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Electrochemical properties of aluminium alloys containing indium, gallium and thallium

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The electrochemical behaviour of aluminium alloyed with small amounts (up to 0·2%) of indium, gallium and thallium has been investigated. It has been found that these additions result in:

(a) A considerable shift of the rest potential in the negative direction (to 1·4–1·7 V versus SCE),

(b) A significant increase of the passivating current density (up to 0·1–1 A cm^{-2}) and

(c) A considerable decrease in the negative difference effect (increase of the faradaic efficiency to 99·5%) compared to the behaviour of pure aluminium. Except for the gallium alloy, the rate of corrosion of the alloys in neutral salt solutions is also decreased compared to that of pure aluminium. A ternary alloy, Al–0·01 In–0·01 Ga, exhibited a more negative rest potential than the Al–In alloy and a corrosion stability superior to that of the Al–Ga alloy. The negative difference effect was found to depend on the cation of the neutral salt in solution. The lowest effect was obtained in ammonium chloride solutions.

1. Introduction

Aluminium is a metal of great electrochemical potential. Its oxidation into hydrated oxide, $Al_2O_3 \cdot 3H_2O$, in aqueous solutions is accompanied with a standard free enthalpy change of 11 700 Wh kg^{-1} [1] convertible into electricity at a theoretical voltage of 3·92 V. It is surpassed only by hydrogen and a small number of other elements (Li, Be, B). Yet it has the advantage of easier handling over hydrogen and of much greater availability and much lower price over the other elements, since it represents the major product of electrochemical industry, taking up 60% of its total production in terms of the consumed electrical energy.

However, the major cause for the lack of success of the attempts to use it as an electrochemically active substance in the chemical energy sources and in corrosion protection, is the irreversibility of its reaction with oxygen in aqueous media. This created the present situation in which it has found exclusive use as a construction and electronic material, while the two above-mentioned fields of application remained dominated by zinc, although the latter has a 5 times lower energy density and is 4–7 times more expensive per unit energy content than the former at the present rate and technology of production.[†]

Three phenomena are responsible for the irreversible behaviour of aluminium in the process of oxidation and recovery:

(i) In the direction of anodic dissolution, a highly resistive oxide layer is formed which prevents the process occurring at rates which could be of practical use (passivity) and – even more important – shifting the rest potential so much in the positive direction with respect to the theoretical potential, that most of its energetic potential is lost;

(ii) In the direction of cathodic recovery of the metal, water decomposition is a process which takes place at a lower voltage and hence aluminium is not obtainable. This is due to the fact that even the highest hydrogen overvoltages known, as e.g. that on mercury which allow even lithium to be recovered from aqueous solutions [2], are insufficient for aluminium.

(iii) Finally, difficulties connected with the

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[†] According to 'Metal Statistics 1963–73' the price ratio of zinc to aluminium varied in 1973 between 0·83 in the USA and 1·42 in Great Britain with a tendency to increase.

transformation of the gelatinous aluminium hydroxide into crystalline hydrated oxide as the end product of the reaction are far from negligible.

Overcoming any of the above phenomena improves the prospects of using aluminium as a valuable electrochemically active material.

One should note that as far as the anodic dissolution is concerned, there are means of removing the protective oxide film. Thus, alkaline hydroxides dissolve it and reveal the bare aluminium surface. However, in such a situation the potential of aluminium is made sufficiently negative for it to displace hydrogen from water at a high rate and, hence, intensive corrosion takes place, so that the electrochemical yield is low.

One should note also the anomalous behaviour of aluminium during anodic dissolution known as the 'negative difference effect' (NDE). As the potential is driven positive from the rest potential value in the attempt to dissolve aluminium (or some other metals), the rate of hydrogen evolution increases almost linearly with the increase in the dissolution current density [3], maintaining almost constant, or in some cases even increasing, the percentage of aluminium lost by hydrogen corrosion. Among other possible causes, this is likely to be due to unexpected changes in the protective capacity of the oxide film.

Hence, an obvious direction for attempting to improve electrochemical activity (reversibility) of aluminium on the anodic side is not to disrupt nor to remove the protective oxide layer, but to modify its properties so as to obtain:

(a) A more negative rest potential;

(b) A higher limiting current density leading to passivity;

(c) A lower NDE, i.e. an increased faradaic yield in the dissolution process.

Moreover, these effects should be achieved with as little foreign material as possible for, in an adverse case, many of the qualities of pure aluminium (high energy density, availability, low price) would be lost. Several attempts have been made in this direction. A very extensive study, involving some 2500 alloys was reported by Reding and Newport [17], who found some evidence for the beneficial effect of small amounts of a number of metals (Mg, Ba, Zn, Cd, Hg, Ga, In, Sn) on (a) as well as on the potential of aluminium at low anodic current densities of the order of 1 mA cm^{-2} in sea-water. Sakano *et al.* [18] stressed the influence of indium, particularly on the anodic behaviour of Al–Zn alloys. Ivanov *et al.* [4] demonstrated that small additions of mercury (up to 0·8% w/w) provided both (a) and (c). However, mercury has long been known to disrupt the protective oxide layer to such an extent that aluminium becomes a highly unstable material in the presence of air.

In the course of our research it was found that the beneficial effects of adding indium, gallium and thallium or, their combinations, surpass those found by the above-mentioned authors [17, 18], and in fact achieve all the above aims. Preliminary results have been reported [5] and described in more detail [6] elsewhere. The purpose of this communication is to give a fuller account of the improvement in the anodic behaviour of aluminium achieved up to the present by alloying it with small amounts of the above metals.

2. Experimental

2.1. *Preparation of alloys*

Alloys have been made from reagent grade aluminium ('Merck', Darmstadt, pro anal). Indium was 99·9%, produced by Cinkarna, Celje (Yugoslavia). Gallium was 99·99%. Thallium was 99·97%.

Al–In, Al–Ga, Al–Tl and Al–In–Ga alloys have been prepared. The alloying components have been added in amount ranging from 0·01–0·5% w/w.

Fusions were carried out in quartz ampoules placed in an induction furnace (binary alloys) and in graphite crucibles placed in an ordinary laboratory type high temperature furnace (ternary alloy). In the latter case contact with the air was prevented by covering the material with a low melting salt mixture NaCl–KCl. Some difficulties were experienced in homogenizing the alloy melt because of the considerable difference in density of the components in the case of In and Ga, and because of the fact that Tl is immiscible with Al even in the liquid phase. In such cases one resorted to making a more concentrated alloy and then diluting it with pure aluminium.

Spectrographic analysis of all the samples has been made for the alloying components as well as for impurities (As, B, Au, Si, Mn, Fe, Mg, Pb, Sn, Ni, Cr, Bi, Mo, Cu, Ag, V, Zn, Ti and Sb).

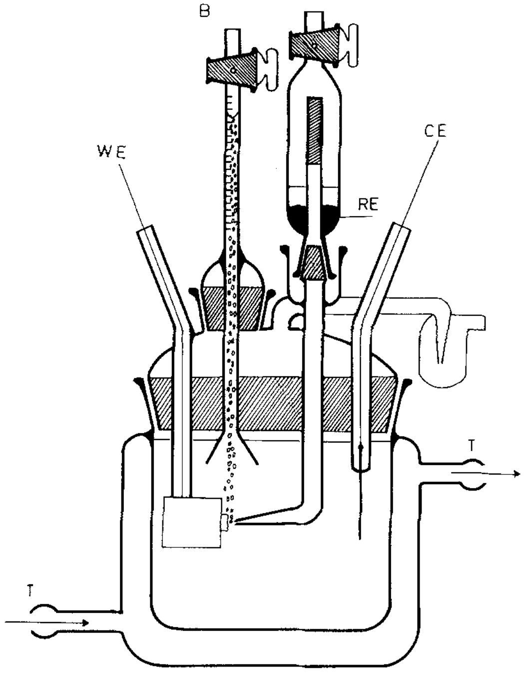

Fig. 1. Electrochemical cell for simultaneous anodic dissolution and hydrogen evolution measurements. WE–electrode under test; RE–reference electrode; CE–counter electrode; B–gas burette; T–thermostat liquid inlet and outlet.

