

REVIEW

Anomalous dissolution of metals and chemical corrosion

DRAGUTIN M. DRAŽIĆ^{1,2*#} and JOVAN P. POPIĆ^{1#}

¹*Institute of Chemistry, Technology and Metallurgy–Center for Electrochemistry, Njegoševa 12, P. O. Box 473, 11001, Belgrade and* ²*Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia and Montenegro (e-mail: dmdrazic@eunet.yu)*

(Received 10 November 2004)

Abstract: An overview is given of the anomalous behavior of some metals, in particular Fe and Cr, in acidic aqueous solutions during anodic dissolution. The anomaly is recognizable by the fact that during anodic dissolution more material dissolves than would be expected from the Faraday law with the use of the expected valence of the formed ions. Mechanical disintegration, gas bubble blocking, hydrogen embrittlement, passive layer cracking and other possible reasons for such behavior have been discussed. It was shown, as suggested by Kolotyrkin and coworkers, that the reason can be, also, the chemical reaction in which H₂O molecules with the metal form metal ions and gaseous H₂ in a potential independent process. It occurs simultaneously with the electrochemical corrosion process, but the electrochemical process controls the corrosion potential. On the example of Cr in acid solution it was shown that the reason for the anomalous behavior is dominantly chemical dissolution, which is considerably faster than the electrochemical corrosion, and that the increasing temperature favors chemical reaction, while the other possible reasons for the anomalous behavior are of negligible effect. This effect is much smaller in the case of Fe, but exists. The possible role of the chemical dissolution reacton and hydrogen evolution during pitting of steels and Al and stress corrosion cracking or corrosion fatigue are discussed.

Keywords: corrosion, electrochemical corrosion, anomalous dissolution, chemical corrosion, iron, chromium, steels.

CONTENTS

1. Introduction
2. Electrochemistry of metal dissolution and corrosion
3. Anomalous behaviors in metal dissolution
 - 3.1. Transitory or uncommon ion mechanism
 - 3.2. Disintegration of the electrode surface
 - 3.3. Film control mechanism
4. Chemical dissolution of metals and corrosion
 - 4.1. Dissolution of Na and K

* Author for correspondence.

Serbian Chemical Society active member.

- 4.2. Other metals
- 4.3. New evidence for the chemical dissolution of metals
- 5. Conclusions

1. INTRODUCTION

The Faraday law is one of the fundamental laws of electrochemistry and was for long time the basis for the definition of coulomb as one of the important units of the International System of Units (SI). The coulomb was defined as a quantity of electricity, which must pass through a circuit to deposit 0.0001180 g of Ag from a solution of silver nitrate.¹ This system was chosen since during the electrodeposition of Ag no other electrochemical process occurs which interferes with the Ag deposition. If that would not be so, the apparent valence calculated using the Faraday law and the weighed amount of Ag, knowing the used amount of electricity, would be less than 1, which is to be expected for the deposition of Ag from the solution of Ag⁺ ions.

Apparent valences smaller than those electrochemically expected are often encountered in electrochemical systems, specially during the electrochemical deposition of metals. It usually occurs when simultaneously with the deposition process of the metal of interest some other electrochemical process takes place, *e.g.*, hydrogen evolution, oxygen reduction, impurities reduction or oxidation of impurities, *etc.* In such cases it is customary to use the term current efficiency, which is defined as the amount of current used for the effective deposition of the desired metal divided by the total amount of current passed through the electrolytic cell. The current efficiency and apparent valence are two different ways to quantitatively express the deviations from the direct application of the Faraday law. For example, a current efficiency, η_j , smaller than one is the same as the statement that the apparent valence, z_{ap} , is larger than the corresponding valence of the deposited metal ion, z . On the other hand, if during the metal dissolution $\eta_j > 1$, the apparent valence will be smaller than expected, *i.e.*, $z_{ap} < z$. Only these examples will be considered and analyzed in this paper. In general, in the literature they are often considered as "anomalous" dissolution² but some other terms related to the similar behavior of metals during dissolution are used in the corrosion literature, *e.g.*, negative difference effect,³ decreased anodic current efficiency,⁴ *etc.*, as well as the abovementioned lower apparent valence.

2. ELECTROCHEMISTRY OF METAL DISSOLUTION AND CORROSION

Local electrochemical cell action was proposed a long time ago by de la Rive⁵ as the explanation of the spontaneous corrosion of metals in which cathodic processes are occurring on the inclusions on the surface of the anodically dissolving corroding metal. Hence, without separated cathodic parts of the local cell, corrosion is not to be expected. This model explained the action of macro corrosion cells or even micro cells for the heterogeneous alloys most often used in technical applications. However, corrosion of extra pure metals, even in the single crystal form

also occurs, albeit at a lower rate in some cases. The electrochemistry of corrosion on homogeneous surfaces based on the laws of electrochemical kinetics was probably first formulated by Wagner and Traud.⁶ Their model was based on the assumption of potential equality over the whole surface of the corroding metal and the *assumption* that the reduction and metal oxidation processes follow the electrochemical kinetic laws. For the case when both, the anodic and cathodic electrochemical reactions are activation controlled (*i.e.*, can be represented by Tafel relations), the Wagner–Traud model can be schematically represented by the diagram shown in Fig. 1. The partial anodic, j_a , and partial cathodic, j_c , current densities are presented as Tafel straight lines (dashed lines), with the intersection at the corro-

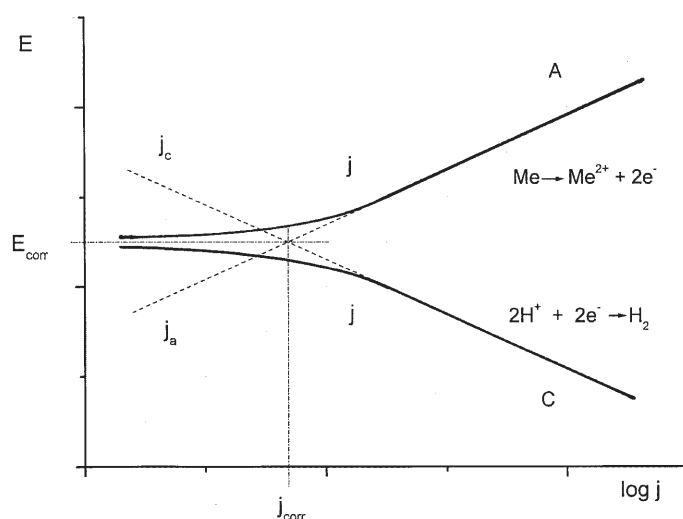


Fig. 1. Wagner–Traud electrochemical corrosion model; j_a – anodic partial current density; j_c – cathodic partial current density; j – effective anodic or cathodic current densities.⁵

sion potential, E_{corr} , which spontaneously forms when the net current at the metal surface, *i.e.*, the electrode of the electrochemical cell, j , is zero. Since the net current (full lines) which are usually experimentally measured in the external circuit, are always the difference between the anodic and cathodic current densities ($j = j_a - |j_c|$), an important conclusion of the Wagner–Traud approach is that the partial anodic and cathodic processes occur simultaneously at any potential of the corroding metal, but at rates corresponding to the electrode potential, and that both processes occur at the same surface randomly. Some authors call this model the homogeneous corrosion model, in contrast to corrosion of heterogeneous metal surfaces when different phases are exposed to the corrosive agent, which might be considered as short-circuited local micro or even macro cells. However, even micro and macro cell action in the multiphase systems can be treated electrochemically as a short-circuited multi-electrode system,⁷ each of them behaving according to the Wagner–Traud model.

The intersection of the Tafel lines at the corrosion potential (see Fig. 1) represents the anodic dissolution current density at E_{corr} , which is, at the same time electrochemical corrosion current density, j_{corr} . Experimental measurements of the polarization curves of the type presented in Fig. 1, small polarization measurement for $\eta < 10$ mV and the use of the concept of polarization resistance, R_p , (Stern and Geary)⁸ and electrochemical impedance measurements⁹ are all based on the Wagner–Traud model and have found wide application among corrosion practitioners and research workers, and also among the manufacturers of electronic devices aimed at producing in a short time experimental data on the corrosion rates of various metals and alloys. However, it was pointed by Prazak¹⁰ that in many cases differences appear between the gravimetrically or analytically determined corrosion rates and those determined electrochemically by the polarization resistance method. Hence, he suggested the use of correction factors for the electrochemically obtained corrosion data, *i.e.*, experimentally determined constant B . It should also be mentioned, that electrochemical determination of corrosion rates at elevated temperatures could produce totally wrong results.¹¹ Nevertheless, electrochemical methods for corrosion rate measurement are still widely used and applied without the necessary caution¹² and verification by other direct methods (weight-loss, analytical, *etc.*).

