ELECTRODISSOLUTION OF ELECTRODEPOSITED IRON OXIDES

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ABSTRACT

The galvanostatic reduction of ferric oxide has been studied in phosphate solutions over a range of pH values. The oxides were prepared on gold by anodic electrodeposition from dilute ferrous borate solution. With increased pH the potential of the reduction arrests decreased and the charge associated with the arrest increased. A dependence of -60 mV/pH was observed except between pH 7.5 and 8.5 where the slope approximated -180 mV/pH. Above pH 7.5 the slope was consistent with the thermodynamic predicted slope of -180 mV/pH expected from reductive dissolution of ferric oxide forming soluble ferrous ions. At higher pH values, a slope of -60 mV/pH has been accounted for by oxide reduction to form a solid lower valent oxide.

INTRODUCTION

Passivity breakdown on iron in dilute aqueous solutions occurs in two distinct stages: at higher potentials pits initiate, passivity is undermined and corrosion remains highly localized similar to that observed on stainless steels. With growth of pits the potential falls. A change in the mode of corrosion takes place when a sufficiently negative potential is reached and reduction of the passive film occurs around the pits. Corrosion then spreads out from the pits becoming more generalised but leaving some distinct areas that remain passive. A possible explanation for the separation between the active and passive areas is a difference in local pH. A high pH due to oxygen reduction at the passive areas may protect the passive oxide from reduction, as it offsets both the drop in potential and the decrease in pH due to hydrolysis at and around the areas of corrosion (1).

There are few studies on the effect of pH on the reduction of passive films on iron: the Flade potential is of note (2) and has a dependence of -60 mV/pH. Flade potential measurements were mainly conducted in acidic sulfate solutions but a similar standard reaction potential and pH dependence is indicated with sulfate solutions at higher pH values (2, 3). Significantly different behaviour was observed in borate solutions over a pH range of 6.4 to 10.5 (4) and gave a dependence of about -120 mV/pH. At the lower pH values difficulties arose due to the dissolution of underlying iron during the reduction

of the passive oxide (4). The value of -120 mV/pH suggests that FeOH^+ rather than Fe^{2+} is the soluble reduction product, also the anionic species may play a direct role and affect the observed pH dependence.

In order to study the effect of pH on the reduction of oxides in more detail without having to separate the electrochemistry of the oxide from that of underlying iron metal, thin deposited oxide layers were used to model the behaviour of the passive film. Ferric oxide layers have been electrodeposited on to gold using the methods of Markovac and Cohen (5). The films produced were of the $\gamma\text{-FeOOH}$ type with small amounts of incorporated boron; the boron has been shown not to affect the reduction process (5). Reduction of the oxide layers was then performed in phosphate solutions over a wide pH range; standard electrochemical techniques and XANES measurements were employed.

EXPERIMENTAL PROCEDURE

Ferric oxide layers were electrodeposited on to gold surfaces from a well deaerated ferrous borate solution at 300 mV_{sce} using the approach developed by Markovac and Cohen (5). The ferrous ion solution (concentration $\sim 4 \times 10^{-4}$ M) was produced by potentiostatically dissolving Fe metal at -450 mV_{sce} in borate solution. A standard 3-electrode electrochemical cell was used comprising a Pt counter, saturated calomel reference electrode (SCE - against which all potentials are quoted), and the working electrode. The gold was cleaned with HCl prior to use. A charge of 22 mC cm⁻² was passed during the deposition, resulting in an oxide film thickness of 27 nm assuming 100% current efficiency for the reaction:

The $\gamma\text{-FeOOH}$ deposits were dried in air prior to galvanostatic reduction at a current density of -20 $\mu\text{A cm}^{-2}$ in a range of phosphate solutions with pH from ~ 2 -11.

X-ray absorption near edge spectroscopy (XANES) measurements were made with samples and a cell geometry that followed the approach used previously (6) in which the sample under investigation forms an x-ray window in an electrochemical cell. The measurements are made at beam line X10C at the National Synchrotron Light Source. Each sample consists of a Mylar film 6 μm thick with an evaporated 200 Å Au film. The evaporated Au acts as the working electrode onto which is deposited Fe oxide following the same procedure used for the solid Au foil but omitting the cleaning with HCl. Incident x-rays enter, and the measured fluorescence exit through the gold and thin plastic film. XANES measurements are made during galvanostatic reduction of the Fe oxide deposits at -5 $\mu\text{A cm}^{-2}$.

RESULTS AND DISCUSSION

The Fe-oxide electrodeposited from borate solution with dissolved ferrous ions was reduced in phosphate solutions at different pH. Figure 1 shows selected examples of

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the variations in the potential transient arrests with pH during the galvanostatic reduction. There are two distinct changes that are observed. The potentials of the arrests decrease and the period of the arrest increases with increasing pH.

