Chemical Dissolution of Iron in Aqueous Solutions*1

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Abstract—By anodic oxidation of hydrogen on the Pt ring of a metal-disk–Pt-ring rotating electrode in aqueous acid (pH 0.5–3) sulfate solutions, it is shown that during the polarization of the metal disk hydrogen co-evolves by two parallel reactions. One is the well known electrochemical charge transfer process, while the other one is a direct chemical reaction of the metal, i.e. iron, with water molecules from the electrolyte. This process was proposed a long time ago by Kolotyrkin and co-workers, but their experimental results were subjected to serious criticism which is taken care of in the present paper. The chemical reaction is potential- and pH-independent and, depending on the actual conditions during the corrosion processes (actual potential, pH, etc.), can be of greater or smaller importance in the overall process. The consequences of the existence of this direct chemical reaction of metal with water molecules (i.e. H2O-induced corrosion or chemical corrosion) on pitting and stress corrosion cracking of metals is discussed.

INTRODUCTION

It was observed by Kolotyrkin, Florianovich and co-workers [1–8] that the effective dissolution rates of a number of metals, including iron, in aqueous solutions do not follow the exponential current versus potential relationship as expected for electrochemical processes. It appeared that they were larger than expected, which means that another dissolution process was occurring simultaneously. This was observed experimentally in the cathodic polarization range as a deviation of the anodic partial current density from the expected linear potential-logarithm of the current density dependency (i.e. Tafel line) towards larger current density values. Their experimental data for the partial anodic current densities during cathodic polarization were obtained indirectly from the analytical data of accumulated iron ions during prolonged cathodic polarization using the Faraday law.

These partial anodic dissolution rates appeared to be practically independent of potential at more negative polarizations, which lead Kolotyrkin and co-workers to conclude that the second dissolution process occurring simultaneously with the electrochemical one is an exclusively chemical process (i.e. potential independent), which at negative polarizations becomes dominant because the electrochemical anodic partial current density decreases exponentially with negative polarization. This “anomalous” dissolution was also observed by other authors for the dissolution of Mn [9, 10], Co [11], Zn [12, 13], Al [14] and Cr [2]. Kolotyrkin and co-workers proposed a chemical dissolution mechanism for these processes in which the metal directly reacts with water molecules by the general scheme

\[
\text{Me} + \text{H}_2\text{O} = \text{MeOH} + \text{H}_{\text{ads}},
\]

\[
\text{MeOH} + \text{H}^+ \longrightarrow \text{MeOH}^+ + \text{H}_{\text{ads}},
\]

\[2\text{H}_{\text{ads}} = \text{H}_2.\]

One can consider this process as the chemical corrosion process which should not be mixed up with the well known electrochemical corrosion processes.

A number of authors [15–18] tried to explain this effect by disintegration of metal and hydrogen ambroilment during prolonged cathodic polarization which was inevitable in order to accumulate a quantity of iron ions sufficient for analytical determinations (typically 10–20 min). In experiments in which the iron working electrode was made magnetic, Vorkapic and Dražić [19] showed that the anomalous dissolution rate was 6 to 7 times smaller than when non-magnetic iron material was used. The idea was that iron particles which might be chunked off by mechanical disintegration (the so called “chunk effect”) would stay at the iron surface and, being in electrical contact with the surface, be cathodically protected from spontaneous corrosion in acid solution. In contrary, chunked off particles floating independently in the solution should spontaneously corrode and increase the total iron concentration in the analytical determinations, leading to erroneous conclusions. However, from these experiments it was not possible to conclude whether the still existing, but smaller, anomalous dissolution effect was due either to the really existing chemical dissolution process as suggested by Kolotyrkin and co-workers, or to the insufficient strength of the magnetization of the iron surface allowing smaller metallic particles to escape from the surface into the bulk.

* Dedicated to the ninetieth anniversary of Ya.M. Kolotyrkin’s birth.

1 This article was submitted by the authors in English.
The experimental results presented in this contribution were obtained from measurements in the domain of active anodic polarization where embrittlement and the chunk effect cannot exist. As it will be shown, the results strongly suggest that, in parallel to the electrochemical dissolution of iron, a chemical dissolution process is also in operation, even though at a rather low rate. The important fact is, however, that this process produces hydrogen which might interfere with the anodic dissolution process and might also be of crucial importance in stress corrosion cracking.