2.2. *Thermal treatment of the alloys*

After melting at about 720° C, in the induction oven, all the samples were rapidly cooled by immersing the quartz ampoules in water. The ternary alloy was cast into a steel mould.

All binary alloys were also submitted to additional thermal treatment (T-alloys), which consisted of heating the alloy at 340° C for 10-14 h, and then cooling it slowly down to room temperature overnight.

2.3. *Measurement of polarization properties*

Small cylinders have been cut out of each alloy, 0·5 cm in diameter and about 1 cm in length, and imbedded into a Teflon holder. This was connected to a glass tube containing a metal wire for contact, to make the electrode for the electrochemical investigations. The electrodes were placed in the closed Pyrex glass cell shown in Fig. 1, which enabled parallel measurements of electrode polarization and of hydrogen evolution at a given potential.

The counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE) connected with the tested electrode via a Luggin capillary.

The electrolyte in the cell was a neutral 1 M NaCl solution, in all cases except those when the effect of cations or of concentration was investigated. Recrystallized reagent grade chemicals and triply distilled water were used to prepare the solutions. Additional purification was carried out by shaking the solution with aluminium powder. (It was found, however, that this purification did not have a significant effect, since some results obtained with commercial salt and ordinary tap water were quite similar to those obtained with purified electrolyte). The solutions were de-aerated by evolving hydrogen on a platinum electrode prior to measurements. The cell was thermostated to 25 ± 0·1° C.

Polarization measurements were made by the potentiostatic technique. The electrode potentials were controlled by a Wenking potentiostat and the current followed with time on a Hewlitt–Packard vacuum tube instrument. Steady-states were attained usually after a few minutes. To correct for the ohmic drop, pseudo-ohmic polarizations were determined at each electrode by a few galvanostatic pulses, the time response being observed on a Tektronix CRO.

2.4. *Measurement of simultaneous hydrogen evolution*

Hydrogen gas evolving from the electrode was collected without difficulty in a measuring burette placed above the electrode (cf. Fig. 1). Volumetric measurement of the rate of hydrogen evolution at a given constant potential could thus be made as a function of time.

2.5. *Corrosion at rest potential**

Rectangular samples, 1 cm × 1 cm × 0·5 cm, were cut out of each alloy. They were suspended in open beakers filled with electrolyte, about 3 cm under the surface. The weights of the samples were measured occasionally over a period of several months.

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* These measurements were carried out at the Institute of Physical Chemistry, Faculty of Technology, University of Zagreb.

2.6. *Determination of the protective capacity**

In order to determine the capacity of the alloy to provide cathodic protection of steel against corrosion, a cell was made up consisting of an alloy anode and a steel cathode of equal surface area facing each other and immersed in 3% NaCl solution. The potential of each electrode could be measured with respect to a SCE, via a Luggin capillary. The Hoar–Evans diagrams were constructed in the usual manner.

Since steel is cathodically protected against corrosion when its potential becomes more negative then − 600 mV, the current density at which that occurs is recorded as the protective current density.

3. Results

3.1. *Constitution of the alloys*

Spectrographic analysis revealed As, Pb, Si and Mo as the major impurities. At low contents of the alloying elements (below 0·05%) the amounts of some of these impurities up to 500 ppm were of the same order as those of the alloying element. Hence, the results concerning the properties of these particular alloys must be taken with caution. All other investigated elements were in trace amounts only (below 50 ppm). A typical result, e.g. that for the ternary alloy having the best electrochemical properties, reads (in ppm): Ga 1220; In 1360; Pb 160; As 125; Mo 106; Sn 48; Fe 45; Cu 45; Zn and Sb below 20; Mg 18·5; V and Ti below 10; Mn, Ni, Bi, Ag and B below 5.

Metallographic investigations of all the alloys indicated that the excess of the alloying element over its solubility (which is known to be extremely low) precipitated into a separate phase. Thermal treatment produced no visible changes.

The mechanical properties of the alloys, especially after the thermal treatment, resembled those of aluminium itself. The alloys could be cut, cold worked, deep drawn etc.

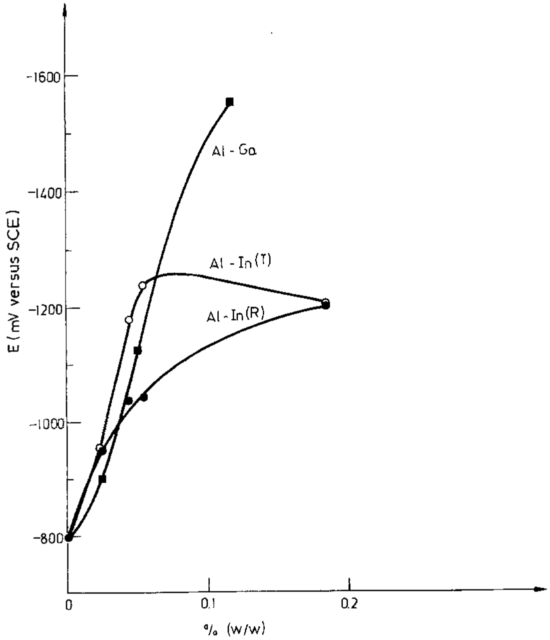

Fig. 2. Rest potentials of different aluminium alloys as a function of the content of the alloying component. (R)–regular alloys; (T)–thermally treated alloys.

3.2. *Rest potential and polarization characteristics of the alloys*

The addition of alloying components to aluminium produced in all cases a considerable shift of the rest potential in the negative direction. Fig. 2 shows the dependence of that shift on the content of the alloying component for binary alloys.

The alloy with thallium exhibited a rest potential of − 1·750 mV while that of the ternary alloy, Al–In 0·14%–Ga 0·12% was at − 1·620 mV versus SCE, i.e. about 800 mV more negative than that of pure aluminium in the same solution.

The rest potentials took some time to become constant if the alloy was left in the electrolyte on open circuit. This time was shortest for Al–In alloys (seconds), somewhat longer with Ga and very long in the case of Tl as the alloying component (20 days). Once established they were very stable in all cases. Faster attainment of the steady rest potential could be achieved by anodic activation.

3.2.1. Alloying with indium. This led to the Tafel plots shown in Figs. 3 and 4. They have been obtained by increasing the current density from one point to another, and after allowing sufficient time for the steady-state to be established (5–10 min).

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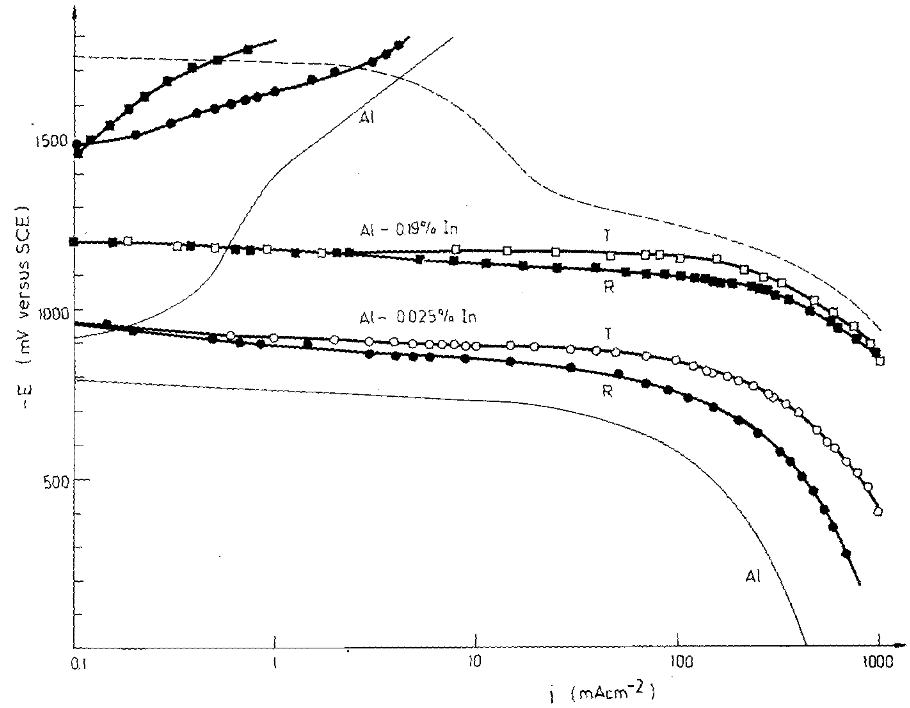

Fig. 3. Tafel plots for Al–In alloys of different In content. (R)–regular alloys; (T)–thermally treated alloys; dashed line-specially treated solution (cf. text).

