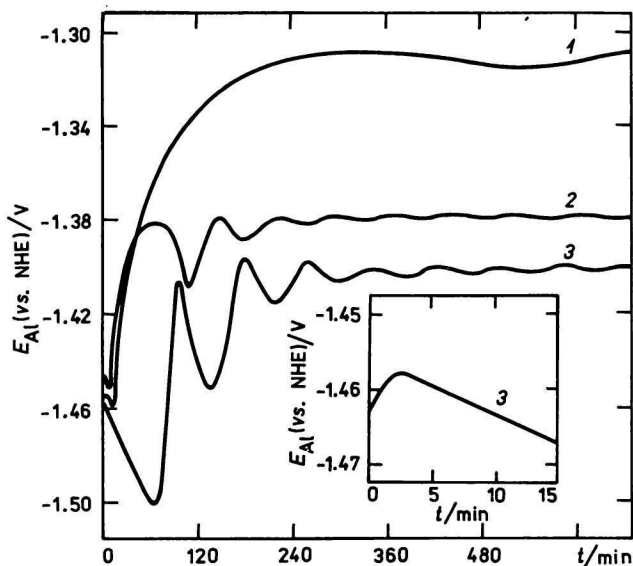

Fig. 3. Variation of potential with time for Al {110} and different concentrations of NaOH. $c(NaOH)/(mol\ dm^{-3})$: *1.* 1; *2.* 2; *3.* 3.

In addition, some damped and at concentration 4 mol dm^{-3} even nondamped oscillations of potential were observed on the face Al {110} in line with paper [2], but the values of period and maximum deflection of oscillations were different and the induction period varied between 60 and 150 min. The typical dependence of potential on time with monotonous as well as oscillating course is represented in Fig. 3.

If KOH was used, the oscillating character of potential was observed on the face Al {100}, too, while for nondamped oscillations observed already in 3.5 M solution of KOH the mean value of potential between the maximum and minimum height of oscillations was regarded as stationary value. The nondamped course of oscillations for the face Al {100} in comparison with the monotonous course of potential observed for the face Al {111} is represented in Fig. 4. A more detailed study of the potential oscillations for aluminium monocrystals has been described in paper [13].

We may assume that the fast specific adsorption of the OH$^-$ ions and their interaction with the surface atoms of metal results in instantaneous formation of a high surface concentration of intermediates of the Al(OH)$^{2+}$ and Al(OH)$_2^+$ type which are stable only in weakly acid medium [14, 15] and are rapidly

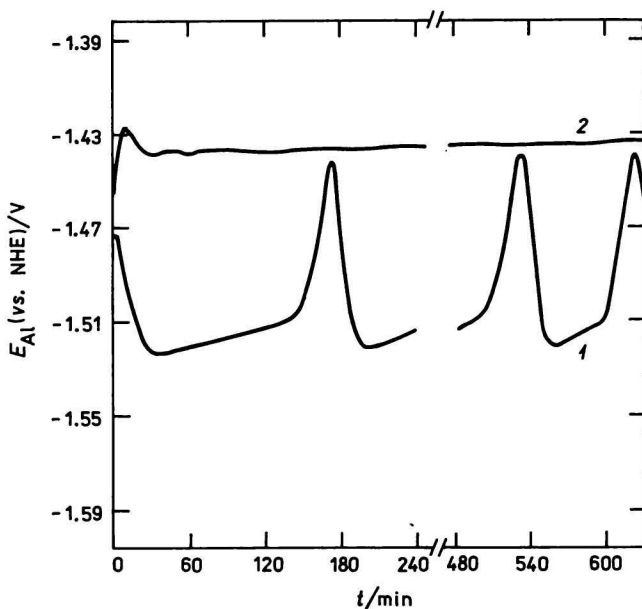*Fig. 4.* Variation of potential with time for 4 M-KOH and aluminium crystal faces. *1.* Al {100}; *2.* Al {111}.

