ELECTROCHEMICAL AND CHEMICAL CORROSION OF CHROMIUM

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It was shown that chromium in deaerated sulfuric acid of pH 1 exhibits two stable corrosion potentials, depending whether the metal had previously been in contact with air or subjected to activation by cathodically evolving hydrogen. Electrochemical polarization measurements, as well as the measurements of the actual metal dissolution rate at the corrosion potential, anodic or cathodic polarization, using the analytical determination of Cr ions in the solution, or volumes of hydrogen evolved, showed that hydrogen can evolve on chromium by three different reaction mechanisms. The first one is the electrochemical hydrogen evolution reaction from H⁺ ions at the bare chromium surface obtained by cathodic activation. This reaction and the active anodic dissolution of chromium determine one stable corrosion potential. The second reaction is the reaction of H⁺ ions on the oxidized chromium surface which, coupled with the anodic dissolution of passivated chromium determines the other stable corrosion potential. The third one is the “anomalous” or chemical reaction of chromium with water molecules and hydrogen ions whereby hydrogen is liberated. This is a potential independent reaction, occurring on the bare metal surface, and which is at pH 1 several times faster at the corrosion potential than the electrochemical hydrogen evolution reaction. The consequence is that the overall corrosion rate is several times faster than that determined by the usual electrochemical methods. The measurements were performed in the temperature interval 20 – 65 °C and apparent energies of activation for anodic, cathodic and anomalous dissolution reactions were estimated as 63.1, 19.5 and 66.9 kJ mol⁻¹, respectively. This implies that the anomalous dissolution rate increases more with the increase of temperature than the electrochemical corrosion rate. The applicability of the different methods of measuring electrochemical corrosion rates is discussed.

Keywords: chromium; corrosion; hydrogen evolution; anomalous dissolution; energies of activation

INTRODUCTION

After the pioneering work of Volmer, Erdey-Gruz and Horiuty almost 70 years ago in which the fundamentals of electrochemical kinetics were laid down [1, 2] Wagner and Traud [3] applied them to the problems of corrosion of metals in a rather successful way, so that modern corrosion of metals was interpreted as the simultaneous occurrence of at least two opposing electrochemical reactions (anodic, i.e. dissolution or corrosion of the metal) and cathodic (electrochemical reduction of some corrosion supporting substance, e.g. hydrogen ions oxygen, etc.). The electrochemical theory of measuring corrosion was developed by a number of known electrochemists and corrosionists so that the methods of measuring the electrochemical corrosion rate (e.g., Tafel line extrapolation [3], Stern-Geary polarization resistance method [4], electrochemical impedance spectroscopy [4], inflection point method [5], etc.) are widely used in technical practice. However, in a number of practical cases it appeared that the electrochemical methods and some direct corrosion rate measuring methods (e.g., weight loss, hydrogen evolution, analytical methods) might differ in their results by more than the expected experimental errors would allow. One can find in the literature a number of attempts to establish correction factors (always larger than one!) by which electrochemical results should be multiplied to obtain the real corrosion rate data [7, 8]. An extensive review of such cases of “anomalous” metal dissolution resulting in “anomalous valences” always lower the electrochemically expected ones was presented by James [9]. These effects were most often registered during the an-
odic dissolution of Al, Mn, Be, Ga, Ti In, Cd, Cu, Fe, Mg, Zn, etc. James suggests that the anomalous lower valence or the often called negative difference effect can be the result of mechanical disintegration of the metal, lower intermediate valence (e.g., Al⁺, Mg⁺, etc.) and chemical disproportionation of such ions, reaction of lower valence ions with solvent molecules, or similar. However, Koltunyrtkin and his coworkers [10–16], after a careful analysis of many experimental results, came to the conclusion that the “anomalous” dissolution of Fe, Be, Mn, Co, Cr, etc. is due to the direct chemical reaction of H₂O molecules with no interference of electron transfer reactions, i.e., the process is potentially independent. In the present work a more detail experimental analysis of the anomalous dissolution of chromium in sulfuric acid is presented.