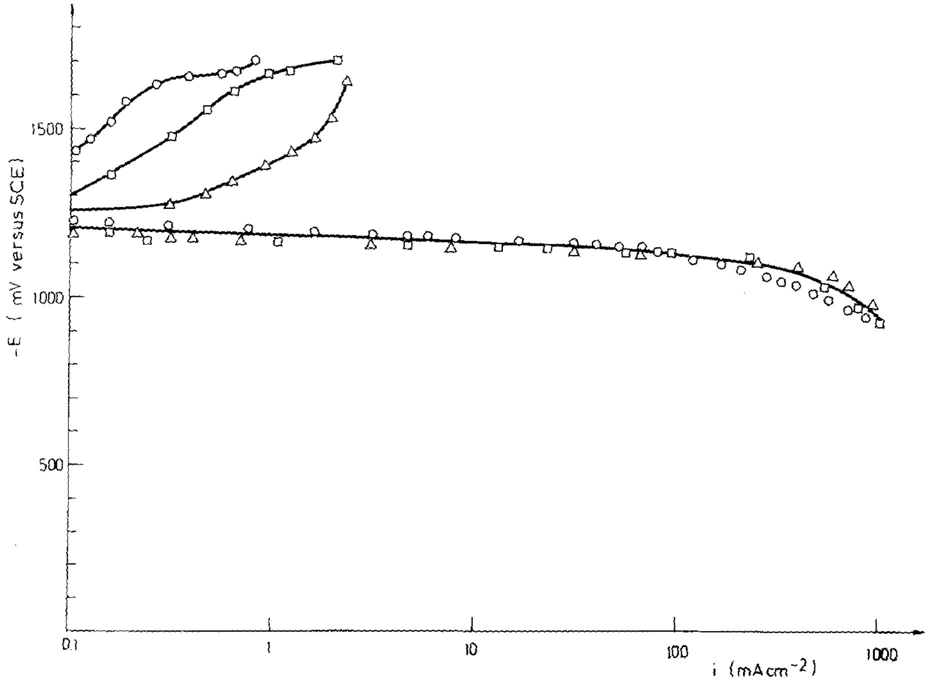

Fig. 4. Tafel plots for a thermally treated Al–In (0·055%) alloy in 1 M solution of different chlorides. ○–NaCl; △–$CaCl_2$; □–$BaCl_2$.

It is interesting to note that at low current densities (< 1 mA cm^{-2}) a decrease in current was recorded with time, while the opposite phenomenon was observed for higher current densities.

If the electrodes were left on open circuit after having been polarized for some time with high anodic currents, a considerable shift of the rest potential in the negative direction (about 200–300 mV) was observed. Irreproducible Tafel plots were obtained if measurements were made immediately afterwards. After the rest potential had attained its original value, good reproducibility of the Tafel plots was found. The anodic Tafel plot for pure aluminium under the same conditions is given in all the figures for comparison (thin line).

As seen in Fig. 3, indium has a significant effect even at a concentration of 0·025%. At this concentration thermal treatment has a substantial beneficial effect especially in the region of limiting current density. Practically no effect could be noted at 0·18%.

It is interesting to note that at intermediate In contents, Tafel lines for regular alloys are all close to those for 0·025% In, while those for thermally treated ones are close to that for 0·18% In.

Anodic Tafel lines are linear over several powers of ten in current density. The slopes are very low, and in most cases have values between 24 and 30 mV dec^{-1}. The addition of indium appears to produce a simple translation of the line for pure aluminium in the negative direction and, as far as the occurrence of passivity (limiting current) is concerned, in the direction of higher current densities.

The cathodic lines, reflecting the rate of (some) oxygen reduction and hydrogen evolution, were less reproducible than the anodic lines. Nevertheless, the intercepts with the anodic lines, defining the corrosion current density, all fell between 10^{-4} and 10^{-5} A cm^{-2}.

Purification of the solution in a standard manner for attaining high purity conditions and a thorough deoxygenation by prolonged hydrogen evolution produced a pronounced change in the rest potential (shifting it to − 1·740 mV) and in the anodic polarization behaviour, as shown by the dashed line in Fig. 3. However, the effects were not very reproducible and were not long lasting enough to be useful. Hence, all subsequent experiments were carried out under the conditions described earlier (cf. 'Experimental').

The effect of changing the cation in the electrolyte has also been investigated. As seen in Fig. 4 the rest potential and the anodic polarization line were hardly affected. Some effect has been noted for the cathodic lines.

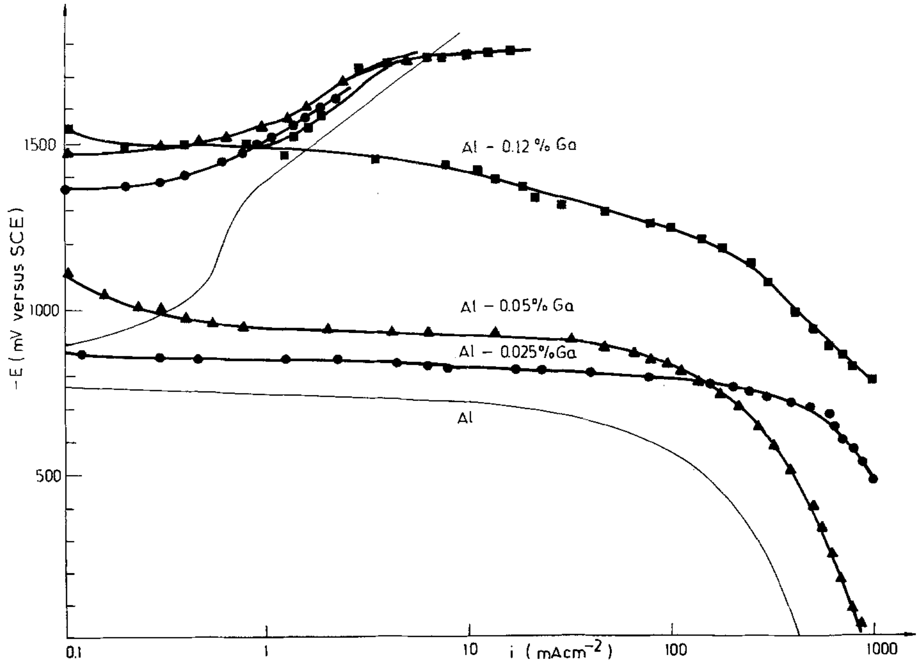

Fig. 5. Tafel plots for Al–Ga alloys of different Ga content.

