

PRELIMINARY COMMUNICATION

Dissolution of chromium in sulfuric acid

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(Received 8 August 2002)

Abstract: By combining electrochemical corrosion rate measurements and spectrophotometric analysis of the electrolyte it was shown that at room temperature chromium dissolves in deaerated 0.1 M Na₂SO₄ + H₂SO₄ (pH 1) solution as Cr(II) and Cr(III) ions in the ratio Cr(II) : Cr(III) ≈ 7 : 1. This process was stable over 4 h without any detectable change. The total corrosion rate of chromium calculated from the analytical data is about 12 times higher, than that determined electrochemically by cathodic Tafel line extrapolation to the corrosion potential. This finding was confirmed by applying the weight-loss method for the determination of the corrosion rate. This enormous difference between these experimentally determined corrosion rates can be explained by the rather fast, “anomalous” dissolution process proposed by Kolotyrkin and coworkers (chemical reaction of Cr with H₂O molecules) occurring simultaneously with the electrochemical corrosion process.

Keywords: chromium, corrosion, acid solutions, corrosion products, anomalous dissolution.

INTRODUCTION

Many authors in the past considered that the product of the dissolution of chromium in deaerated sulfuric acid was Cr(II) species (Hittorf,¹ Weidinger and Lange,² Basiouny and Haruyama,³ Okuyama *et al.*⁴). Heumann and Diekötter⁵ claim that Cr(III), neither in the ionic form, nor as a solid oxide surface layer can be formed. Hurlen *et al.*⁶ concluded that the primary product of the electrochemical reaction was Cr(I) which with water react further forming Cr(II) species. However, Weidinger and Lange,² and in particular Kolotyrkin *et al.*⁷ allowed that some Cr(III) species can be formed in the active-to-passive potential region. Pourbaix⁸ states that Cr(II) ions are very unstable and in acid solutions react very fast with oxygen, if present, and also that they reduce H₂O molecules with formation of H₂. Safonov⁹ recently reported that Cr(II) was the main reaction product, mentioning some instability during the dissolution process, which might be ascribed to Cr(III) species.

The purpose of this communication is to clarify this inconsistency and report the first results obtained in carefully carried out experiments intended to qualitatively and quantitatively define the corrosion reaction products, and the rates of their formation.

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EXPERIMENTAL

All the experiments were carried out with a metallic (Merck, p. a.) chromium electrode sealed in epoxy resin with an exposed surface of 2 cm^2 . Before each experiment, the electrode surface was mechanically polished with 400 grade emery paper and rinsed with distilled water. A three-compartment electrochemical cell was used with a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference. Potentials are referred to SCE. The electrolyte was $0.1 \text{ M Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH 1.0) made from Merck p. a. chemicals and double distilled water. Hydrogen purified with exceptional care¹⁰ was used for purging the solution. The cell volume was about 60 ml. For some corrosion rate measurements, volume of evolved hydrogen was measured in another cell provided with a marked burette. The experiments were carried out at room temperature, $22 \pm 2 \text{ }^\circ\text{C}$.

The surface of chromium exposed to air oxidizes spontaneously, and hence it was necessary to polarize the chromium cathodically at -0.9 V for 90 s to activate it. After establishing a stable corrosion potential the electrode was left in the solution for a time sufficient to accumulate the necessary concentration of the corrosion products in the solution for analytical determination.

For the determination of the chromium ion concentration, a Hewlett-Packard HP8452A spectrophotometer with a stoppered cuvette was used in order to eliminate possible oxidation of Cr(II) ions by air oxygen. Also, care was taken during the transfer of the samples from the electrochemical cell, which had a stopcock at the bottom enabling the sample solutions to be fed directly into the cuvette, to avoid any contact of the electrolyte with air.