Potential changes for all measured data are shown in Figure 2 for the start and end potentials. The average of the measured values for the half-wave potentials are also plotted in Figure 2. With increasing pH the range of potential over which the arrest occurs increases. Except for the inflection in the curve around pH 8 the half-wave potentials show a -60 mV/pH dependence. The results at a pH of 8.4 compare well with other data (3-6) in borate solutions.

Figure 3 shows the relevant Pourbaix diagram for Fe (7) and the arrest potential from the present work along with those of other workers for comparison (2,4). The lines separating the regions in the Pourbaix diagram are for a 1 mM solubility rather than 0.001 mM, generally used. Comparison of all the results in Figure 3 indicates a dependence on the anion present in the solution; of particular note is the high potentials for sulfate. This is the Flade potential, mainly derived from acidic sulfate solutions. When extrapolated to the higher pH values the Flade potential is distinctly more positive than other measurements in other solutions. The greater susceptibility for oxide reduction in sulfate solution may offer a possible explanation for the ability of sulfate ions to reactivate passive Fe surfaces even when compared to chlorides (1,8).

The data of Sato et al (4) in borate with a slope of about -120 mV/pH agree fairly well with those measured in phosphate in the range of pH from 7 to 9 but the present results more closely approximates a slope of -180 mV/pH and can be accounted for by the reaction

which is the thermodynamically expected behaviour around neutral and acidic pH values. In alkaline solutions the reactions involves only solid reactants and products. A -60 mV/pH variation is expected for the reduction reaction of the form

This was observed in phosphate solutions above pH 8.5 but not for the borate solutions up to a pH of about 11 (4).

The differences in the reduction of the oxides may offer a general explanation for the dependence of corrosion susceptibility of Fe and steels in different solutions. However, these present indication must await further measurements. Other variables are also still under investigation and include concentration and mixture of anions as well as preparation of oxides.

The variation with pH in acidic phosphate solution in Figure 3 was unexpected as it suggested a solid reactant/ solid product reaction. As discussed above a slope of -180 mV/pH for Eq. 2 was the thermodynamically predicted reaction. Recently, measurements of the reduction of sputtered iron oxides have been reported that are of direct interest (9). From galvanostatic reduction in acid solutions in conjunction with charge density and XANES measurements, it was concluded that chemical dissolution of a very thin surface

layer of Fe_3O_4 formed on the Fe_2O_3 . The dissolution of this surface layer competed with the reductive dissolution of ferric oxide (Eq. 2) and the reaction in Eq. 3 becomes rate limiting (9). This process would produce the observed -60 mV/pH dependence in the acidic solution in Figure 3. This approach suggests that at both high and low pH, Eq. 3 determines the pH dependence but only a partial reaction occurs at the lower pH and the reaction approaches completion at high pH. The transition results when dissolution of the oxide occurs only after the Fe_3O_4 is further reduced.

The periods of arrest in Figure 1, that showed the marked increase with pH were all produced at the same current density. It therefore would appear that the current efficiency for the reduction of the oxide increased markedly at the low pH. However, the XANES measurements in Figures 4 and 5 showed that Fe still remained on the sample surface following the tests, and very little iron had dissolved at the lower pH. This was seen from the decrease in the height of the curves with time. Over 75% of the oxide dissolved at the higher pH but only about 10% at the lower pH. The edge position of the curves all remained close to 7125 eV indicating the presence of the original oxide. The cessation of oxide reduction appears to be associated with the initial cathodic reduction disruption of the electrochemical contact between the oxide and the gold. The disruption occurred more readily at the lower pH and isolated oxide was no longer reduced. It is interesting to note that without the XANES measurements the explanation based on increased current efficiency with decreasing pH would have been a logical conclusion.

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Figure 1. Effect of pH on galvanostatic transients for a $22 mC cm^{-2}$ (approx. 27 nm thick) electrodeposited ferric oxide layer in phosphate solutions reduced at $-20 mA \cdot cm^{-2}$.

Figure 2. Variation of arrest half-wave potentials for reduction of electrodeposited ferric oxide with pH.

Figure 3. Observed half wave potentials and predicted thermodynamic potentials based on a solubility of 0.001 molar metal ion.

Figure 4. XANES measurements made during galvanostatic reduction of electrodeposited oxide in phosphate solution of pH 9.1. Scans were started every 220 s and repeated until no significant changes were observed.

Figure 5. XANES measurements made during galvanostatic reduction of electrodeposited oxide in phosphate solution of pH 4.2. Scans were started every 220 s and repeated until no significant changes were observed.

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