**EXPERIMENTAL**

The experiments were performed with Armco iron or commercial stainless steel (AISI 304) of the following composition obtained by the analysis: Cr—17.88%, Ni—8.52%, Si—0.31%, P—0.009% and C—0.06%. Disks made of these materials were inserted into the interchangeable metal disk–Pt-ring PINE rotation system. The system was slightly modified by changing the original ring, which was made of an about 1 mm thick Pt part welded to an upper stainless steel part, with a ring made only of Pt. This was necessary as the sealing of the insulating part to the Pt ring in the PINE system was never ideal and, hence, small leaks to the welded Pt to steel joint caused instabilities in ring-current measurements in the micro current scale. Most of the measurements were performed at a rotation speed of 1600 rpm. The collection efficiency for the geometry used (disk 0.2 cm², Pt ring 0.18 cm²) was calculated [20] to be $N = 0.21$, while the experimentally determined value using the $[\text{Fe(CN)}_6]^{4-}/[\text{Fe(CN)}_6]^{3-}$ system [21] was $N_{\text{exp}} = 0.20 \pm 0.02$. Before each experiment, the disk and ring surfaces were polished with SiC paper (1000 grit) and washed with distilled water in an ultrasonic bath. It appeared, however, that the real collection efficiency for hydrogen evolving on the disk, experimentally obtained when hydrogen was evolving on the disk at certain cathodic polarization, was somewhat smaller, i.e. about 0.11. It is interesting that this experimental collection efficiency was even smaller when thiourea was present as the inhibitor, dropping even to about 0.02. Chloride ions and quinoline, which are both anodic and cathodic inhibitors, influenced the collection efficiency parameter much less (i.e. 0.10 and 0.06, respectively). This lowering of the collection efficiency factor to 0.11 can be explained by the fact that some of the evolved hydrogen forms bubbles which escape the ring surface. In the case when inhibitors were present, by their preferential adsorption, they probably decrease the hydrogen molecule adsorption and dissociation at the Pt surface, which in fact cause the reaction limiting current in the $\text{H}_2$ oxidation process at the ring, which on the other hand is proportional to the hydrogen concentration.

All the experiments were performed in aqueous mixtures 0.1 M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ with the concentrations of acid adjusted so that the pH was in the range 0.5 to 3. Merck p.a. chemicals and doubly distilled water were used for the preparation of the solutions. An all-glass electrochemical cell with a platinum foil as the counter electrode and a saturated calomel reference electrode (SCE) was used. All the potentials are referred to SCE. The solutions were continuously deaerated with purified nitrogen. The experiments were carried out at room temperature ($22 \pm 2^\circ\text{C}$).

Prior to the measurements, the electrodes were in contact with the solution for 60 min. In order to clean Pt surface immediately before the ring measurements, Pt was electrochemically treated for 5 min by potential cycling in the range −0.3 to 1.1 V, with a scan rate of 0.5 V s⁻¹. As explained elsewhere [22], during the chosen cathodic or anodic polarization (or sweep of the potential) of the disk, the ring potential was kept at ca. 0.1 V to ensure the efficient anodic oxidation of the hydrogen transported from the disk used. This potential corresponds to the limiting current of hydrogen oxidation in the solutions used [22]. However, in the experiments with the inhibitors, there were some small inhibitor oxidation currents at these potentials (as observed from independent cyclic voltammetry curves on the Pt ring) so that it was necessary, prior to the start of the disk-ring measurements, to adjust the ring potential to the zero current potential by observing the cyclic voltammograms or steady state polarization curves in a narrow potential window of ca. ±100 mV from the expected zero current potential (see inset in Fig. 1).

**RESULTS**

Cathodic and anodic polarization curves for Armco iron at pH 1 are depicted in Fig. 1 with open signs. The curve with the filled signs represents the hydrogen evolution rates expressed as the equivalent current densities calculated from the current data registered on the Pt ring and corrected with the collection efficiency factor 0.11 in the manner explained in the Experimental Section. As seen, the hydrogen evolution Tafel line with a slope of about $−120 \text{ mV dec}^{-1}$ measured directly (open signs) in the range of negative electrode polarizations coincides with the hydrogen evolution rate calculated from the Pt ring currents. However, at potentials more positive than the corrosion potential, i.e. in the anodic side of the diagram, the anodic Tafel line (open signs) obtained by a gradual increase of anodic polarization has a slope of about $50 \text{ mV dec}^{-1}$. On the other hand, the ring detected currents, recalculated into the equivalent hydrogen evolution current densities, represented by the curve marked with filled signs, does not follow the corresponding Tafel line for the partial hydrogen evolution as expected from the Wagner–Traud electrochemical corrosion model [23], marked in the diagram by the dashed line. It deviates from it and eventually becomes vertical, indicating the independence of the hydrogen evolution rate on the potential. In fact, this experimentally obtained curve can be separated into two parts, one represented by the dashed Tafel line for