RESULTS AND DISCUSSION

Corrosion products

The corrosion potential of the Cr electrode activated by cathodic polarization as described in the Experimental, was about -0.714 V . After a rather short time the color of the

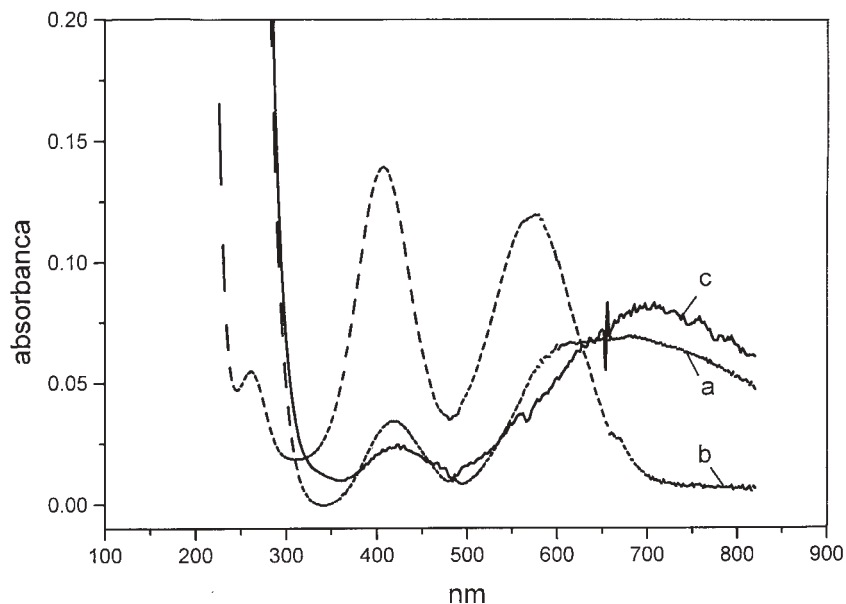


Fig. 1. Absorption spectra of chromium ions: a) in the electrolyte after contact with the Cr electrode for 100 min at the open circuit potential (corrosion potential); b) in a solution of $\text{KCr}(\text{SO}_4)$ ($c = 1.14 \times 10^{-2} \text{ mol dm}^{-3}$);

solution became greenish and after 100 min was taken for spectrophotometric analysis (see Fig. 1, curve a). It appeared that the spectrum is complex, composed of the spectra of Cr(II) (Fig. 1, curve b) and of Cr(III) (Fig. 1, curve c) in sulfuric acid at approximately the same concentrations. According to Ref. 11 Cr(II) ions have a broad absorption band at 714 nm ($\epsilon \approx 6.7 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) but we observed also another but smaller peak at 422 nm ($\epsilon \approx 2.2 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). Cr(III) ions have a higher peak at 404 nm ($\epsilon \approx 14 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) and also at 574 nm ($\epsilon \approx 12 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). As can be seen in Fig. 1, curves b and c are in good agreement with the data of the cited reference. However, it should be pointed out that a similar spectrum for Cr(II) ions presented in Fig. 20 in Ref. 12 is erroneous showing only an absorption peak at 574 nm, and nothing at 714 nm, as stated in Ref. 11, and as presented for Cr(II) in this work (see Fig. 1). The Cr(II) ion solutions used in the present experiments were prepared by the reduction of aqueous solutions of $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ with Zn amalgam.¹³ On the other hand, in the literature there are various statements regarding stability of Cr(II) ions in aqueous solutions. As mentioned before, Pourbaix⁸ considers Cr(II) to be a very strong reducing agent that reacts with water molecules producing H_2 , while in the presence of oxygen it very easily oxidizes Cr(II) to Cr(III) state. This would imply that solutions of Cr(II) ions are unstable and that conclusions regarding the concentrations of Cr(II) in the quantitative evaluations of the experimental results should be analyzed with extreme care. Our experience was that aqueous solutions of Cr(II) ions prepared by the reduction of Cr(III) ions with Zn amalgam, using the method mentioned before, showed the same absorption spectrum as presented in Fig. 1, curve a, even after several hours if left in the closed cuvette of the spectrophotometer. This means that the statement on the reactivity of Cr(II) with H_2O presented in Ref. 8 is not correct, at least over time intervals of several hours. On the other hand, removing the stopper from the cuvette the spectrum of Cr(II) ions was converted almost completely to that of Cr(III) ions (*i.e.*, curve c in Fig. 1. was changed into curve b) over a period of several tens of minutes. When air was bubbled through the cuvette, this conversion was completed in several minutes.