EXPERIMENTAL

The experiments were performed with metallic chromium (Merck, lumps). The electrodes were made in the form of a piece of metal sealed in epoxy resin so that the exposed surface was 1 cm². All the experiments were performed in aqueous mixtures of 0.5 M Na₂SO₄ + H₂SO₄, the concentrations of the acid being adjusted so that the pH was 1.0. Merck p.a. chemicals and doubly distilled water were used for the preparation of the solutions. An all glass, three-compartment electrochemical cell with a platinum foil as a counter electrode and a fritted-glass separator and a saturated calomel reference electrode (SCE) with a glass stopcock as a separator was used. The cell was thermostated in a water bath with a ±1 °C temperature control. All the potentials were referred to the SCE which was situated outside the water bath (i.e., its temperature was equal to the ambient temperature (22 ± 2 °C). This was done in accordance with the recommendation given in Refs. 17 and 18 for measuring the electrode potentials at temperatures other than the standard temperature. The solutions were continuously deaerated with purified nitrogen. The potential scan rate of the Cr electrode was 2 mV s⁻¹, which was thought to be sufficiently slow to be able to consider the polarization curves as having been obtained under a quasi-steady state condition. Prior to the measurements, the electrodes were activated by cathodic polarization at −0.9 V for 90 s, since the spontaneous formation of the open circuit potential of an electrode, which had previously been in contact with air, was at about −0.450 V, which corresponded to the passive state of the chromium surface.

A Hewlett-Packard HP8452A spectrophotometer was used for the determination of chromium ion concentration. A stoppered quartz cell was used in order to eliminate possible oxidation of Cr(II) ions by air oxygen. Care was also taken during removal of the samples from the cell, which had a stopcock at the bottom enabling the solution samples to be passed directly into the quartz cell. Details concerning the difficulties involved in the spectrophotometry of Cr(II) ions and mixtures of Cr(II) and Cr(III) ions have been presented elsewhere[19]. Some of the corrosion rates were determined gravimetrically by weight-loss measurements.

RESULTS AND DISCUSSION

After introduction of the Cr electrode into the electrolyte the spontaneously established potential was about −0.420 to −0.450 V (SCE) and only after cathodic activation, explained in Experimental had the more negative open circuit potential, representing the corrosion potential of active Cr, in the range of −0.720 V obtained. The first corrosion potential of the passive surface was designated as $E_{\text{corr.1}}$, and the second one as $E_{\text{corr.2}}$ (see Fig. 1). The same potential of about −0.420 V was obtained when a Cr electrode was anodically polarized to the passive state at −0.200 V, so that it can be concluded that surface oxide formed spontaneously on contact with air before the introduction of the electrode into the solution and the electrochemically formed passive oxide were similar in nature. Anodic polarization of the passive Cr gave, as shown in Fig. 1, a Tafel straight line dependence with a slope of $b_{a,\text{ox}} \approx 0.120$ V dec⁻¹. Cathodic polarization resulted in a cathodic Tafel line with the slope of $b_{c,\text{ox}} = −0.080$ V dec⁻¹. Since the anodic and cathodic Tafel lines intersect at the open circuit potential, $E_{\text{corr.1}}$, this potential can be considered as having the character of the real corrosion potential in the sense of the Wagner-Traud electrochemical corrosion model [2].
A similar situation exists with an activated Cr electrode. The open circuit potential, $E_{\text{corr},2}$, is positioned at the intersection of the anodic polarization curve with a short Tafel line with a slope $b_a \sim 0.120 \text{ V dec}^{-1}$ and the cathodic Tafel line with a slope $b_c \sim -0.120 \text{ V dec}^{-1}$, as it is usually obtained for the electrochemical hydrogen evolution reaction. The intersection of both Tafel lines at the open circuit potential indicates that the open circuit potential of the active Cr electrode is the real corrosion potential in terms of the above-mentioned Wagner-Traud electrochemical corrosion model. On extrapolation of the cathodic Tafel line for the activated Cr electrode to the range of the cathodic Tafel line for the passivated surface, it can be seen that both cathodic lines practically overlap. This should mean that the rate of the electrochemical hydrogen evolution reaction at the bare and at the oxide covered Cr surface proceed at practically the same rate. On the other hand, the active and passive surfaces differ, as expected, in the rates of the anodic dissolution reactions. It is obvious that the differences of the open circuit (i.e., corrosion) potentials are due to the differences in the rates of the anodic reactions on the active and passive chromium electrodes.