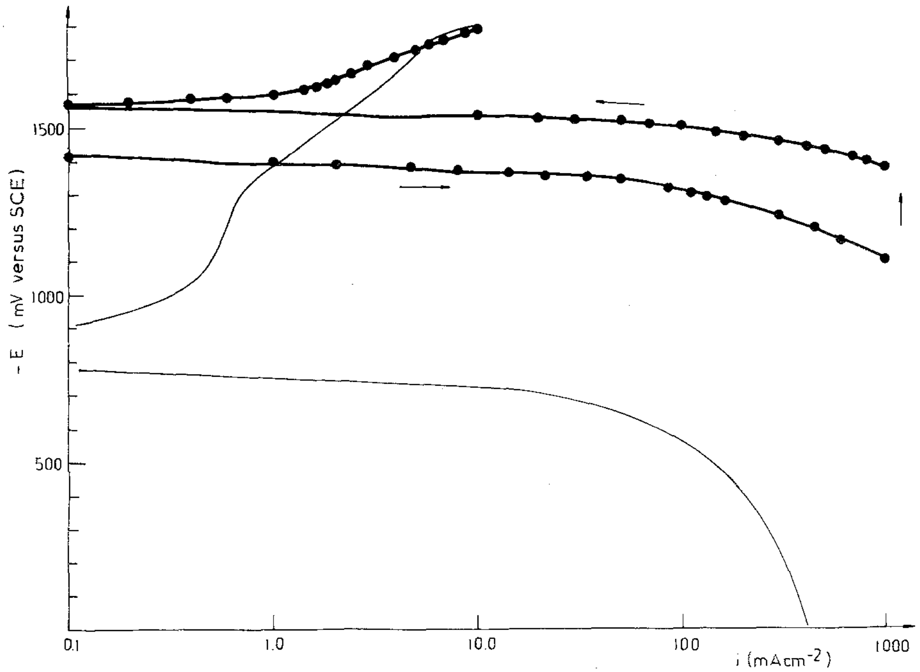

Fig. 6. Tafel plots for an Al–Tl alloy.

3.2.2. Alloying with gallium. As seen in Fig. 5, this produced very similar changes in polarization properties as the addition of indium. Even more negative rest potentials were reached. However, reproducibility was somewhat poorer and the cathodic polarization lines indicate larger corrosion current densities (increases of about an order of magnitude).

3.2.3. Alloying with thallium. This gave the result shown in Fig. 6, which must be considered as preliminary since only one sample has been tested so far. Nevertheless, the result shows that similar or better effects than those obtained with the other two elements can be expected. Without any thermal treatment the sample attained a very negative rest potential comparable to that for the highest gallium content, and a Tafel line superior to that of the latter, inasmuch as it was very flat up to a current density of 1 A cm^{-2}.

It is interesting to note that holding the electrode for some time at this high current density and returning it gradually to lower current densities gave a Tafel line shifted by another 150 mV in the negative direction. A rather large corrosion rate, however, of about 1 mA cm^{-2}, is suggested by the cathodic Tafel line.

3.2.4. Ternary alloy, Al–In–Ga. This led to (Fig. 7) a similar Tafel plot to that for the Al–Ga alloy of the highest Ga content. The corrosion current is difficult to estimate with precision from the plot, but is of the order of 1 mA cm^{-2}.

3.3. *Hydrogen evolution during anodic polarization of the alloy*

All alloys exhibited a negative difference effect (NDE) of much the same character as that on pure aluminium. However, from the quantitative point of view alloying had a profound effect.

A typical set of lines showing the dependence of the rate of hydrogen evolution, expressed in terms of current density, on the current density of anodic dissolution, is shown in Fig. 8. Since all the lines are practically straight, the slopes, $\Delta i_{H_2}/\Delta i_{an}$, can be taken as a measure of the NDE while the intercept should reflect the corrosion current. This at the same time gives the percentage of aluminium lost for the faradaic (i.e. electrical energy producing) process, i.e. reflects the faradaic yield of the dissolution. Fig. 9 shows the dependence of this loss on the alloying component content for three types of alloys. Although following the same decreasing trend at low alloying element contents as

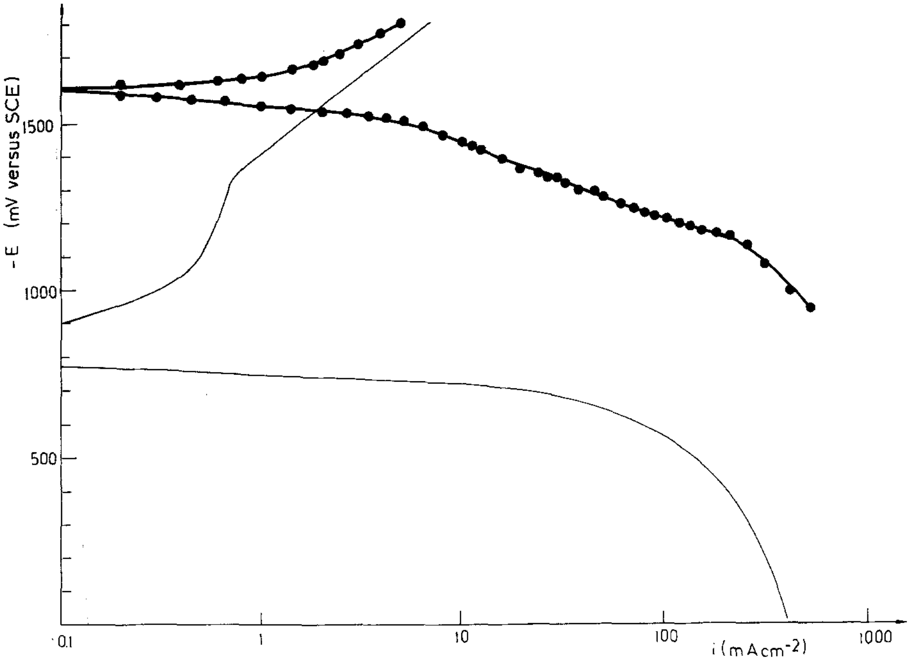

Fig. 7. Tafel plot for a ternary alloy Al–In–Ga.

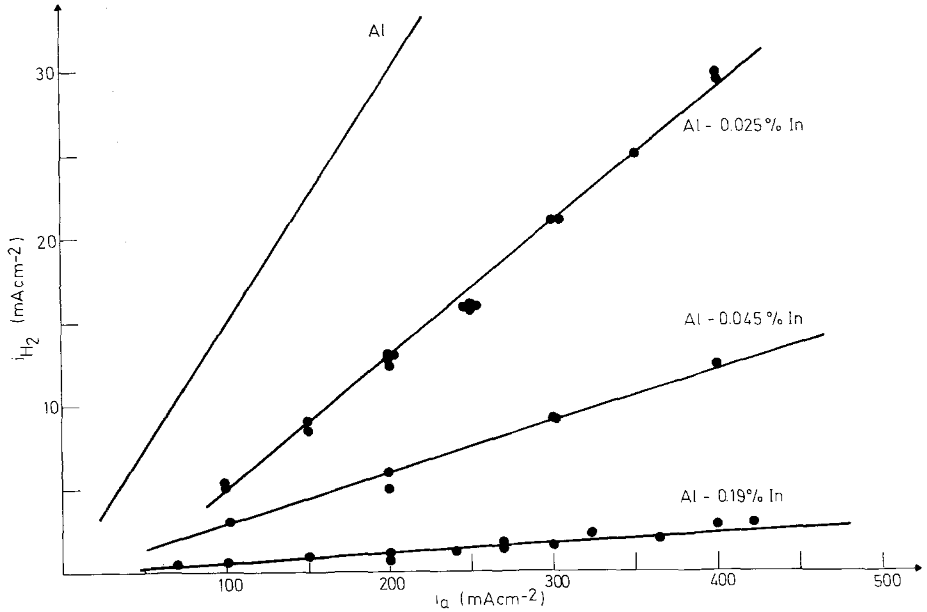

Fig. 8. Rate of hydrogen evolution as a function of anodic current density for thermally treated alloys of different indium content.

the indium alloys, the gallium alloys of high gallium contents suddenly gave very large negative difference effects surpassing that of pure aluminium. The thallium alloy exhibited a loss of about 7·7%. The ternary alloy Al–In–Ga did not follow the linear dependence of hydrogen evolution rate on anodic current density, as shown in Fig. 10. A rather high rate of corrosion of some 6 mA cm^{-2} is measured at the rest potential. After exhibiting a NDE similar to that on pure aluminium at low

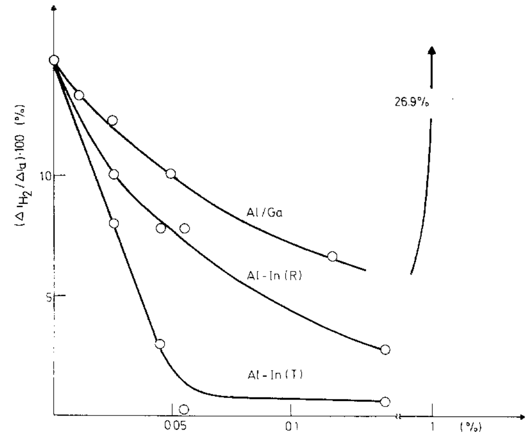

Fig. 9. Loss of aluminium during anodic dissolution due to hydrogen corrosion as a function of content of alloying component. (R)–regular alloys. (T)–thermally treated alloys.