3. ANOMALOUS BEHAVIORS IN METAL DISSOLUTION

Examples and possible reasons for the experimentally detected anomalous dissolution of metals is well documented in an elaborate review prepared by W. J. James,² and the reader is advised to consult the original review for a number of interesting examples and literature citations. In considering the possible mechanisms by which the effective valence (*i.e.*, the apparent valence) calculated using the Faraday law and the measured amount of electricity passed during the anodic dissolution is smaller than expected, three different mechanisms were proposed: (i) the transitory or uncommon ion mechanism; (ii) the anodic disintegration of metal surface mechanism and (iii) the film controlled mechanism.

3.1. Transitory or uncommon ion mechanism

In the case when the dissolving metal forms ions of higher valence than one, it is reasonable to assume that the electrochemical reaction proceeds stepwise, most probably through single electron exchange reaction steps.¹³ It has been established that many metals during dissolution pass through the stage of a simple monovalent ion in a form Me^+ (*e.g.*, Cu,¹⁴ Zn,¹⁵ Be⁺,¹⁶ In⁺,¹⁷ *etc.*), or hydrated form, MeOH or something similar (*e.g.*, Fe,¹⁸ Co,¹⁹ *etc.*).

It can be expected that such lower valence ion can diffuse into the electrolyte if they are not adsorbed at the electrode surface, as was experimentally proved by

Raush *et al.*¹⁶ for Be^+ and by Hadži Jordanov and Dražić for Zn .²⁰ In such cases, the rates of diffusion of the lower valence ion into the bulk depend on the hydrodynamics and therefore the lower apparent dissolution valence should depend on hydrodynamics in the vicinity of the electrode surface. However, if the lower valence intermediates are strongly adsorbed to the electrode surface, no diffusion into the bulk can be expected, and, therefore, no decrease of the apparent valence for this reason can be obtained.

In some cases, the lower valence ions can be expected to be strong reducing agents for H_2O from the electrolyte, as suggested by Pourbaix²¹ for Cr^{2+} ions. Unstable monovalent ions might also be reducing agents, but the reactivity of various ions of this kind cannot be determined since their instability does not allow knowledge of their thermodynamic properties. However, since the chemical reaction of such ion has to result in anomalous hydrogen evolution during anodic dissolution, this can be an indication that such ion react with the solvent. This will again decrease the apparent valence to a value dependent on the ratio of the rate of the overall electrochemical reaction and that of the chemical reaction of the lower valence ion with water molecules. In a study of Al dissolution in aqueous perchlorate solution, Epelboin *et al.*²² concluded that the appearance of large amount of Cl^- ions is caused by the chemical reduction of perchlorate ions with the Al^+ formed as an intermediate. Przulski and Palka²³ came to a similar conclusion in the case of the dissolution of Mg in Cl^- containing solutions, *i.e.*, that Mg^+ ions are formed which react with H_2O on the one hand to form a hydroxide film on the surface, and on the other hand, gray metallic Mg particles which accumulated in the oxide film, formed by the disproportionation reaction



The effect of the disproportionation reaction on the kinetics of metal dissolution was also elaborated by Losev.⁷

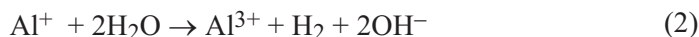
3.2. Disintegration of the electrode surface

Mechanical disintegration of the metal surface during anodic or cathodic polarization has been proposed as the reason for the lower apparent valence during anodic dissolution or the relative increase of the metallic ion concentration above the expected value during cathodic polarization (higher apparent valence). James and Stoner²⁴ reported that in all cases where Zn and Cd exhibited anomalous anodic behavior, a gray-black film was observed on the anodic surface. Straumanis and coworkers²⁵ analyzed the anomalous dissolution of Zn and Al and concluded that the mechanical disintegration (chunk effect) was responsible for the lower apparent valence. They proposed a mechanism for the process of anodic disintegration in which the anodic current is in some way undercutting groups of atoms on the surface which, as metallic particles, stay loosely attached to the surface or are

transported hydrodynamically into the bulk. If the electrolyte is aggressive to the metal, *e.g.*, H_2SO_4 or HCl , spontaneous corrosion of such particles in the electrolyte is to be expected, resulting in the accumulation of metallic ions in the solution at a higher rate than corresponds to the amount of current passed, and also, additional hydrogen evolution. Hence, an apparent valence smaller than expected can be experimentally registered. Marsh and Schaschl²⁶ concluded that Fe in H_2SO_4 solutions of pH 2 corroded 2 times faster than expected from electrochemical measurements because of disintegration (*i.e.*, chunk effect). However, Straumanis *et al.*²⁷ reported that high-purity Fe did not show any sign of disintegration during cathodic polarization in H_2SO_4 solution unless the current density was larger than *ca.* 2 A cm^{-2} . Vorkapić and Dražić²⁸ demonstrated that anomalous dissolution of iron in sulfuric acid solution during prolonged cathodic polarization is also due to mechanical disintegration (hydrogen embrittlement) and not only to the chemical dissolution as proposed by Kolotyркиn and Florianovich.²⁹ Namely, in experiments with a magnetized iron electrode in sulfuric acid solution, the anomalous dissolution rate, determined experimentally by spectrophotometric analysis on Fe^{2+} ions, was decreased considerably, probably because of the cathodic protection of loose iron particles hooked to the magnetized cathodic iron surface. However, some anomalous dissolution still remained indicating that besides mechanical disintegration, some other mechanism of anomalous dissolution exists.

3.3. Film control mechanism

Film control mechanisms have been proposed, as pointed out by James,² to account for the anomalous anodic behavior of metals as manifested by the decreased current efficiencies and negative difference effects, often encountered during the dissolution of Mg, Zn and Al. Various versions of the film control mechanism can be found, most of them are based on the fact that these metals during anodic dissolution are covered with a passive film which is ruptured, occasionally being repaired, and depending on the composition of the electrolyte, some of its constituents, (*e.g.*, Cl^- ions), change the properties of the film. It is worth pointing out that all these processes are connected with the appearance of pits. It should also be mentioned, that the negative difference effect is evidenced by an *increase* of hydrogen evolution with *increasing anodic* current density. This dependence is most often linear and for example for Al in chloride containing solution has a slope 0.15, *i.e.*, the anodic current efficiency for all current densities is about 15 %, but it does not depend on the pH in the range 2 – 7.³⁰ However, alloying of Al with even very small amounts of In or Ga (less than 0.2 wt. %) can decrease the negative difference effect to less than 0.5 %.³¹ Hydrogen evolution during anodic polarization is usually explained either by the formation of Al^+ ions and their reaction with H_2O molecules



or by the acidity at the bottom of the pits increasing due to the hydrolysis reaction of Al^{3+} ions with water containing NaCl



whereby the pH becomes about 4 (or for FeCl_3 hydrolysis even 2) and, therefore, the hydrogen evolution reaction is stimulated. However, the values of the negative difference effect are independent of pH in the range 2–7,³⁰ showing that hydrogen evolution at large anodic current densities is not due to AlCl_3 hydrolysis and local acidification. This is more so if one considers the experimental fact that an Al surface dissolving anodically at *ca.* 100 mA cm⁻² in 0.5 M NaCl had a shiny surface, with no visible pitting, as observed at much lower current densities. It could be imagined that the entire surface become the bottom of a giant pit.³²

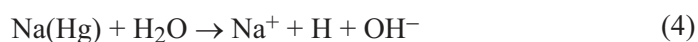
Hydrogen evolution during anodic dissolution is a problem that appears in the different mechanisms of stress corrosion cracking or corrosion fatigue of austenitic and martensitic stainless steels.³³ Namely, theories of pit growth during the pitting of many materials, including ferritic stainless steels,³⁴ assume that pits are formed by anodic reaction at the bottom of cracks in the passive film and cathodic reaction (*e.g.*, oxygen reduction) at the film surface (*i.e.*, by the action of the local cells). However, the rate of electrochemical hydrogen evolution during anodic polarization is considerably depressed at the bottom of pits in accordance with the laws of electrochemical kinetics (*cf.* Fig. 1, by one order of magnitude for each 120 mV of anodic polarization in acid solutions). Since the corrosion potential in acid solutions is $E_{\text{corr}} \approx -0.2$ V (SHE), it is easy to see that in this potential range (*i.e.*, -0.2–0.0 V) the rate of hydrogen evolution has to decrease by *ca.* 100 times. However, since active dissolution before passivation can proceed up to *ca.* 0.5 V (Flade potential for Fe³⁵) electrochemical hydrogen evolution is thermodynamically impossible if the bottom of the pits operate at these anodic potentials. This was experimentally proved by SAYS *et al.*³⁶ who showed, by measuring the local potentials inside the cracks, that the actual potentials of the assumed cathode are more positive than the thermodynamic potentials for hydrogen evolution and therefore the thermodynamics of hydrogen forbid electrochemical evolution of hydrogen at such places. On the other hand, a number of authors, using sophisticated techniques experimentally demonstrated the existence of dissolved hydrogen in the metal and hydrogen embrittlement at the crack tips (see Ref. 33). A possible explanation of the origin of this hydrogen is discussed in Section 4.