In the range of active corrosion of Cr the amounts of volumetrically collected hydrogen (dashed line, Fig. 1) considerably exceed the amounts expected according to the partial cathodic hydrogen Tafel line (thin dashed straight line, Fig. 1). At the corrosion potential, $E_{\text{corr},2}$, about four times more hydrogen was collected (filled circle, $j_{\text{tot},H}$) than was expected to be obtained by electrochemical corrosion at the same potential, i.e., corresponding to $j_{\text{corr},el}$. The difference between the total hydrogen evolved and the electrochemically evolved hydrogen (open circle, i.e., $j_{\text{an},H} = j_{\text{tot},H} - j_{\text{corr},el}$) might be attributed to the anomalously evolved hydrogen, or anomalously corroded (or dissolved at the corrosion potential), as proposed by Kolotyrkin et al. [10 – 16]. Similar result was obtained by analytically determined amount of Cr after corrosion in the same solution (for 10 – 30 min) and recalculated by using Faraday’s law as the corresponding total corrosion current density (filled
square, \( j_{\text{tot.anal}} \), at \( E_{\text{corr.2}} \). Open square represents the difference between the total dissolution current density determined from analytical data and electrochemical corrosion current density, similarly as calculated for the collected hydrogen gas data. It should be, also considered as the excess dissolution rate over the electrochemical dissolution rate at the corrosion potential due to the anomalous dissolution of chromium. Small difference in the positions of open square and open circle should be attributed to the experimental errors of two different experimental methods used. There are reasons to believe that volumetric measurements can give somewhat lower current densities values (molecular gas dissolution into the nitrogen saturated electrolyte). Even more interesting was that at –0.650 V, when the anodic dissolution current was about 1.5 mA cm\(^{-2}\) (see anodic Tafel line in Fig.1), the equivalent metal dissolution rate, calculated from the analytical data was about 4.1 mA cm\(^{-2}\) (filled square). The difference between these two dissolution current densities is represented by an open square at = 0.680 V which has the approximately the same value as the anomalous dissolution current density at the corrosion potential. A similar situation appears for the cathodic potential of –0.800 V when the anomalous dissolution current density (open square) again has the approximately the same value. This means that the anomalous dissolution current densities do not depend on potential as is indicated in Fig. 1 by a vertical double dot dash line, and what is in accord with the proposed chemical mechanism of the anomalous dissolution of metals proposed by Kolotyrkin et al.

As mentioned in the Introduction, Kolotyrkin and coworkers [10–16] proposed that this anomalous behavior of some metals including chromium is due to the direct reaction of H\(_2\)O with the electrode metal, without any electrochemical reaction step. For Cr this anomalous hydrogen evolution and also simultaneous metal dissolution, since this process is also pH dependent [19], the total chemical reaction, without further elaboration of the detailed reaction mechanism, can be presented as

\[
\text{Cr} + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{Cr}^{2+} + \text{H}_2 + \text{OH}^-. \tag{1}
\]

Other processes summarized in the work of James [9], such as mechanical disintegration during fast anodic dissolution or hydrogen embrittlement, disproportionation of the lower valence ions, negative difference effect, and similar reasons for the anomalous metal dissolution cannot be considered valid in the case of chromium, since the anomalous process (vertical double dot dash line) has the same rate, irrespective of cathodic or anodic polarization. Therefore, the only rational explanation of the observed effect of the anomalous hydrogen evolution and chromium dissolution is this one proposed by Kolotyrkin et al. (reaction (1)).

Another important conclusion from these experiments is that the electrochemically determined corrosion rates for chromium in sulfuric acid of pH 1 is more than five times smaller than the real corrosion rate determined by the loss of material; determined analytically, and also by the loss of weight of corroding chromium under the same conditions as explained elsewhere [19]. It should be mentioned here that the results presented in Ref. 19 gave almost twice higher dissolution rates than presented here, even though formally the same chromium material was used in both cases. Since the electrode used in these experiments were made from another lump from the same batch, and the structure of the metallic chromium consisted of large crystals (up to 0.7 mm in diameter) it could be that this difference in macrostructure of different electrodes resulted in somewhat different corrosion rates. The examination of the electrode crystal structure on the electrochemical behavior is presently under way. The large difference between the electrochemically determined corrosion rates and analytically determined corrosion rates, which is in this case at the ambient temperature more than five times larger than the electrochemical one raises a serious question about the reliability of electrochemical methods for the determination of corrosion rates, which is otherwise widely accepted as a standard method (ASTM, DIN, etc.). This problem is even more serious for the elevated temperature when the anomalous dissolution is even more pronounced, as it will be shown in the following text.