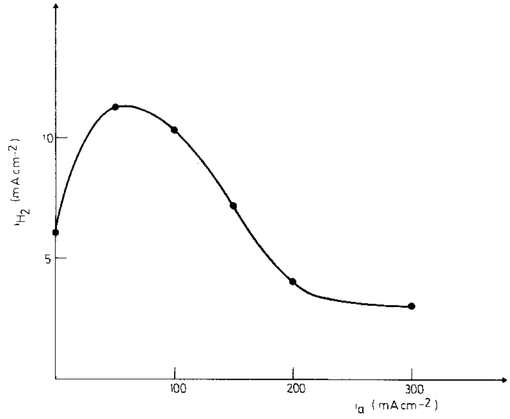

Fig. 10. Rate of hydrogen evolution as a function of anodic current density for the ternary alloy Al–In–Ga.

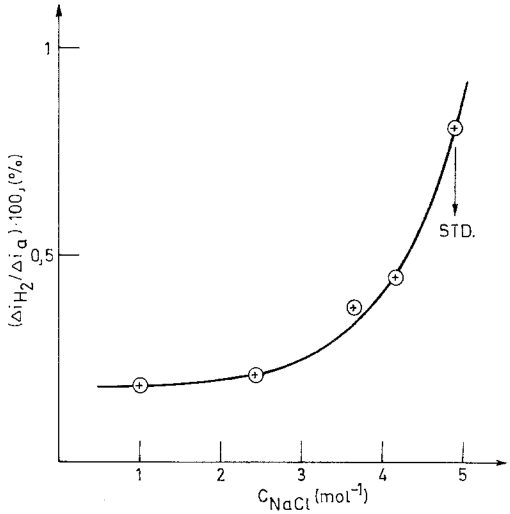

Fig. 11. Loss of aluminium as a function of concentration of NaCl in solution for Al–In alloy with 0·055% of indium.

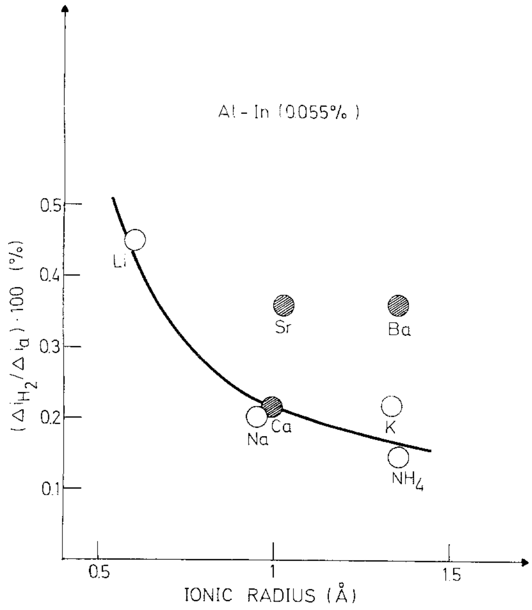

Fig. 12. The loss of aluminium as a function of the cation constituting the electrolyte for Al–In alloy with 0·055% of indium.

current densities, the rate of hydrogen evolution decreases, thus giving a positive difference effect which tends to zero at high current densities.

A typical Al–In alloy was investigated for the dependence of the NDE on concentration of the salt in solution as well as on pH. The NDE and hence, the loss of aluminium was found to depend fairly strongly on the concentration of the electrolyte as shown in Fig. 11, especially when close to saturation. On the other side, it was not found to depend on pH in the pH region between 1·4–11. The NDE also depended on the type of cation constituting the salt, as the plot versus the ionic radius of the cations shows (Fig. 12). The lowest loss is obtained with the ammonium chloride solution. The same was found to be true for the Al–Ga alloys.

An interesting relationship was found between the NDE and the rest potential of the alloys as seen in Fig. 13. It seems to be a logarithmic one, although with slopes depending on the alloying element as well as on the treatment of the alloy.

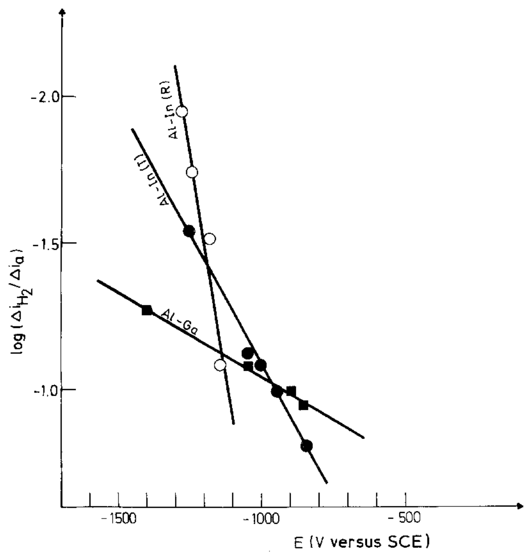

Fig. 13. Relationship between the loss of aluminium and the rest potentials of alloy electrodes. (R)—regular alloys; (T)—thermally treated alloys.

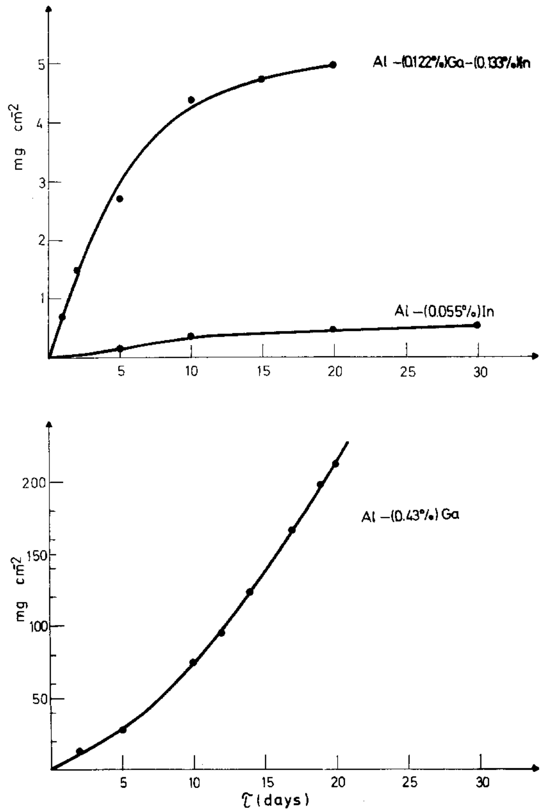

Fig. 14. Weight loss of samples of different alloys submerged in 3% NaCl solution as a function of time.