One variant of the film mechanism is the suggestion of Abe *et al.*,³⁷ who observed very intensive anomalous dissolution of pure Fe and steels 430 and 304 in sulfuric acid during cathodic polarization, that the high dissolution rate was caused by a layer of hydrogen bubbles which block the surface for cathodic protection. The final effect would be anodic dissolution at rates similar to that at the corrosion potential.

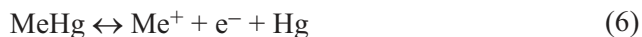
4. CHEMICAL DISSOLUTION OF METALS

4.1. Dissolution of Na and K amalgams

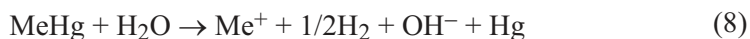
In their study of the hydrogen evolution reaction on mercury or alkaline (K, Na, Li) metal amalgams in aqueous hydroxide solutions Bockris and Watson³⁸ came to the conclusion that the reaction mechanism involves a primary fast deposition of alkali metals atoms, which react irreversibly with water molecules to produce hydrogen and alkali metal hydroxide



This was further experimentally verified by Korshunov and Iofa³⁹ and Frumkin *et al.*⁴⁰ in their studies of the dissolution of alkali metal amalgams (*i.e.*, corrosion). They observed that the dissolution rate of metal from the amalgam followed the relationship $j = kc_{\text{amalg}}^{0.5}$, instead of being $j = kc_{\text{amalg}}$, valid for the electrochemical mechanism of amalgam dissolution. They suggested that the reason for this was the direct chemical reaction of H₂O with alkaline metal from the amalgam. Also, they proposed two parallel reactions for the overall amalgam dissolution process:



for the electrochemical corrosion reaction, and



for the chemical reaction. Based on this model the overall decomposition (*i.e.*, corrosion) rate can be expressed as

$$j_{\text{corr}} = j_{\text{elch}} + j_{\text{ch}} = k_1 [\text{H}_3\text{O}^+]c_{\text{amalg}}^n + k_2 c_{\text{amalg}} \quad (9)$$

where $n < 1$. Depending on the pH, either the electrochemical (at lower pH values), or the chemical mechanism (at higher pH values) could be dominant.

4.2. Other metals

In the period 1965 – 1980, Kolotyркиn and coworkers published a number of papers reporting experimental evidence of the anomalous dissolution of metals during corrosion and cathodic polarization of corroding metals. The technique used was to polarize cathodically a metal at different cathodic polarization values

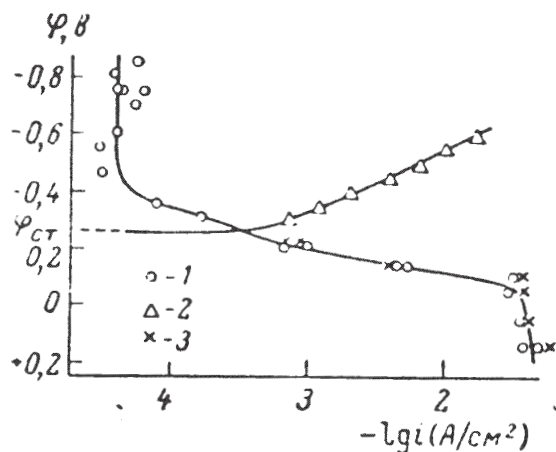


Fig. 2. Dependence of the rate of dissolution of iron in 0.05 M H_2SO_4 solution on the potential, determined analytically at 20 °C (open circles). Cathodic (2) and anodic (3) polarization curves under the same conditions.²⁹

for time long enough to allow accumulation of the corresponding ions in the solution to reach concentration sufficiently high to enable their determination by analytical methods. The obtained results were used to calculate the equivalent dissolution rates in terms of anodic current density with the help of the Faraday law and compare them with the expected electrochemical dissolution rates at these (cathodic!) potentials. For many metals it was found that the overall dissolution rate was much higher than expected, and even more important, that it did not depend on

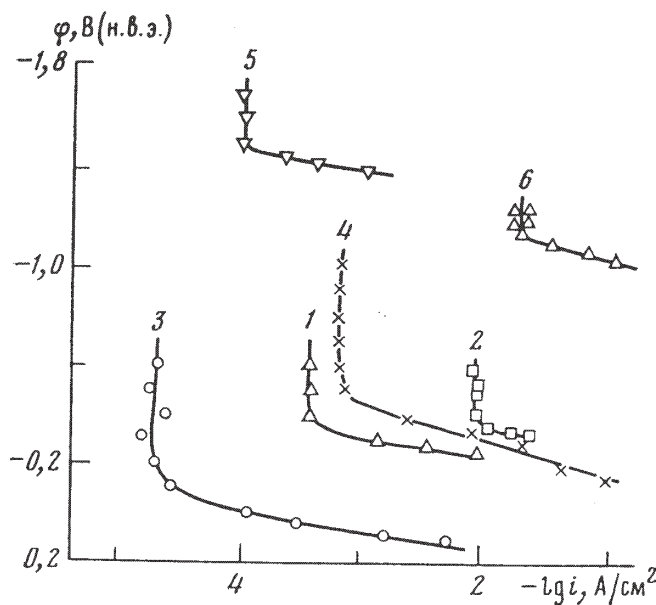
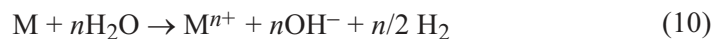


Fig. 3. Dependence of the dissolution rate of iron (1), chromium (2), nickel (3), aluminium (4), zinc (5), and manganese (6) on the potential, determined analytically, under different conditions: (1) - (3) - in 0.05 M H_2SO_4 ; (4) - 0.05 M H_2SO_4 + 0.1 M NaCl; (5) - 0.05 M H_2SO_4 + 0.25 M Na_2SO_4 ; (6) - 0.05 M H_2SO_4 . Temperature: (1) - (3) - 50 °C; (4) - (6) - 25 °C.⁴⁵

the metal potential, *i.e.*, it appeared that the dissolution process was potential independent. These facts lead Kolotyrkin to conclude that this anomalous behavior was due to a chemical dissolution process. Anomalous dissolution was observed for Fe, Mn, Co, Cr, Be, steels and some other metals.^{28,29,41–46} Figure 2 depicts the dependence of the analytically determined dissolution rates of iron on potential (open circles) and the electrochemically measured cathodic (triangles) and anodic (crosses) curves for the same conditions as presented by Fig. 5 in Ref. 29. Figure 3 depicts the polarization diagram for the anodic dissolution for several metals obtained experimentally by determining analytically the concentrations of the corresponding ions, as presented by Fig. 1 in Ref. 45. Note that the vertical parts of these curves are in the potential range of cathodic polarization, *i.e.*, they are more negative than the corresponding corrosion potential, which, *e.g.*, for Fe in the employed concentration of sulfuric acid is about -0.2 V (SHE). Note also that instead of the anodic polarization curves being Tafel straight lines, as expected from the Wagner–Traud model (see Fig. 1), all of them deviated at more negative potentials, becoming vertical, *i.e.*, the dissolution becomes potential independent. In electrochemical terms, these parts indicated anomalous metal dissolution with apparent current efficiencies higher than one, or apparent valence lower than the corresponding true valence of the dissolved metal ion. Interestingly, contrary to the other metals studied, the anomalous dissolution of iron was also pH dependent, *i.e.*, H^+ ions accelerated the dissolution. The overall reaction was presented as.²⁹



while for the pH dependent processes for Fe and Cr a more complex mechanism was proposed:



More details about the anomalous or chemical dissolution of metals can be found in a recent review article prepared by Florianovich.⁴⁷

Other authors also reported findings on the chemical dissolution of some metals. For example for Ni,^{48,49} Zn,⁵⁰ In amalgam,⁵¹ Co,⁵² Al,^{53,54} steel⁵⁵ and Fe.^{28,56}

4.3. New evidence for the chemical dissolution of metals

Chemical analyses of the electrolyte after prolonged electrolysis, necessary for the accumulation of a sufficient amount of the corresponding ions needed for analytical determination, allow quantitative studies of the anomalous dissolution of metal only in the region of cathodic polarizations, as presented in Figs. 2 and 3.