Temperature has a considerable influence on the kinetics of the electrochemical reaction on a Cr electrode in sulfate solutions of pH 1 [20]. The diagrams in Fig. 2, representing anodic and cathodic polarization curves at four different temperatures, 293, 308, 323 and 338 K, respectively, illustrate this. The anodic dissolution process is more affected by temperature than the cathodic hydrogen evolution and, as a consequence, the corrosion potential \( E_{\text{corr.2}} \) shifts in the negative direction with increasing temperature (by almost 80 mV for the increase of temperature of 45 °C).
These different effects on the anodic and cathodic processes are due to the differences in the apparent energies of activation, $E_a$, for these processes. The Arrhenius type diagrams representing the anodic and cathodic current densities at constant potentials (−0.680 V and −0.800 V, respectively) versus the reciprocal temperature show straight line dependences for both processes. From their slopes, the apparent energy of activation for the anodic process, $E_{a,a} = 63.1$ kJ mol$^{-1}$ (circles) and for the cathodic hydrogen evolution, $E_{a,H} = 19.5$ kJ mol$^{-1}$ (squares) are calculated. Since, as explained previously, the difference between the total dissolution current determined analytically, $J_{\text{tot.anal}}$, and the electrochemical corrosion current density, $J_{\text{corr.el}}$, represents the anomalous dissolution of chromium obtained from the analytical data, $J_{\text{an.anal}}$. These differences for different temperatures, when plotted in the diagram in Fig. 3 also gave a straight line (triangles) with a slope close to the slope of the anodic dissolution dependence and hence a similar apparent energy of activation for the anomalous dissolution reaction, $E_{a,an} = 66.9$ kJ mol$^{-1}$, but with a somewhat larger pre-exponential factor. By extrapolation of straight lines for anodic dissolution and anomalous dissolution to $1/T = 0$, the pre-exponential factors can be compared. It turns out that for an anodic potential of −0.680 V, the pre-exponential factor for the anomalous dissolution is about 5 times larger than that for the anodic reaction. This means that the anomalous dissolution reaction is faster than the anodic electrochemical reaction at the same potential and that, as a result of the rather high apparent energy of activation, the dissolution rate increases faster with increasing of temperature then the electrochemical reaction. One should bear in mind, however, that the apparent energies of activation for the electrochemical reaction, both anodic and cathodic, by definition are also dependent on potential, in contrast to the chemical, anomalous dissolution reaction, the apparent energy of activation of which does not depend on potential since the anomalous dissolution reaction does not depend on potential. Therefore, the apparent energies of activations for electrochemical reactions should be compared only for a defined value of the potential [17, 18]. Therefore, it is not allowed to discuss and even “measure” the
apparent energies of activation of corrosion processes during corrosion under open circuit potential conditions, i.e. at the spontaneously formed corrosion potentials, since these values depend on temperature in a different way than either the anodic or cathodic reaction. Even though the Arrhenius plots of corrosion rates versus reciprocal temperature might give an apparent straight line the calculated energy of activation has no theoretical background and should be considered only as an artefact, similar to the case of the old fashioned “decomposition voltage”, obtained by extrapolation of the polarization curve to I = 0 in an I – V coordinate system.

Fig. 3. Arrhenius plots for an active Cr electrode in a solution of pH 1.

However, from a practical point of view, the effect of temperature on the total corrosion rate with the increasing of temperature is more important. This is presented in Fig. 4 with triangles for the total corrosion dissolution rate, \( j_{\text{tot,anal}} \), determined analytically after corrosion at the corresponding corrosion potential and temperature, and the electrochemically determined corrosion current densities, i.e. rates, as a function of temperature (open circles). As it can be seen, the total corrosion rate increases much faster with temperature than the electrochemical corrosion rate. Since the differences between the total corrosion rates and electrochemical rate are the anomalous dissolution (i.e. corrosion) rates, it is obvious that the anomalous dissolution rate increases with temperature much faster than the electrochemical one. In other words, the anomalous dissolution and corrosion become more important when the temperature is higher.