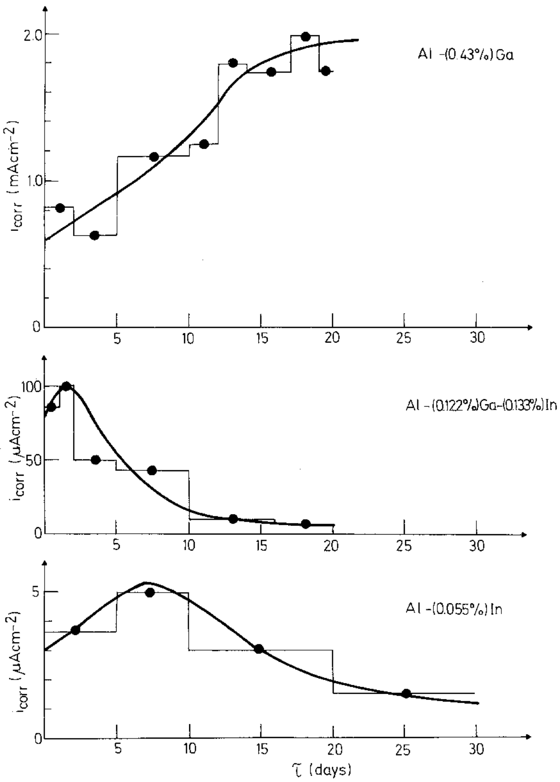

Fig. 15. The corrosion current density, calculated from weight loss, of different alloys as a function of time.

3.4. *Corrosion of the alloys at the rest potential**

The rate of corrosion of all the samples submerged in 1 M NaCl solution open to the atmosphere, varied with time. Fig. 14 shows the weight losses of three typical alloys – that with 0·18% indium, that with 0·13% gallium and, the ternary alloy, that with 0·14% indium and 0·12% gallium. The average rate of corrosion between two measurements has been calculated from the change in weight and is plotted against time in Fig. 15.

The alloy with indium exhibited a very good stability which was comparable initially to that of zinc under the same conditions but increased with time to a state in which corrosion could be considered negligible for all practical purposes.

On the contrary, gallium caused a very rapid dissolution of the sample at corrosion rates of the order of several mA cm^{-2}. Some increase of the rate with time is observed. One should bear in

* These measurements were carried out at the Institute of Physical Chemistry, Faculty of Technology, University of Zagreb.

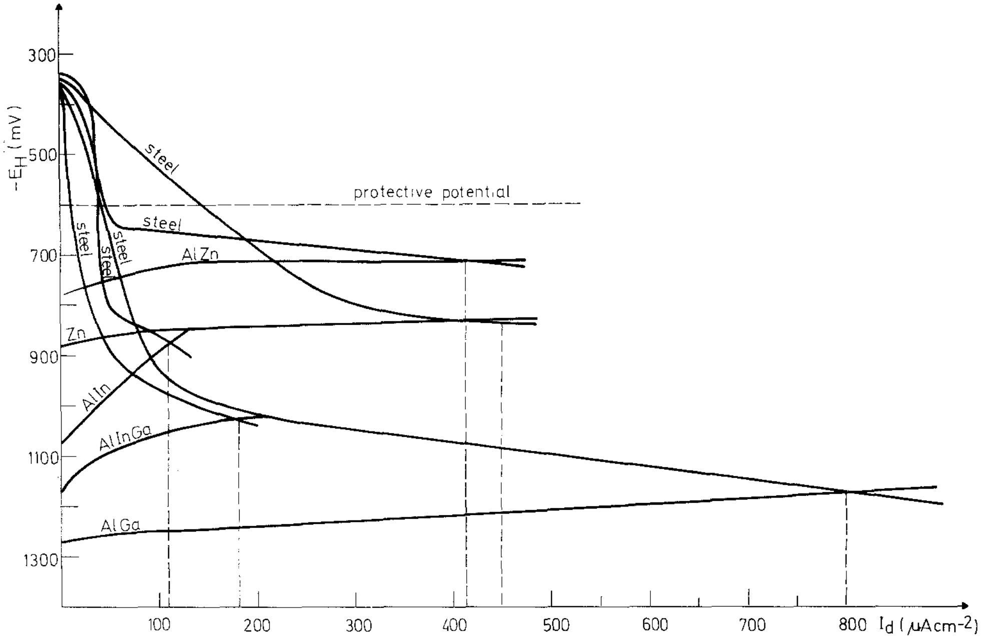

Fig. 16. The Hoar–Evans diagrams for coupling steel with zinc and different alloys providing cathodic protection.

mind, however, that due to the rapid corrosion process and uneven dissolution, the surface area of the sample increased simultaneously. Hence, as a first approximation the rate of corrosion of that alloy can be considered to be constant.

The ternary alloy preserved the good qualities of the indium alloy, although at an order of magnitude a higher rate of corrosion. The virtual steady-state value attained after some 15 days, of about 6 $\mu A\,cm^{-2}$, gives the alloy a satisfactory corrosion stability.

3.5. *Protective properties of the alloys**

Hoar–Evans diagrams for estimating the protective capacity of the alloys in the cathodic protection of steel in 3% NaCl solution, simulating such media as e.g. sea-water, were constructed. The result is shown in Fig. 16. Diagrams of steel coupled with zinc as well as with an aluminium–zinc alloy (70 : 30 w/w), obtained in the same laboratory, are given for comparison.

The interesting feature is that not only the anodic dissolution curves of the alloys are different, as already shown above, but also that the polarization of steel is strongly affected by the presence of the dissolution products. Aluminium itself has some effect on the polarization of steel (compare effect of the Al–Zn alloy with that of pure zinc). The protective currents (i.e. those at − 600 mV versus the NHE) in the case of the alloys are very much the same and much lower than that for pure zinc. An additional inhibitive effect, however, is achieved with the combination Al–In–Ga, where a very small current density of only 15 $\mu A\,cm^{-2}$ provided complete cathodic protection.

4. Discussion

4.1. *Constitutional and structural effects of alloying*

In all samples, except those with the lowest contents of the alloying elements, two phases are present: that of almost pure aluminium and that containing the excess of the alloying component over the amount dissolved in the former phase.

Even at the lowest investigated contents of alloying elements, where the situation with the precipitation of the second phase was not clear and where their contents were comparable with those of the major impurities, the addition of the

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alloying element produced pronounced effects on two major electrochemical properties – the rest potential and the NDE.

If one assumed an even distribution of the alloying component throughout the metal, 1 atom in 10 000–50 000 atoms of aluminium would be producing these effects. This is a very unlikely situation. Moreover, prolonged heating of the samples close to the melting point (the thermal treatment) made both effects even more pronounced.

Obviously, such a treatment could only make the alloy approach an equilibrium situation if aluminium had been supersasturated by the alloying component when the alloy was produced. Three consequences of such an equilibration can be forseen:

(1) The content of the alloying component in the aluminium rich phase must be decreased;

(2) The amount of the other phase must be increased;

(3) If the alloying component is surface active with respect to aluminium, there can be an accumulation of the former component at grain boundaries (i.e. adsorption at the inside of the crystal grain surfaces).

Effect (1) could not lead to improved electrochemical behaviour and effect (2) could have a positive effect only if the electrochemical properties were dominated by impurities and if the second phase had a greater affinity for impurities than pure aluminium and hence its precipitation had a purifying effect. Both of these seem rather unlikely. Otherwise, the second phase could either give rise to centres of increased cathodic activity (and thus lead to a more positive rest potential and increased rate of hydrogen evolution) or be inert compared to the electrochemical activity of the main phase. Considering all of the observed effects the latter seems to be the case.

Hence, (3) seems to be the major reason for the beneficial effect of the thermal treatment and at the same time offers an explanation for the marked influence of minor amounts of added element.

The fact that all the thermally treated alloys of indium, except those with the lowest content of the alloying component, exhibit practically the same electrochemical properties, lends support to the above reasoning. In well-equilibrated alloys with excess of indium above the solubility limit both the content of the alloying component in the solid solution and its adsorption at the grain boundaries are the same in all samples and independent of the overall indium content. Indium contents larger than the limiting solubility, merely incrêase the amount of the second phase, which is inert.