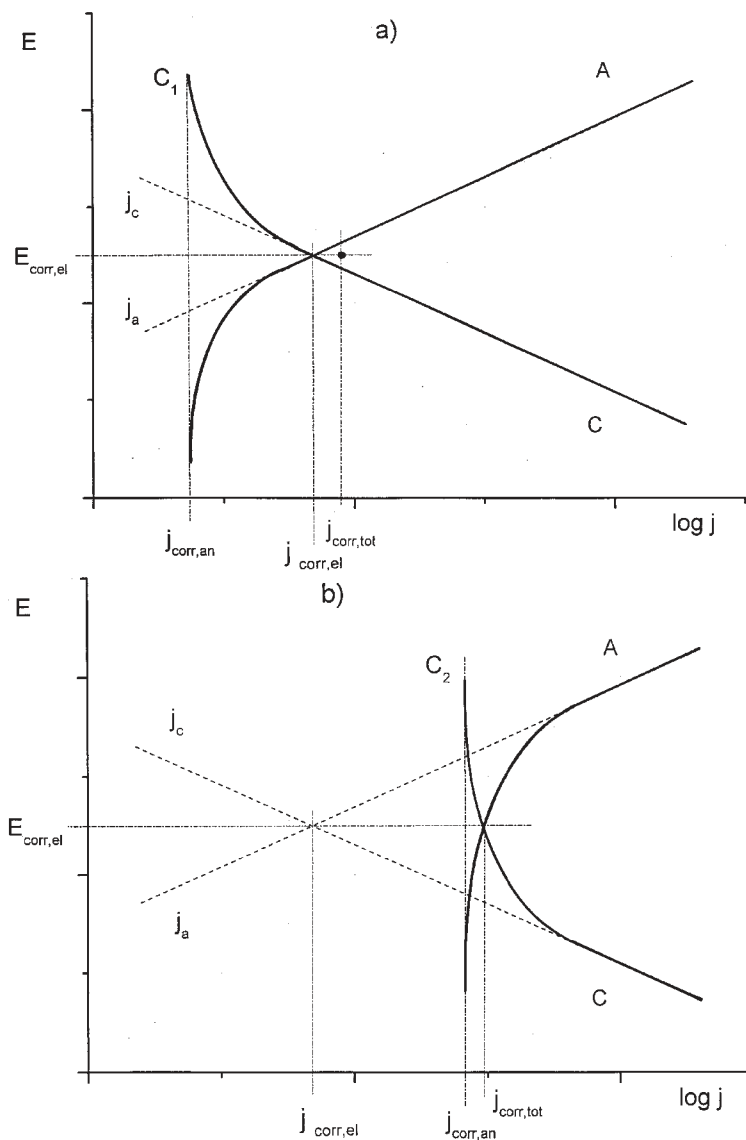


Fig. 4a and b. Schematic representation of the Wagner–Traud electrochemical corrosion model with superimposed chemical dissolution when the chemical dissolution rate is smaller than the electrochemical corrosion rate (a), and when the chemical corrosion rate is larger than electrochemical corrosion rate (b).

In the range of anodic polarizations, the electrochemical dissolution rates are almost always higher than the chemical dissolution rates (see Fig. 4a), and therefore it is difficult to ascribe the small differences between the obtained analytical and electrochemical data to the chemical (or any other kind of anomalous) dissolution, or to experimental errors in the analytical determinations. On the other hand, the

analytical method used by Kolotyrkin and coworkers, and other cited authors, has the problem that simultaneous cathodic polarization can cause surface distintegration and, therefore, false conclusions. Also, the purity of the electrolyte might play an important role since, during prolonged cathodic polarization, metal impurities might be electrodesposited at the surface and change its properties, as was discussed in the case of Na amalgam in the work of Frumkin *et al.*⁴⁰

According to the view of Kolotyrkin, the chemical dissolution of a metal, whether following reactions (10) or (11) – (13), should be a potential independent reaction and, therefore, in an electrochemical diagram of the Wagner–Traud type presented in Fig. 1, should be represented by a vertical line, as depicted in Fig. 4a. Its position in the diagram is determined only by the rate of the chemical reaction with water (*e.g.*, the kind of metal, temperature, and pH for a pH dependent reaction). As seen, for the case when the rate of chemical dissolution is much smaller than that of electrochemical corrosion (vertical straight line C_1), deviations from the electrochemical anodic partial current density line (*i.e.*, anodic Tafel line A – dashed line) on the overall partial dissolution current density–potential dependence line (heavy line A) can be observed only in the range of cathodic polarizations. In the case when the rate of chemical dissolution is higher than that of electrochemical corrosion (vertical straight line C_2), as presented in Fig. 4b, deviations from the anodic partial current density line might start much before the corrosion potential, *i.e.*, in the domain of actual anodic polarization (see Fig. 4b). The important point in this case is that the corrosion potential is determined solely by electrochemical reactions, in accordance with the Wagner–Traud model, but the actual dissolution rate, or the real corrosion current density is much higher than expected from the intersection point of the anodic and cathodic Tafel lines (*c.f.* Fig. 4b). In this case the apparent (anomalous) valence determined electrochemically should depend on the anodic current density, being smaller at the corrosion potential and slowly increasing with an asymptotic tendency to the real value with increasing anodic polarization.

These diagram can also be analyzed by considering the cathodic reaction, *i.e.*, the partial electrochemical hydrogen evolution current density line (*i.e.*, the cathodic Tafel line C – dashed line). Since molecular hydrogen is also produced in the chemical reactions (10) or (11) – (13), the overall hydrogen production as a function of potential should be the sum of the partial cathodic (dashed C) and chemical reaction vertical line (C_1 for Fig. 4a or C_2 for Fig. 4b). The heavy C lines in both figures depict these sums. Therefore, in the case of the existence of parallel chemical reaction of the Kolotyrkin type the hydrogen evolution rates (measured, *e.g.*, volumetrically) would deviate from the overall equivalent (calculated by using the Faraday law) hydrogen current density line C, either as depicted in Fig. 4a or Fig. 4b. If the hydrogen evolution during anodic polarization could be measured sufficiently precisely and its rate coincided with the chemical metal dissolution line determined by the analytical

method used by Kolotyrkin and coworkers the chemical dissolution hypothesis of Frumkin, Kolotyrkin and others would obtain a very serious confirmation.