From these findings three important conclusions can be drawn:

1. Chromous ions do not react with H_2O molecules at a detectable rate as is sometimes assumed, *i.e.*, aqueous solutions of Cr(II) ions are stable in reasonable time intervals, at least at pH 1. The detection of Cr(II) ions during the dissolution of the Cr disc on the ring by its electrochemical oxidation should be possible, if there would be no other interference (*e.g.*, hydrogen co-evolution).
2. Chromous ions really react pretty fast with dissolved oxygen. The rather slow oxidation observed after exposure of the solution to open air is due to the slow diffusion of oxygen into and through the bulk of the solution.
3. The data in Ref. 12 regarding the absorption spectrum of Cr(II) ions are erroneous probably because of the inadequate protection of the solution from air. We experienced similar problems when the purging gas was purified by bubbling through a $\text{Va}(\text{SO}_4)_2$ solution, as is often the practice in many laboratories¹⁴ for the removal of oxygen. A slow increase of the Cr(III) ion concentration was observed after longer bubbling of so-purified

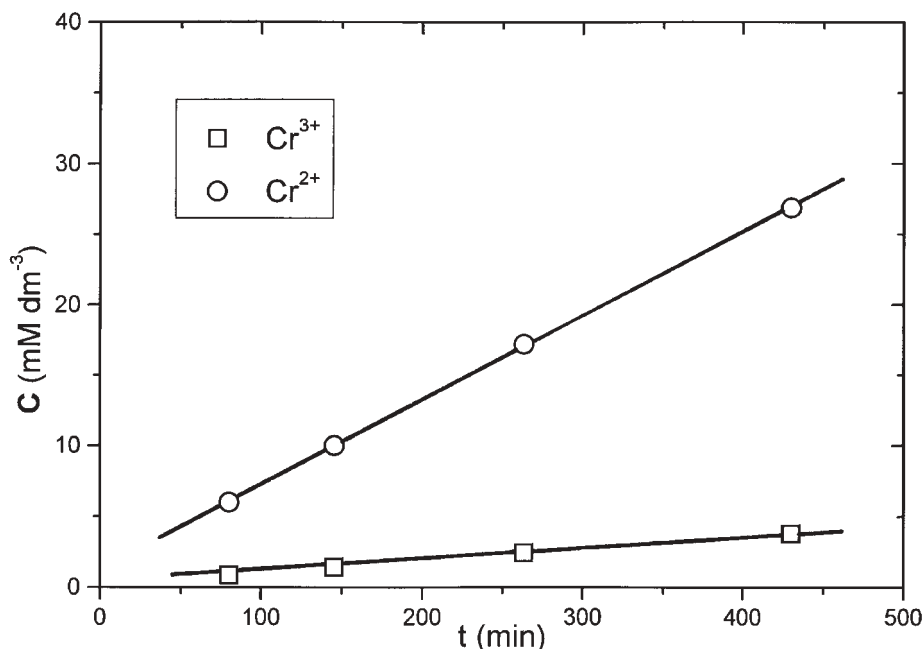


Fig. 2. Increase of the concentration of Cr(II) and Cr(III) ions in the electrolyte (pH 1) over time during the corrosion of a Cr electrode at the open circuit potential.

hydrogen or nitrogen through the Cr(II) ions containing vessel. Only after the purification train as explained in the Experimental was used even several hours bubbling with the purging gas did not affect the observed Cr(II) spectrum in a visible manner.

Bearing in mind the aforesaid it can be concluded that the experimentally obtained spectrum shown in Fig. 1, curve a, for the electrolyte containing corrosion products doubtlessly indicates the simultaneous formation of both Cr(II) and Cr(III) ions during the corrosion process. After taking samples several times during the Cr corrosion over 5 h it was shown, as presented in Fig. 2, that the rate of the corrosion process was constant over this time interval, and also that the ratio $c(\text{Cr(II)})/c(\text{Cr(III)}) \approx 7$ was constant over this time period.