4.2. *The rest potential of aluminium and its alloys*

The very positive rest potential of aluminium and its shift in the negative direction due to alloying cannot be explained in terms of the usual model involving the hydrogen corrosion couple and the theoretical value of the reversible potential of aluminium arising from the thermodynamics of Al to $Al_2O_3 \cdot 3H_2O$ oxidation, for the following reason.

The anodic dissolution is shown to follow the Tafel Law with a very small and constant slope of about 30 mV dec^{-1}. If this slope were maintained down to the reversible potential of aluminium, the obtained value of the exchange current density would be unreasonably small. Subtracting the oxygen electrode potential in neutral electrolyte (0·81 V versus NHE) from the theoretical cell voltage of 3·8 V, one obtains the reversible potential of the aluminium electrode as $-$3·0 V. Hence, the rest potential of about $-$0·6 V versus NHE recorded for pure aluminium in 1 M NaCl solution, would signify an overpotential for anodic dissolution of aluminium of 2·4 V. With the above value of the Tafel slope and a corrosion current of the order of 10^{-4} A cm^{-2}, this leads to an i_0 value of 10^{-84} A cm^{-2}. Even if the Tafel slope were to change at current densities lower than the corrosion current, to, say, 120 mV dec^{-1}, the i_0 value would still be of the order of 10^{-24} A cm^{-2}.

Moreover, although (as pointed out by Ivanov *et al.* [4]) there is a remarkable correlation between the shift of the rest potential caused by alloying and the hydrogen overvoltage on the alloying element, the shift is due mainly to the change in the anodic activity of the metal, while cathodic activity seems to be more or less independent of alloying, as seen in Figs. 3–7.

Hence, an altogether different explanation must be sought. As far as the problem of the improbably low i_0 value of aluminium dissolution is concerned, it is quite likely that not only the effects on the kinetics should be taken into account, but also that the possibility of shifts of the reversible potential of aluminium with respect to the calculated value must be considered.

It is only that part of the free energy change in a complex overall reaction, pertaining to steps which are sufficiently reversible such that equilibrium between all states to which they lead and the initial state can be established, which can be transformed into electrical energy. If the final state of the overall reaction is cut off by a very slow chemical reaction occurring outside the electrical double layer, that part of the total free energy change is converted into heat and cannot contribute to the electrical energy obtained from the system, i.e. to the potential of the electrode concerned.

This could be the case in the investigated system. If a very compact oxide layer of very low porosity is formed upon the dissolution of the metal it is quite likely that it will by the anhydrous one, as the transport of the water through the crystal lattice is bound to be slow. Hence, the reversible potential should be that for the formation of Al_2O_3 at the metal–oxide film interface rather than that for $Al_2O_3 \cdot 3H_2O$, the hydration occurring as a purely chemical process far outside the electrical double layer when the film starts cracking and allowing the water to enter. The difference in the free energy of the two states is so large, that the theoretical cell voltage of the formation of the anhydrous oxide is only 2·72 V, and hence, the theoretical potential of aluminium facing the oxide is $-$ 1·9 V. The overpotential of 1·3 V would still suggest an i_0 value of 10^{-43} A cm^{-2}. The origin of this will be discussed below.

One serious objection could be raised against such a model if one wanted to preserve the classical concept of the complex reaction kinetics. It is related to the question of what controls the overall rate of reaction. If the last chemical step is to be so much cut off from the electrochemical ones that a different overall reaction can be ascribed to the latter, leading to the corresponding reversible potential, the kinetics of the process as a whole must be controlled by the cut off step. In such a case one would not expect the Tafel law to be obeyed, with a slope indicating control by some step in the electrochemical stages.

One should invoke, however, a particular feature of the process of anodic oxide layer formation – the development of porosity farther away from the surface, due to mechanochemical effects. Thus, the chemical reaction of the oxide with water and final hydration can keep up with the rate of oxide formation as the layer cracks and develops its surface area. The overall kinetics is in such a case still governed by that at the metal–oxide interface.

The effect of the alloying component in such a model remains rather obscure in both features – the effect on the anodic activity and the lack of effect on the cathodic activity. The former will be discussed below in connection with considerations of the possible reaction mechanism, while the latter can be explained by assuming that the hydrogen evolution which determines the rest potential does not take place either on bare parts of the metal surface revealed by rupture of the oxide film or on some separate centres of cathodic activity (precipitated impurities) but rather on the surface of the oxide layer. One does not expect to find the alloying components there, for even if they are ionized together with the dissolving aluminium, they are likely to precipitate back immediately because of their considerably more positive standard potentials.

This model requires, however, the oxide layer to exhibit some electronic conductance. This can be the case if a degree of non-stoichiometry appears during anodic dissolution, which is not an unlikely situation, as will be seen below.

4.3. *The mechanism of the anodic oxidation*

The Tafel slope can be used as one diagnostic criterion to help to elucidate the reaction mechanism. Its constancy over a significant range of current densities indicates that one step only in the complex mechanism is rate-determining and that all the others are in virtual equilibrium.

In such a case the meaning of the value of the transfer coefficient, $\alpha = 2$, arising from the obtained value of the slope (0·030 mV dec^{-1}) can be analysed using the equation which relates it to the mechanistic parameters of the process [7]:

$$\alpha_a = (1 - \beta_d) z_d + \frac{f'_a z' + f''_a z''}{\mu_d} \qquad (1)$$

where z_d is the number of electrons exchanged in the rate determining step (rds), z' and z'' are those of electrons exchanged before and after it respectively, β_d and μ_d are the symmetry factor and the stoichiometric number of the rds, while f_a' and f_a'' are the complexity factors. The latter should have two sets of values only: (i) $f_a' = 1; f_a'' = 0$, and (ii) $f_a' = f_a'' = 0{\cdot}5$. If one assumes a $\beta_d = 0{\cdot}5$, and the $z-s$ to be integers, there are only two combinations satisfying Equation (1) in the case (i) and none in the case (ii).

The first possible mechanism (a) would consist of a non-electrochemical step as the rds, prior to which two electrons are exchanged forming Al(II) species as the intermediate, while the third electron is exchanged in some step after the rds. It is quite likely that some fast chemical steps are also preceding the rds, for it is unlikely that Al(II) is a bare Al^{2+} ion. The split of the second electron would be difficult from an already positively charged species. Hence, it is more likely that Al^+ intermediate reacts with oxygen before giving away the second electron.

The second possible mechanism (b) would be that of a fast electron transfer to form Al(I) as the intermediate and slow exchange of the remaining two electrons in a single act. Again a fast chemical reaction between Al^+ and oxygen is likely to precede the slow step.

Both mechanisms seem reasonable. However, in the case of mechanism (a) one has difficulties in understanding the catalytic activity of the alloying component, which in this case should speed up the formation of the chemical bond between Al (II) and oxygen.

This is more easily understood if mechanism (b) is assumed. Simultaneous transfer of two electrons is likely to be a very slow process, leading to the very low i_0 value in the case of the oxidation of pure aluminium. Cases are known in homogeneous reaction kinetics of such transfers being catalysed by some redox couples acting as transmitters which open up an alternative reaction path (e.g. Ce^{4+}/Tl^+ catalysis by the Mn^{2+}/Mn^{4+} couple [8]). Hence, it is forseeable that indium, gallium and thallium can undergo reversible redox reactions at the metal–oxide interface transferring electrons from the Al^+ ion surrounded by oxygen in the oxide lattice to the electrode.

The existence of the intermediate species and catalysis of further charge transfer also offers good grounds for explaining the observed influence of the alloying components on the NDE as will be seen below.

4.4. *Hydrogen evolution during anodic dissolution of aluminium*

Changes in the rate of hydrogen evolution with the increase of current density of anodic dissolution of a metal, traditionally carry the name of the difference effect [9, 3]. The positive difference effect is well-understood in modern electrode kinetics and corrosion science as due to the normal decrease of the rate of hydrogen evolution with the potential going anodic.