In their work with a Fe-disc-Pt-ring rotating electrode, Popić *et al.*⁵⁷ showed that hydrogen co-evolution at the disc electrode could be measured up to equivalent current densities of less than $10 \mu\text{A cm}^{-2}$ by electrochemical oxidation of the hydrogen collected at the Pt disc. Using this method, Dražić and Popić^{30,58} studied the negative difference effect and anomalous dissolution of Al during pitting, and also analyzed the hydrogen co-evolution during anodic polarization of Fe and steel in aqueous sulfuric acid solutions.^{56,59,60}

The important experimental results presented in Ref. 56 are depicted in Figs. 5 – 7. Figure 5 represents the polarization curves for Armco iron in $0.1 \text{ M Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH 1) determined electrochemically (open circles) starting from the corrosion potential going in the anodic direction. The filled circles represent the oxidation currents (corrected for the collecting efficiency experimentally determined for the used experimental set-up) for hydrogen evolved on an iron disc and collected at the Pt ring. It can be seen that cathodic Tafel lines obtained by direct electrochemical

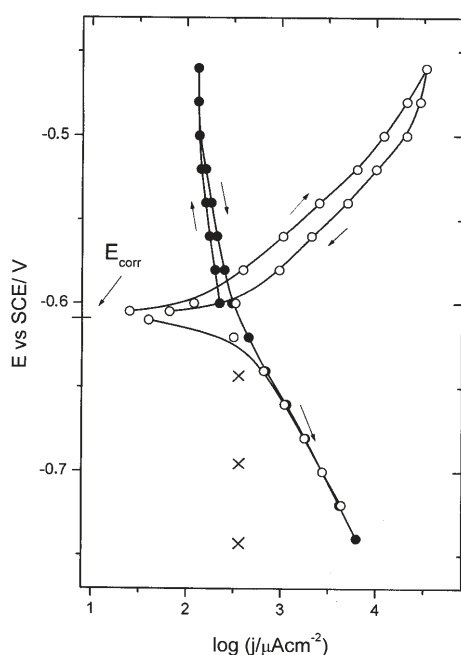


Fig. 5. Anodic and cathodic polarization curves for Armco iron in $0.1 \text{ M Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH 1) aqueous solution (open circles) and H_2 evolution current densities detected by the Pt ring of a rotating Fe-disc-Pt-ring electrode (filled circles). The arrows indicate the direction of polarization.⁵⁶

(x) – Results from Fig. 3, curve 1.

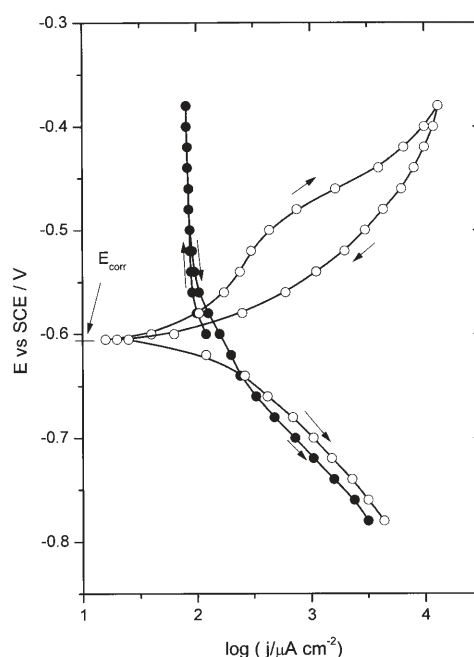


Fig. 6. Anodic and cathodic polarization curves as shown in Fig. 5 but with the addition of 0.03 M NaCl .⁵⁶

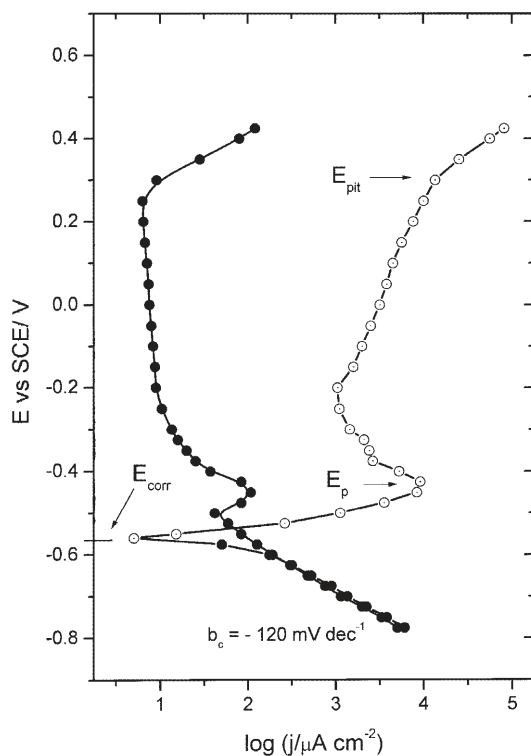


Fig. 7. Anodic and cathodic polarization curves for 304 stainless steel in 0.1 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M NaCl}$ solution (open circles) and the simultaneously detected H_2 evolution on a Pt-ring (filled circles).⁵⁶

measurements (open circles) and indirectly by collecting evolved hydrogen on Pt ring (filled circles) overlap in the cathodic potential region, while in the anodic region, the partial hydrogen evolution deviates from the Tafel line eventually forming a vertical line, similar to that predicted in Fig. 4a for the case of a chemical dissolution reaction of a Kolotyrkin type occurring simultaneously with the corresponding electrochemical reactions (hydrogen evolution and anodic dissolution). Figure 6 depicts a similar diagram for Armco iron in the same solution as for Fig. 4a, but with the addition of 0.03 M NaCl. The presence of chloride ions had an inhibiting effect on the anodic polarization curve, as is known from previous experience⁶¹ However, chloride ions had no detectable effect on the anomalous co-evolution of hydrogen during anodic dissolution, but a small inhibiting effect on the cathodic evolution of hydrogen, as is also known from previous experience.⁶² Another important conclusion from these experiments (Ref. 56, Fig. 2) was that the anomalous hydrogen evolution was not pH dependent in the pH range 0.5 to 3, which is contrary to the findings of Kolotyrkin and Florianovich.⁴⁵ Also of importance is the fact that, as shown in Fig. 6, the presence of chloride ions practically had no influence on the anomalous dissolution process, even though anodic dissolution reaction was inhibited in a known manner.⁶¹ On the other hand, a very important point is that the crosses in Fig. 5 representing the experimental points for iron in a very similar solution (Fig. 2a pre-

sented in Ref. 45) are positioned at practically the same vertical line (dotted line C_1) as experimental points for anomalous hydrogen evolution during anodic polarization (filled circles) presented in Fig. 5. This is the experimental proof that the model presented in Fig. 4a, *i.e.*, chemical dissolution proposed by Kolotyrkin and coworkers, is acceptable. None of the other mechanisms proposed in Section 3 can produce a potential independent process in both the cathodic and anodic potential range, as can the one presented schematically in Fig. 4a and experimentally in Fig. 5.

The obtained results strongly support the proposal made by Kolotyrkin and coworkers that the anomalous dissolution and hydrogen evolution on iron can be considered as a chemical mechanism of iron corrosion, occurring simultaneously with electrochemical processes and electrochemical corrosion



Since the chemical reaction (14) does not involve free electron exchange, the electronic balance between the metal and solution is achieved when the electrochemical partial processes occur at equal rates, *i.e.*, at the corrosion potential. Therefore, the corrosion potential of iron (and other metals corroding chemically in a similar manner) is determined *only* by electrochemical reactions, while the chemical corrosion process has no influence on it.

Figure 7 depicts the polarization diagram for stainless steel 403 (open circles), and equivalent hydrogen current densities obtained by the same rotating disc-ring technique as for iron (filled circles) (*cf.* Figs. 5 and 6). It is interesting that in the anodic potential region hydrogen evolution starts even to increase after passing through the corrosion potential region, but at potentials more positive than the passivation potential, E_p , decreases to very small values in the range of the passive state. In other words passivation of the surface strongly inhibits the anomalous hydrogen evolution. This can be simply explained by a blocking of the direct contact of H_2O molecules with the metallic surface which is required for reaction (14) to occur. The further increase of the hydrogen current on the ring after the pitting potential, E_{pit} , confirms the often-reported literature data^{2,33} that hydrogen gas is evolved during pitting (negative difference effect).

Results obtained with metallic chromium in a series of similar experiments performed by Popić and Dražić^{63–67} are even more important for clarification of the role of chemical reactions in corrosion.

The immediate reason for the study of the behavior of chromium was the rather strange peak in Fig. 7 on the hydrogen evolution line for stainless steel in the region of anodic potentials. Since the only difference between the polarization diagrams for iron (Fig. 5) and stainless steel (Fig. 7) was the rather high content of Cr (*ca.* 18 wt.%), it was assumed that this increases of hydrogen evolution rate during anodic dissolution in the active dissolution potential range might be related to the presence of Cr.