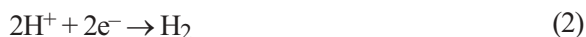
Corrosion rates

Corrosion rates were determined electrochemically by extrapolation of the polarization curves (Tafel lines), from the spectrophotometric Cr(II) and Cr(III) ions concentration data, from the volume of evolved gaseous hydrogen and from the weight-loss data (gravimetric data). The corrosion data are expressed as the equivalent corrosion current densities calculated from the originally measured data and bearing in mind that the ratio between the concentrations of Cr(II) and Cr(III) ions during the corrosion process was always about 7. (*i.e.*, the apparent valency for Cr dissolution was $n = 2.12$). These results are summarized in Table I. As can be seen the corrosion rates determined electrochemically

TABLE I. Corrosion rates (equivalent current densities in mA cm⁻²) of Cr in aqueous 0.1 M Na₂SO₄ + H₂SO₄ (pH 1) solution determined by different techniques

Method	Corrosion rate	“Anomalous” dissolution rate	Ratio of rates (2; 3 or 4) : 1
1. Cathodic Tafel line extrapolation (electrochemical)	0.79		
2. Weight loss (gravimetry)	10.9	10.2	13.8
3. Evolved hydrogen (volumetry)	8.9	8.1	11.3
4. Spectrophotometry of the electrolyte for Cr(II) and Cr(III) ions (analytically)	9.6	8.8	12.2

are only 0.8 mA cm⁻² while the rates determined by the other otherwise accepted techniques are more than ten times larger, and do not differ much from each other (about 10 ± 1 mA cm⁻²). This shows that besides the electrochemical corrosion process occurring in acid solution, that is



another corrosion process occurs simultaneously, which in this case is about 12 times faster than the electrochemical one. It could be well assumed that the process assigned as an “anomalous dissolution” proposed by Kolotyrykin *et al.*⁷ is the dominant process which can be schematically written as



in which the reaction proceeds without the participation of electron charge transfer, as in reactions (1) and (2) and which, therefore should not have a potential dependent rate. We have found similar behavior for Fe, stainless steel and Al,¹⁵ confirming the findings of the Kolotyrykin school, but the effect was an inverse one, *i.e.*, the electrochemical rate was about 12 times faster than the “anomalous dissolution”. Our experimental results show that the dissolution of Cr proceeds both to Cr(II) and Cr(III) species in the ratio ≈ 7:1, respectively. Therefore, reactions (1) and (3) should be considered as tentative. At this moment it is not clear in which reaction Cr(III) species are formed, since neither the electrochemical nor the “anomalous” reaction satisfy the observed ratio Cr(II): Cr(III) = 7:1, suggesting that the faster reaction (3) probably proceeds as a complex reaction with two reaction products Cr(II) and Cr(III) being produced at the observed reaction rate ratio. Not much can be said about the reaction mechanisms at this moment. Further kinetic studies of these processes are necessary.

Finally, it became quite clear that the often used electrochemical techniques for corrosion rate determination should be applied with great care, and only when the parallel “anomalous” dissolution process rate is negligible in comparison with the electrochemical one. In the case of corrosion of chromium in acid solutions this condition is obviously not satisfied.

ИЗВОД

РАСТВОРАЊЕ ХРОМА У СУМПОРНОЈ КИСЕЛИНИ

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Комбиновањем електрохемијског мерења брзине корозије и спектрофотометријске анализе електролита показано је да се на собној температури у деаерираним раствору састава $0,1 \text{ M Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (рН 1) хром раствара у облику Cr(II) и Cr(III) јона у односу Cr(II):Cr(III) \approx 7:1. Овај процес је био стабилан током 4 часа без икакве знатније промене. Укупна брзина корозије хрома израчуната из аналитичких података била је око 12 пута већа од брзине корозије одређене електрохемијском методом екстраполације Тафелове праве до корозионог потенцијала. Ови резултати потврђени су и одређивањем укупне брзине корозије методом губитка масе. Ова огромна разлика у експерименталном одређивању брзине корозије електрохемијском методом и другим методама може се објаснити релативно бржим процесом "аномалног" растварања који су предложили Колотиркин и сарадници (хемијска реакција Cr са молекулима H_2O), а који се одиграва једновремено са електрохемијским процесом корозије.

(Примљено 8. августа 2002)

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