The NDE, however, being an abnormal phenomenon, requires a special model and three causes have been suggested so far in the literature:

(i) The occurrence of uncommon valency [10, 11] – because of a slow exchange of the last electron(s), some intermediate ions, e.g. Al(I), leave the electrode and release the electron(s) in a chemical (redox) reaction, away from the metal–oxide interface. The probability of such an event is proportional to the rate of anodic dissolution, and hence the linear dependence between the rate of hydrogen evolution (which is the product of the chemical reaction) and the anodic current density;

(ii) The rupture of the oxide layer and an increased steady-state porosity should lead to an increased rate of hydrogen evolution on the bare parts of the metal [3, 12–15]

(iii) The 'chunk' effect model [16] follows from the fact that small pieces of metal have been observed splitting away from the electrode and corroding freely in the solution, thus increasing the anodic current efficiency and the rate of hydrogen evolution.

The two latter models have difficulties in explaining the constancy of the NDE, i.e., the linearity between the two rates, found in the majority of cases. Both the rupture of the oxide layer and splitting away of pieces of the metal are likely to be stochastic processes, affected by factors not related to the mechanism of the reaction (e.g. mechanical stress created in the surface). Hence, they are likely to lack reproducibility and could hardly be expected to render the above-mentioned linearity. Moreover, since the rate of hydrogen evolution on a bare metal should be inversely proportional to the rate of anodic dissolution to some power depending on the Tafel slopes, the oxide film rupture should have a higher power dependence on anodic current density to provide the linearity between the increase in the rate of hydrogen evolution and the latter. No reasons can be seen for such a dependence.

The uncommon valency model seems to obtain further support from the observations made in this work. The slower the rds, the more ionic intermediate will accumulate at the surface and hence, the larger will be its flux through the oxide layer towards water. The concentration of the intermediate at the surface should increase proportionally to the current densiy. Hence, so should the flux through the oxide and consequently the rate at which hydrogen evolves as the reaction product between Al(I) and water.

The catalytic effect of the alloying component leads to a decrease in the concentration of Al(I) at the surface for a given current density, and, in line with the above mechanism, the rate of hydrogen evolution should be correspondingly decreased.

Hence, the decrease in the rate of h.e.r. is in this model in no way related to the inhibitive qualities of the alloying element with respect to the h.e.r. on the latter. Any correlation between the two is thus incidental.

The dependence of the NDE on the type of cation of the inert electrolyte as well as the fact that the anodic behaviour is affected by the type of anion (passivation of pure aluminium is known to be different for different anions, and the presence of chloride seems to be essential to account for the recorded polarization behaviour of aluminium) indicates that events both at the metal–oxide and the oxide–electrolyte interface are somewhat more complex than would appear in the above considerations.

Thus, it is possible that alkali metal ions act as mediators in the electron transfer from Al(I) to water since they do not affect the anodic polarization but do affect the NDE. Their catalytic effect is the larger the smaller is their hydrated radius. Nevertheless this does not affect the validity of the model as a whole.

4.5. *Corrosion of the alloys and their protective properties*

The corrosion of such materials consisting of at least two different phases and a substantial number of impurities must be a complex phenomenon. Three sources of hydrogen evolution are likely to exist at such a surface:

(i) Hydrogen evolution at the surface of the oxide layer which is unaffected by the alloying component;

(ii) That at some centres of cathodic activity (impurities deposited at grain boundaries or the second phase of the alloy) which could be affected by the dissolution products of the alloy;

(iii) That due to the chemical reaction between the aluminium ions of intermediate valency and water, occuring again at the surface of the oxide layer, but affected indirectly by the alloying component as discussed in Section 4.4.

The first source may be dominant in the cathodic evolution of hydrogen, the third accounts for the NDE, while both the first and the second may determine the corrosion stability of the alloy. One is led to such a conclusion by the time dependence of corrosion demonstrated in Fig. 15, which leads in all cases (except in the cases of alloys containing substantial percentages of gallium) to such low corrosion rates that the materials can be considered as corrosion resistant.

This could be due to two causes. The oxide layer may be growing in thickness in its compact part, so that the conductance of the layer decreases with time and, hence, the corrosion couple acquires an increased internal resistance, leading to a decrease in the corrosion current. However, the centres of cathodic activity may also be affected by the products of dissolution of the alloys.

The existence of such effects has already been noted in connection with the protective capacity of the alloys, for this is the only way to explain the remarkable reduction in the current necessary to provide the cathodic protection of the piece of steel (Fig. 16) when for example, the Al–In–Ga alloy is used, compared to that needed when using zinc.

6. Practical consequences of the results

There appears to be no obstacle to using the alloys described above in primary chemical energy sources as replacements for zinc. Economically such a replacement seems very favourable since with present world wholesale metal prices the Al–

In–Ga alloy, for example should be 4–7 times cheaper in raw materials then zinc, while the processing cost remains practically the same.

Two difficulties can be foreseen however. The reaction product is a bulky gelatinous aluminium hydroxide, which swells and uses up significant quantities of water. Also, the material is sensitive to impurities in the electrolyte. Practically all elements deposit on the alloy and, if they exhibit low hydrogen overvoltage, they act as centres of cathodic activity leading to significant increases in the rates of corrosion, i.e. self-discharge of the battery. Hence, careful selection of the other raw materials in the production of a battery must be made.

Similar considerations apply to the application of the alloys for cathodic protection against corrosion. Much cheaper protection than can be obtained with zinc is possible.

If applied in a dispersed form, significantly smaller amounts of material are needed having regard to the reduction in the protective current when the dissolution products remain close to the surface of the protected object.

However, the metal ion impurities in the air or for example, in sea-water, can lead to an acceleration of the corrosion of the alloy and hence remove some of its economic merits.

Investigation of the importance of all of the above factors is in progress.

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References

[1] W. M. Latimer, 'Oxidation Potentials', Prentice Hall, New York, 1952.

[2] J. M. Kolthoff and J. J. Lingane, 'Polarography', Vol. II. Interscience Publishers, New York 1952, p. 513–8.

[3] W. O. Kroenig and V. N. Uspenskaja, *Korrosion u. Metallschutz*, **11**, (1935) 10.

[4] E. G. Ivanov, E. A. Berkman and G. M. Petrova, *Sbornik Rabot po Khimicheskim, Istochnikan Toka*, 9, *Energiya* (1974) 186.

[5] M. M. Purenović, A. R. Despić and D. M. Dražić, *Elektrokhimiya*, **12** (1976) 296.

[6] 'An Electrochemically Active Aluminium Alloy, the Methods of its Preparation and Use', Institute of Technical Science, The Serbian Academy of Science and Arts, Yug. Pat. Appl. No. P-405 (1975).

[7] A. R. Despić, *Bull. T. XLVI Acad. Serbe sci. et arts, classe sci. math. et natur*, **12** (1969) 79.

[8] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism', John Wiley, New York 1961, p. 209.

[9] M. E. Straumanis, *J. Electrochem. Soc.* **105** (1958) 284.

[10] *Idem, ibid* **108** (1961) 1087.

[11] D. V. Kokulana and V. N. Kabanov, *DAN SSSR*, **112** (1957) 692; *DAN SSSR*, **120** (1958) 558; *ZFH*, **34** (1960) 2469.

[12] W. J. Muller, *Trans Electrochem. Soc.* 76 (1969) 167.

[13] M. E. Straumanis and J. N. Wang, *J. Electrochem. Soc.* **102** (1955) 304.

[14] N. D. Tomashoff, *Light Metals* **11** (1948) 505.

[15] M. E. Straumanis, *J. Electrochem. Soc.* **105** (1958) 284.

[16] G. A. Marsh and E. Schaschl, *ibid* **107** (1960) 960.

[17] I. T. Reding and J. J. Newport, *Materials Protection* 5 (1966) 15.

[18] T. Sakano, K. Toda and M. Hanoda, *ibid* 5 (1966) 45.