Several techniques were used to study the anomalous dissolution of chromium; polarization measurements, analytical determination of Cr(II) and Cr(III) concentrations, the evolved hydrogen volume and gravimetric determination of the metal weight loss. The results of these examinations for metallic Cr in a deaerated aqueous sulfuric acid solution of pH 1 with 0.1 M sodium sulfate added are presented in Fig. 8 (Ref. 67, Fig. 1). The anodic and cathodic Tafel slopes were *ca.* 120 mV dec⁻¹ with a rather narrow anodic potential range before passivation. Similar polarization diagrams for pH 2 and 3 showed (Ref. 66, Fig. 2) that the hy-

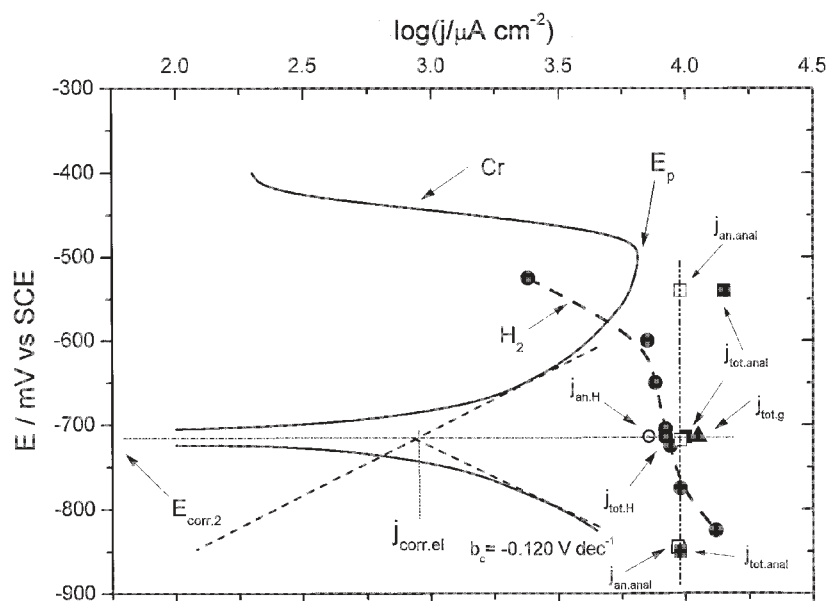
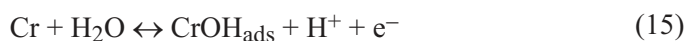
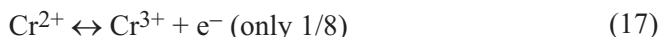
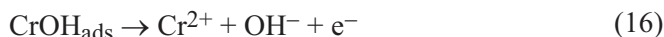


Fig. 8. Anodic and cathodic polarization curves for a Cr electrode at pH 1.0 (0.5 M Na₂SO₄ + H₂SO₄), (—●—) H₂ evolution rates calculated from volumetric data. (---) Partial anodic Tafel line. Total corrosion current densities determined: (●) – volumetrically, (▲) – gravimetrically and (■) – analytically. Electrochemical corrosion current density $-j_{\text{corr,el}}$. The anomalous dissolution current densities (vertical dash and double dots line) are the differences between the total and the electrochemical corrosion current densities. (□ – Calculated from analytical; ○ – from volumetric data). Sweep rate 2 mVs⁻¹.⁶⁷

drogen evolution Tafel line was pH dependent with a reaction order with respect to H⁺ ions of $n_{\text{H}^+} = 1$, while anodic Tafel line was pH independent, even though the passivation potential was pH dependent. Bearing in mind that the dissolution products during the corrosion of Cr in deaerated sulfuric acid are Cr(II) and Cr(III), formed in the ratio Cr(II)/Cr(III) ≈ 7 , as experimentally proved in Ref. 65, the following mechanism for the electrochemical dissolution reaction was postulated.⁶⁷



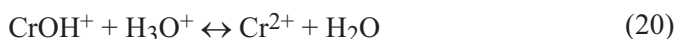
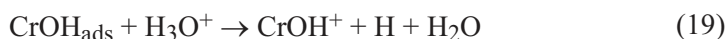


It should be pointed out that active dissolution of Cr proceeds only if the surface was activated by polarization with cathodic current densities of *ca.* 50 mA cm⁻² for several tens of seconds, in order to reduce the thin oxide film which spontaneously forms on contact of Cr with air. The corrosion potentials of non-activated surfaces were more positive by *ca.* 200 mV.

The results of the hydrogen co-evolution measurements, obtained by measuring the volumes of the evolved hydrogen and recalculating into the equivalent current densities, are presented in Fig. 8 by the black dots connected with the dashed curve. As can be seen, the effective hydrogen evolution curve (dashed curve) is in the domain of current densities much larger than the cathodic Tafel line representing the electrochemically evolving hydrogen. This is also the case in the vicinity of the corrosion potential and also in the domain of anodic polarizations. In the domain of the passivation potential, this hydrogen evolution drastically decreases. Since the total hydrogen evolution is the sum of the electrochemical hydrogen evolution represented by the cathodic partial hydrogen evolution line over the whole domain of electrode and some other anomalous hydrogen evolution process (*i.e.*, chemical hydrogen evolution) the difference between the total hydrogen evolution rate (dashed line) and the cathodic Tafel line at any potential should give the dependence of the anomalous hydrogen evolution (equivalent to Cr dissolution, Eq. (10)) on potential. Such differences for three electrode potentials, for the corrosion potential, for anodic polarization in the active dissolution range and during cathodic polarization are lying on a vertical line and these data are presented in detail in Ref. 66, Figure 1. These results are omitted from Fig. 8 in order to make the diagram simpler, except the open circle at $E_{\text{corr}, 2}$, representing the anomalous dissolution rate at the corrosion potential, $j_{\text{an.H}}$. Practically the same result was obtained as presented in Fig. 8, when the analytically determined concentrations of Cr(II) and Cr(III) ions were recalculated into the total dissolution current densities, $j_{\text{tot,anal}}$ (filled squares), for three different electrode potentials and the anodic dissolution current densities corresponding to the same potentials, j_a . These values are represented with open squares and they also lie on a vertical line (dash and dots line) close to the previously described (vertical dashed line). The important point is that these three calculated points lie on a same vertical line (dashed line), as would be expected in the case when the chemical dissolution reactions is faster than the electrochemical corrosion rate (see Fig. 4b). In the same diagram, the filled triangle at the corrosion potential represents the result of the weight-loss measurements of the Cr electrode after prolonged corrosion under the same experimental conditions. It can be concluded here that all three applied measuring methods gave practi-

cally the same result, and supported the view of Kolotyrkin that, besides the electrochemical reactions and corrosion behavior in accordance with the Wagner–Traud model, a parallel dissolution reaction accompanied by an equivalent evolution of hydrogen, practically independent of the electrode potential, is occurring. This fact allows the conclusion that this reaction is a chemical reaction of the Kolotyrkin type, and, in the case of a Cr electrode in acid solutions (addition of Cl⁻ ions has no effects), the rate of this chemical dissolution reaction is up to several times faster than the equivalent electrochemical corrosion rate. This fact is very important since, in corrosion measuring practice, electrochemical corrosion rate methods (*e.g.*, Stern–Geary polarization resistance,⁸ electrode impedance spectroscopy,⁹ *etc.*) are widely applied as the exact method,¹² but, as seen, the results could be seriously erroneous if chemical dissolution processes are ignored. It could be that the problems discussed by Pražak¹⁰ are also related to the neglect of a chemical reaction.

The rate of the chemical dissolution reaction is pH dependent and has an experimental reaction order with respect to H⁺ ions of *ca.* 0.89 in the pH range 0.5 – 3,⁶⁷ *i.e.*, practically one. Bearing in mind the observed diagnostic criteria, and also the fact that most of the electronegative metals, Ni, Fe, Co, Zn, *etc.*, have an affinity for H₂O molecules,⁶⁸ which has found its confirmation in many proposed anodic metal dissolution mechanisms,⁶⁹ the following Cr chemical dissolution mechanism in aqueous acid solutions can be postulated:



which is similar to that proposed by Kolotyrkin for Fe.⁴⁵ It should be pointed out that this reaction occurs only at a bare metal surface, and, as seen in Fig. 8, the formation of a passive layer inhibits this reaction, which is logical since H₂O molecules important for the reaction cannot come in contact with metal atoms.