Fig. 4. Total corrosion current densities obtained analytically (△) and electrochemically (○) at different temperatures

CONCLUSIONS

Corrosion of chromium in sulfuric acid proceeds by electrochemical corrosion accompanied by electrochemical hydrogen evolution and chemical (anomalous) dissolution of chromium resulting from the chemical (non-electrochemical) reaction of \( \text{H}_2\text{O} \) molecules and \( \text{H}^+ \) ions.

The effect is more pronounced in solutions of pH < 3, so that in a solution with pH ~1 chemical dissolution rate is about 5 times faster than the electrochemical dissolution rate.

The apparent energy of activation for the anodic reaction is approximately the same as for the chemical dissolution (\( E_{a,a} = 63.1 \text{ kJ mol}^{-1} \) and \( E_{a,an} = 66.9 \text{ kJ mol}^{-1} \), respectively), while for the cathodic hydrogen evolution it is only \( E_{a,H} = 19.5 \text{ kJ mol}^{-1} \). This difference in energies of activation for the anodic and cathodic processes results in the fact that the corrosion potential (as the potential of the intersection of the anodic and cathodic Tafel lines) changes in the negative direction with increasing
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temperature and the corrosion current density changes to a smaller degree with increasing temperature than does the chemical dissolution rate (or chemically induced corrosion). Therefore one would expect the effects of chemical corrosion to be more pronounced at higher temperatures.

As a result of the considerable rates of chemical corrosion, electrochemical methods of corrosion rate measurement might give much smaller corrosion rates than those determined by the measurement of the weight losses, the concentrations of corrosion product or volume of hydrogen gas produced with time. This effect could be even more pronounced at higher temperatures.

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NOMENCLATURE

$E_{corr,1}$ – corrosion potential of passivated Cr

$E_{corr,2}$ – corrosion potential of activated Cr

$E_p$ – passivation peak potential

$j_a$ – partial anodic current density

$j_{corr,el}$ – electrochemical corrosion current density

$j_{corr,H}$ – electrochemical $H_2$ evolution current density at $E_{corr,2}$ ($=j_{corr,el}$)

$j_{tot,H}$ – total $H_2$ evolution rate at $E_{corr,2}$ (from volumetric data)

$j_{an,H}$ – anomalous dissolution rate at $E_{corr,2}$ (from volumetric data)

$j_{tot,anal}$ – total dissolution rate from analytical data

$j_{an,anal}$ – anomalous dissolution rate from analytical data

REFERENCES


Резиме

ЕНЕРГЕТИЧКА И ХЕМИСКА КОРОЗИЈА НА ХРОМ

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Ключни зборови: хром; корозија; ослободување на водород; аномерно растворување; енергија на активација

Покажано е дека хромот во деаерирани сулфурна киселина при pH 1 покажува два стабилни корозиони потенцијали, во зависност од тоа дали металот претходно бил во контакт со ваздух или бил подложен на активација со катодно ослободен водород. Електрохемиските поляризационо мерења, како и мерената на брзина на растворањето на металот при корозионен потенцијал, катодна или катодна поляризација, користејќи ги аналитичките определувања на хромот во растворот или колумениите на ослободениот водород, покажаа дека водородот може да се ослободи на металот по три различни механизми. Првот е електрохемискиот механизам на ослободување на водород од N⁺-јоните на чиста површина на хромост добиен со катодна активација. Оваа брзина на активното анодно растворување на хромот го определуваат едниот стабилен корозионен потенцијал. Втората реакција е реакција на H⁺-јоните на оксидирани површина на хромот, која во спротиво анодното растворување на пасивизираниот хром го определува другиот стабилен корозионен потенцијал. Третата е „аномерна“ или хемиска реакција на хромот со молекулите на вода и водородниот Јони, со што се ослободува водород. Оваа реакција е независна од потенцијалот, се одвива на чиста метална површина и при pH 1 е неколку пати брзата при корозионит потенцијал од отколку електрохемиско ослободување на водород. Последица е дека целокупната брзина на корозија е неколку пати поголема од онаа определена со вообичаените електрохемиски методи. Мерењата бег изведени во температурниот интервал од 20 до 65 ºC и определените енергии на активација на анодната, катодната и аномерна реакција на растворување изнесуваат 63,1, 19,5 и 66,9 kJ mol⁻¹, соодветно. Ова импицира дека брзината на аномерно растворување се зголемува повеќе со пораст на температурата одколку се брзината на електрохемиска корозија. Дискутирана е применливоста на различните методи на мерење на брзината на електрохемиска корозија.