transformed in products of the $Al(OH)_3$, $Al(OH)_4^-$ or $Al(OH)_6^{3-}$ type. This process might lead to establishment of a certain stationary state characterized by adsorption of products on the surface of electrode and proportional to generation of hydrogen. This fact could be responsible for the initial rise in potential as well (Fig. 3). A certain decrease in OH^- concentration close to the surface probably makes the reaction come into the further stage in which the rate of passage of the products into solution is comparable with the rate of their formation [16]. This state is characterized by a decrease in potential ("denudation of metal surface" sets in). In this way, however, the conditions of specific adsorption of the OH^- ions are still more facilitated and the mentioned steady state is established, *i.e.* the potential shifts to more positive values. Provided a more rapid desorption of the mentioned products into solution takes place again, the steady state is disturbed, which is accompanied with an abrupt change in potential towards more negative values. Then the conditions suited for specific adsorption of the OH^- ions and repeated establishment of steady state are restored. These assumptions are consistent with the idea of stationary and nonstationary diffusion of the OH^- ions towards metal surface [17]. The different electrochemical behaviour of the oriented samples Al $\{100\}$, $\{110\}$, and $\{111\}$ in alkali hydroxide solutions may be related with different solubility of the products of the consecutive reaction steps involved in scheme (C) [18], with influence of the temperature gradient originating in proximity to electrode surface or with different semiconductive properties of the arising and decaying surface layers.

$$Al(OH)_{m-1}^{(m-4)-} + OH^- \ \rightleftarrows \ Al(OH)_m^{(m-3)-} \qquad m = 1\text{—}6 \qquad (C)$$

The stationary values of electrode potential decreased with increasing activity of all hydroxides used towards more negative values (Table 2, Fig. 5) in contrast to the relationship between the rate of metal dissolution and hydroxide activity which exhibited a maximum (Table 1). For all hydroxides and differently oriented samples the course of the relationship $E_{st} = f(a_{MeOH})$ corresponded to empirical relation (1) which was formally identical with the classical Nernst equation

$$E_{st} = k_1 - k_2 \log a_{MeOH} \qquad (1)$$

The linear course of the logarithmic dependence of stationary potentials on hydroxide activity was verified and the parameters k_1 and k_2 of eqn (1) were calculated by regression method. The values of constants k_1 and k_2 as well as the values of regression coefficients r are given in Table 3. It can be seen that the values of prelogarithmic term k_1 are influenced not only by the kind of cation but also by orientation of the used samples, while the parameter k_2 depends on the used hydroxide.
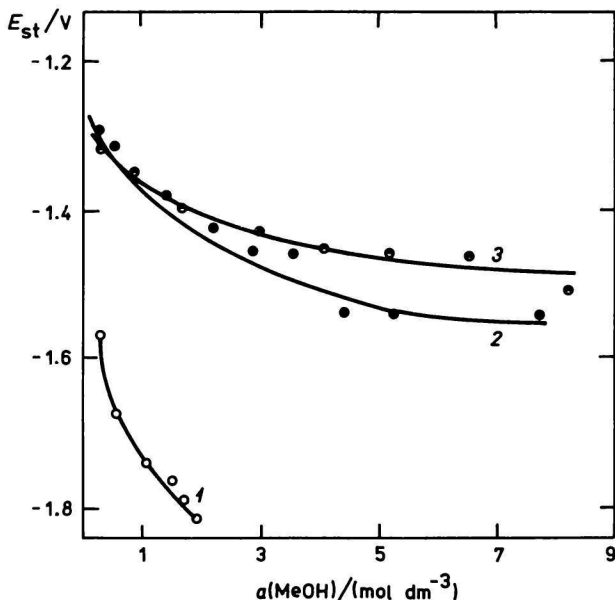
Fig. 5. Stationary value of potential of Al {110} as a function of MeOH activity. *1.* LiOH; *2.* NaOH; *3.* KOH.

Relation between kinetic and electrochemical behaviour of the system

It has been found for monotonous course of potential that the instantaneous reaction rate v_0 did not change after elapsing of induction period (approximately for 15 min), which evidences a rapid formation of the mentioned steady state.