Another important fact is that the temperature dependence of the chemical reaction is more pronounced than that of the electrochemical corrosion. It was shown in Ref. 64 that the apparent energy of activation for the dissolution chemical of Cr is 63.1 kJ mol⁻¹, for the anodic dissolution 66.9 kJ mol⁻¹, but only 19.5 kJ mol⁻¹ for the electrochemical hydrogen evolution. Temperature dependence of the electrochemical corrosion rate is a complex function of both the anodic and cathodic temperature dependences (note that it is unjustified⁶⁴ to use the Arrhenius equation for the determination of the energy of activation of corrosion, as is sometimes found in the literature) but it can be easily estimated that the electrochemical corrosion current, because of the smaller energy of activation for hydrogen evolution

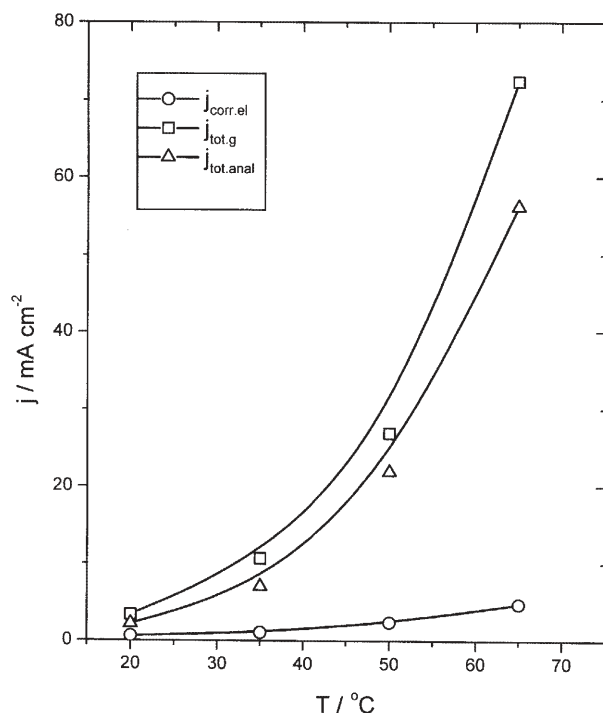


Fig. 9. Total corrosion current densities obtained gravimetrically (\square) or analytically (Δ), and the electrochemically obtained corrosion current densities (\circ) at different temperatures.⁶⁴

has to change slower with increasing temperature, than the chemical dissolution, since both the chemical dissolution and anodic dissolution have approximately the same energies of activation (note that according to the Arrhenius equation processes with the higher energies of activation increase their rates faster than those with smaller ones). This is obvious from Fig. 9 which represents the changes of the corrosion rates with temperature for the rates of electrochemical corrosion (circles) and total corrosion determined analytically (triangles) or gravimetrically (squares). The anomalous, chemical dissolution rates are the differences between the total and the electrochemical rates. As can be seen, the chemical dissolution current increases faster with increasing temperature than the electrochemical one. The temperature dependence of the electrochemical corrosion current in a polynomial form is⁶⁴

$$j_{\text{corr,el}} = 9.3 \times 10^{-6}T^3 + 9.8 \times 10^{-4}T^2 - 0.046T + 1.09 \quad (21)$$

while for the total corrosion current determined analytically is:

$$j_{\text{tot,anal}} = 4.8 \times 10^{-4}T^3 - 0.028T^2 + 0.764T - 5.64 \quad (22)$$

where T is the temperature in degrees Celsius, while $j_{\text{anom}} = j_{\text{tot}} - j_{\text{corr,el}}$. Hence it is simple to calculate the ratio $j_{\text{anom}}/j_{\text{corr,el}}$ for any temperature. For 22 °C this ratio is 3.15 for 65 °C it is 6.34 for 80 °C 13.4, while for the boiling solution, *i.e.*, 100 °C it becomes 16.4, if the extrapolation to this temperature is valid. In this case at ele-

vated temperatures, the electrochemical corrosion rate is negligible in comparison with that of chemical corrosion and, obviously, electrochemical corrosion rate measurements become senseless. The reason for the larger effect of temperature on the chemical dissolution rate than on the electrochemical corrosion rate is the considerable difference in energies of activation for electrochemical hydrogen evolution (19.5 kJ mol^{-1}) and the rather high energies of activation for the chemical dissolution reaction (69.9 kJ mol^{-1}) and the anodic dissolution reaction (63.1 kJ mol^{-1}), as mentioned previously. On the other hand, the very similar energies of activation for the anodic reaction and the chemical reaction suggest that the reaction mechanisms are very similar with similar reaction intermediates participating. This is another argument that the proposed reaction mechanism given by reactions (15) – (17) for the electrochemical dissolution and reactions (18) – (20) for chemical dissolution are probably valid.

5. CONCLUSIONS

During the anodic dissolution of a number of metals the calculated dissolution valence is sometimes lower than expected. The observed values of the valence are termed apparent and the dissolution process anomalous, *i.e.*, deviating from the Faraday law. Disintegration of the metal surface, lower valence ion formation, passivation and the formation various films, hydrogen embrittlement, *etc.* were proposed as the reasons for the anomalous behavior. However, Frumkin and coworkers analyzing the dissolution of alkali metal amalgams, and later Kolotyrkin and coworkers analyzing the anomalous behavior of some other electronegative metals (Fe, Ni, Cr, Mn, Al, Be, *etc.*) during cathodic polarizations in acid electrolytes concluded that simultaneously with the electrochemical anodic reaction, a chemical reaction occurs, whereby metal atoms at the surface react with water molecules forming metal ions and gaseous hydrogen. Recent results of studies of the anomalous behavior of Fe and Cr during cathodic and anodic polarizations made by Dražić and coworkers strongly support the view of Kolotyrkin concerning the role of a chemical reaction in the process of metal corrosion in aqueous solutions. It was also shown that an increase of temperature favors the chemical reaction, so that at higher temperatures, chemical dissolution of chromium can be as much as 10 times faster than the electrochemical corrosion. As chemical dissolution reactions cannot be followed by electrochemical means, electrochemical methods for the determination of corrosion rates, especially at elevated temperatures, give erroneous results. How large the errors can be depends on the actual rate of the chemical process and its ratio against the electrochemical corrosion rate.

Acknowledgements: This work was financially supported by the Ministry of Science and Environmental Protection of the Republic of Serbia (Grant No. 1389) and the Serbian Academy of Sciences and Arts (Project F-7(4)).

ИЗВОД

АНОМАЛНО РАСТВОРАЊЕ МЕТАЛА И ХЕМИЈСКА КОРОЗИЈА

ДРАГУТИН М. ДРАЖИЋ^{1,2} и ЈОВАН П. ПОПИЋ¹¹Институт за хемију, технологију и металургију – Центар за електрохемију, Њеђошева 12, п.бр. 473, 11000 Београд и ²Српска академија наука и уметности, Кнез Михаилова 35, 11000 Београд

Дат је преглед аномалног понашања неких метала при анодном растварању у киселим воденим растворима, нарочито Fe и Cr. Аномалија се одражава у чињеници да се током анодног растварања раствори више материјала него што би се очекивало на основу Фарадејевог закона при стварању одговарајућих јона. Као могући разлози овој појави разматрана је механичка дезинтеграција површине, блокада површине мехурима водоника, водонична кртост, пуцање пасивног слоја, као и неки други могући узроци. Такав могући узрок, по предлогу Колотиркина и сарадника је и хемијска реакција молекула H₂O са металом уз стварања јона метала и издвајања гасовитог H₂ у процесу независном од потенцијала. Показано је да ова реакција тече симултано са електрохемијским процесом корозије, при чему искључиво он контролише корозиони потенцијал. Показано је на примеру Cr и Fe у киселом раствору да је доминантан узрок аномалног понашања управо хемијска реакција растварања, која је код Cr значајно бржа од електрохемијске, као и да повишавање температуре више убрзава хемијско растварање, док је код Fe хемијска реакција спорија од електрохемијске. Разматрана је могућна улога хемијске реакције растварања и издвајања водоника при појави питинга код нерђајућих челика и Al као и појави корозионог замора и лома.

(Примљено 10. новембра 2004)

REFERENCES

1. *CRS Handbook of Chemistry and Physics*, 55th Ed., R. C. West Ed. CRS Press, Cleveland, Ohio, 1974, p. F88
2. W. J. James, Anodic Dissolution of Metals – Anomalous Valence in *Advances in Corrosion Science and Technology*, Vol. 4 M.G. Fontana and R. W. Staehle, Eds., Plenum Press, New York, 1974, pp. 85 – 147
3. A. Thiel, J. Eckell, *Z. Elektrochem.* **33** (1927) 370
4. W. Vielstich, *Brenstoffelemente*, Verlage Chemie, Weinheim, 1965, Chapter. 5.4
5. A. de la Rive, 1830, citation after A. N. Frumkin, *Izabranie trudi: elektrodnie processy*, B. P. Nikoljskiy, Ed., Nauka, Moskva, 1987, p. 183
6. K. Wagner, W. Traud, *Z. Elektrochem.* **44** (1938) 391
7. N. D. Tomashov, *Teoriya korozii i zashchiti matallov*, AN SSSR, Moskva, 1959.
8. M. Stern, A. L. Geary, *J. Electrochem. Soc.* **104** (1957) 56
9. F. Mansfeld, in *Advance in Corrosion Science and Technology*, Vol. 6, M. G. Fontana and R. W. Staehle, Eds., Plenum Press, New York, 1976
10. M. Pražak, *Werkst. Korros.* **25** (1974) 104
11. M. E. Indig, C. Groot, *Corrosion* **25** (1969) 367
12. J. R. Scully, *Corrosion* **56** (2000) 199
13. B. E. Conway, J. O'M. Bockris, *Electrochim. Acta* **3** (1960) 340
14. E. Mattson, J. O'M. Bockris, *Trans. Faraday Soc.* **55** (1959) 1586
15. D. M. Dražić, S. K. Zečević, *Bull. Chem. Soc. Beograd* **43** (1978) 141
16. M. D. Raush, W. E. McEwen, J. Kleinberg, *J. Am. Chem. Soc.* **76** (1954) 363
17. A. I. Molodov, G. N. Markosyan, A. P. Pchel'nikov, V. V. Losev, *Elektrokhimiya* **4** (1958) 1366, 1370
18. J. O'M. Bockris, D. M. Dražić, A. R. Despić, *Electrochim. Acta* **4** (1961) 325
19. K. Heusler, *Ber. Bunsenges. Phys. Chem.* **71** (1067) 620

20. S. A. Hadži Jordanov, D. M. Dražić, *Bull. Chem. Soc. Beograd* **38** (1973) 529
21. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, New York, NY: Pergamon Press, 1966, p. 226
22. I. Epelboin, M. Froment, G. Nomarski, *Rev. Metal.* **55** (1958) 260
23. J. Przyłiski, E. Palka, *Electrochim. Acta* **15** (1970) 853
24. W. J. James, G. E. Stoner, *J. Am. Chem. Soc.* **85** (1963) 1354
25. M. E. Straumanis, *J. Electrochem. Soc.* **108** (1961) 1087 and references therein
26. G. A. March, E. Schaschl, *J. Electrochem. Soc.* **107** (1960) 960
27. M. E. Straumanis, G. E. Welch, W. J. James, *J. Electrochem. Soc.* **111** (1964) 1292
28. L. Ž. Vorkapić, D. M. Dražić, *Corros. Sci.* **19** (1979) 643
29. Ya. M. Kolotyrkin, G. M. Florianovich, *Zashch. metal.* **1** (1965) 7
30. D. M. Dražić, J. P. Popić, *J. Appl. Electrochem.* **29** (1999) 43
31. A. R. Despić, D. M. Dražić, M. Purenović, N. Ciković, *J. Appl. Electrochem.* **6** (1976) 527
32. A. R. Despić, D. M. Dražić, S. K. Zečević, R. T. Atanasoski, *Electrochim. Acta* **26** (1981) 173
33. R. H. Jones, "Stress Corrosion Cracking", in *ASM Handbook, Metals Handbook, Vol. 13, Corrosion*, The Materials Information Society, 1998, pp. 145, 161
34. H. Kaesche, *Die Korrosion der Metalle*, Springer, Berlin, 1979, Russian translation, Metallurgiya, Moskva, 1984, p. 269
35. K. J. Vetter, *Elektrochemische Kinetik*, Springer, Berlin, 1961, Fig. 208
36. A. A. Seys, M. J. Brabers, A. A. Van Haute, *Corrosion* **30** (1974) 47
37. S. Abe, K. Tano, M. Tuchinaga, *Proc. 11th Intern. Corr. Congress*, Florence, 2–6 April 1990, Vol. 3, Associazione Italiana di Metallurgia, Milano, 1990, p. 3.501
38. J.O'M. Bockris, R. Watson, *J. Chim. Phys.* **49** (1952) 70
39. V. N. Korshunov, Z. A. Iofa, *Dokl. AN SSSR* **141** (1961) 143
40. A. N. Frumkin, V. N. Korshunov, Z. A. Iofa, *Dokl. AN SSSR* **141** (1961) 413
41. Ya. M. Kolotyrkin, G.M. Florianovich, *Z. Phys. Chem. (Leipzig)* **231** (1966) 145
42. Ya. M. Kolotyrkin, T. R. Agladze, *Zashch. metal.* **4** (1967) 413
43. V. M. Knyazheva, Ya. M. Kolotyrkin, A. A. Kruzhkovskaya, *Zashch. metal.* **6** (1970) 265
44. Ya. M. Kolotyrkin, G. M. Florianovich, *Elektrokhimiya* **9** (1973) 413
45. Ya. M. Kolotyrkin, G. M. Florianovich, *Zashch. metal.* **20** (1984) 14
46. Ya. M. Kolotyrkin, G. M. Florianovich, *Bull. Chem. Soc. Beograd* **48** (1983) S125
47. G. M. Florianovich, *Russ. J. Electrochem.* **36** (2000) 1037
48. G. G. Penov, Z. Ya. Kosakovskaya, L. A. Botneva, N. P. Zhuk, *Zashch. metal* **6** (1970) 544
49. G. Bech-Nielsen, F. de Fonteney, H. Poulsen, *Electrochim. Acta* **47** (2002) 4279
50. L. A. Chernikova, V. I. Vigdorovich, L. E. Tsigankova, R. V. Glotova, *Zh. prikl. khim.* **6** (1978) 2190
51. E. V. Leontovich, V. V. Losev, M. A. Dembrovskii, *Elektrokhimiya* **5** (1969) 32
52. G. Raichevski, *Izv. po khim. BAN* (1978) 11
53. S. P. Kuznetsova, T. V. Gubenko, N. P. Zhuk, *Zashch. metal.* **11** (1975) 321
54. G. Bech-Nielsen, *New Applications of Corrosion Measurements by Titration*, 47th ISE Meeting, Veszprem, Hungary, 1996, Book of Abstracts, L6a – 2
55. F. Mansfeld, J. V. Kenkel, *Corros. Sci.* **16** (1976) 653
56. D. M. Dražić, J. P. Popić, *Russ. J. Electrochem.* **36** (2000) 1043
57. J. P. Popić, M. Avramov-Ivić, D. M. Dražić, *J. Serb. Chem. Soc.* **61** (1996) 1233
58. D. M. Dražić, J. P. Popić, *ATB Metallurgie, Acta Technica Belgica* **37** (1997) 307
59. D. M. Dražić, "Anomalous Hydrogen Evolution on Some Metals", *Proc. 3rd Kurt Schwabe Symp. on Corrosion*, 30 Aug.- 2 Sept. 2000, Zakopane, Poland, pp. 173–179
60. D. M. Dražić, J. P. Popić, "The Negative Difference Effect and Stress Corrosion Cracking", 5th European Symposium on Electrochemical Engineering, Icheme Symposium Series No. 145, 1999, p. 111
61. D. M. Dražić, V. J. Dražić, V. Jevtić, *Electrochim. Acta* **34** (1989) 1251
62. Lj. Vračar, D. M. Dražić, *J. Electroanal. Chem.* **339** (1992) 269

63. D. M. Dražić, J. P. Popić, *J. Serb. Chem. Soc.* **67** (2002) 777
64. J. P. Popić, D. M. Dražić, *J. Serb. Chem. Soc.* **68** (2003) 871
65. D. M. Dražić, J. P. Popić, *Corrosion* **60** (2004) 297
66. J. P. Popić, D. M. Dražić, *J. Electrochim. Acta* **49** (2004) 4877
67. D. M. Dražić, J. P. Popić B. Jegdić, D. Vasiljević-Radović, *J. Serb. Chem. Soc.* **69** (2004) 1065
68. R. M. Lazorenko-Manevich, L. A. Sokolova, *Elektrokhimiya* **17** (1981) 39
69. D. M. Dražić, Iron and Its Electrochemistry in an Active State, in *Modern Aspects of Electrochemistry*, Vol. 19, B. E. Conway, J.O'M Bockris and R. E. White, Eds., Plenum Press, New York, 1989, Chapter 2, pp. 69 – 192.