Table 3

Values of constants k_1 and k_2 in eqn (*1*) and values of regression coefficient for different hydroxides and differently oriented samples of aluminium monocrystal

MeOH	Face	k_1	k_2	r
LiOH	{100}	−1.7449	0.3017	−0.9919
	{110}	−1.7441	0.3009	−0.9896
	{111}	−1.7448	0.3022	−0.9971
NaOH	{100}	−1.3838	0.1488	−0.9085
	{110}	−1.3714	0.1472	−0.8964
	{111}	−1.3292	0.1438	−0.9880
KOH	{100}	−1.4120	0.1094	−0.9474
	{110}	−1.3828	0.1115	−0.9484
	{111}	−1.3382	0.1103	−0.9921

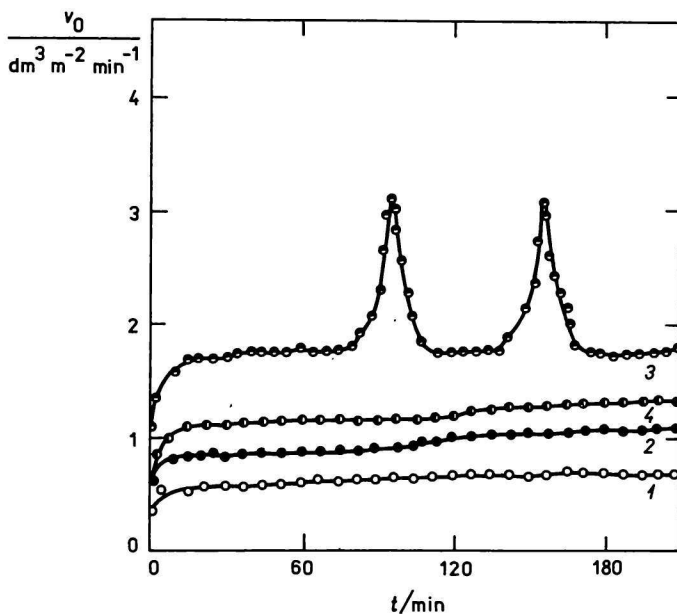*Fig. 6.* Instantaneous rate of dissolution as a function of time for Al {110} and different concentrations of KOH.
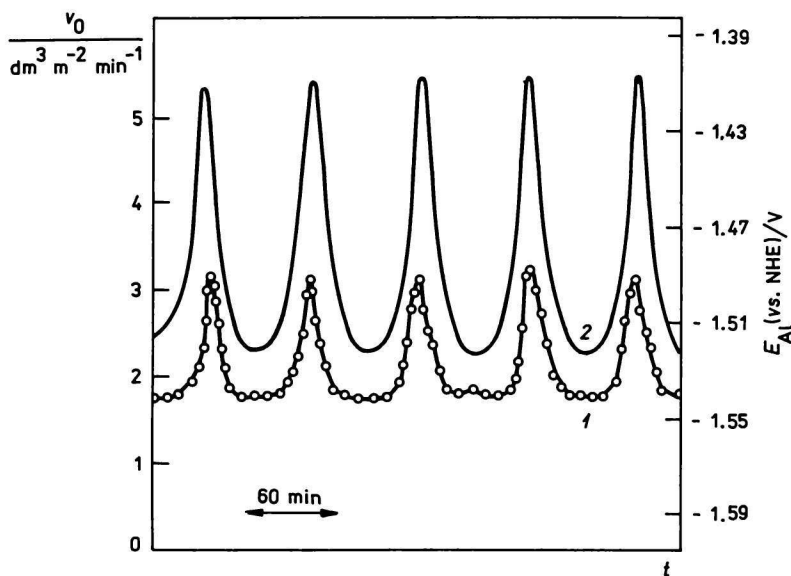$c(KOH)/(mol\ dm^{-3})$: *1.* 0.5; *2.* 1; *3.* 4; *4.* 12.

Fig. 7. Instantaneous rate of dissolution for Al {110} as a function of time (curve *1*) and variation of potential with time for the same sample (curve *2*) in 4 M-KOH.

Probably owing to relatively small variation of potential (± 20 mV at maximum) no changes in instantaneous rate were observed in systems with damped oscillations of potential, either (Fig. 6, curves *1, 2, 4*). A certain increase in instantaneous reaction rate is, as mentioned earlier, evidently connected with the increase in real surface of samples because this change did not manifest itself in the corresponding temporal course of potential. On the other hand, it has been revealed that the oscillation changes in instantaneous rate which appeared in some systems after about 90 min following the reaction start (Fig. 6, curve *3*) and were, to a certain extent, indicated during investigations of the kinetics of aluminium dissolution (Fig. 2, curve *3*) are in direct relation with nondamped oscillations of potential (Fig. 7).

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