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# **Corrosion Mechanisms in Theory and Practice**

Second Edition, Revised and Expanded

edited by

**Philippe Marcus**

*Laboratoire de Physico-Chimie des Surfaces  
Université Pierre et Marie Curie  
Ecole Nationale Supérieure de Chimie de Paris  
Paris, France*



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### **Growth and Stability of Passive Films**

**Barry MacDougall and Michael J. Graham**

*National Research Council of Canada, Ottawa, Ontario, Canada*

#### **INTRODUCTION**

Interest in passivity started with the studies of Faraday [1] and Schönbein [2] over 150 years ago. The lack of metallic corrosion in the case of iron immersed in certain solutions was attributed to either the presence of an oxide film or an electronic change in the metal. This basic argument has persisted in various forms to this day, although the majority of scientific evidence suggests protection by a three-dimensional oxide film. Much has been published on passivity and its breakdown over the last 50 years. This chapter does not attempt to cover all the literature but concentrates on work over the past 10–15 years, emphasizing the passivity of iron, nickel, iron-chromium, and iron-nickel alloys in aqueous environments. Examples are given from the authors' and other selected laboratories.

Iron becomes passive in the absence of an applied current in a variety of solutions ranging all the way from concentrated nitric or sulfuric acids to basic solutions containing oxygen. In more recent years iron has been protected from corrosion in acid solutions by the addition of inhibitors usually containing nitrogen, sulfur, or hydroxyl groups. This complex subject is dealt with in Chapter 14. Here we concentrate on anodic passivity, dealing with the nature of passive films—their composition, thickness, growth, and stability—and their role and influence on pit initiation. Much of the information is obtained from surface analytical techniques like Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and secondary ion mass spectrometry (SIMS).

#### **ANODIC PASSIVITY**

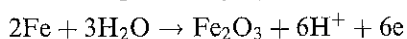
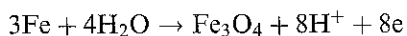
Although there is general agreement today that anodic passivity of metals such as iron and nickel is associated with the formation of a three-dimensional oxide film on the surface and that breakdown of passivity is due to the disappearance of this protective film either locally or generally, there is still considerable controversy concerning the nature, composition, and structure of the passive film. Here the most prominent models for passivity will be presented and the nature of the passive oxide film on common metals such as iron and nickel will be discussed.

The use of Pourbaix diagrams in predicting the stability of metals in various environments will not be detailed in this chapter. The subject has been discussed on many occasions over the past 40 years (see, e.g., Refs. 3–5). It should, however, be pointed out that these equilibrium potential-pH diagrams can be extremely useful in establishing the regions of metal immunity as well as (possible) corrosion and passivation. Since the diagrams do not provide any direct kinetic information, the real rate of corrosion and extent of passivation are not evident from a simple examination of the diagrams. Some oxides (e.g., NiO) dissolve only very, very slowly in certain solutions (e.g., neutral borate buffer) for kinetic as opposed to thermodynamic reasons. It should also be pointed out that the oxide stoichiometries and thermodynamic information given in the Pourbaix diagrams are for thick, bulk oxides, which may be quite different from the very thin (often  $\leq 1$  nm) surface oxide films found on passivated metal surfaces. For this reason, it should not be surprising that the actual composition of passive oxide films is sometimes not identical to that found in the Pourbaix diagrams [e.g., the diagram for nickel does not show the presence of NiO but rather Ni(OH)<sub>2</sub>; see below].

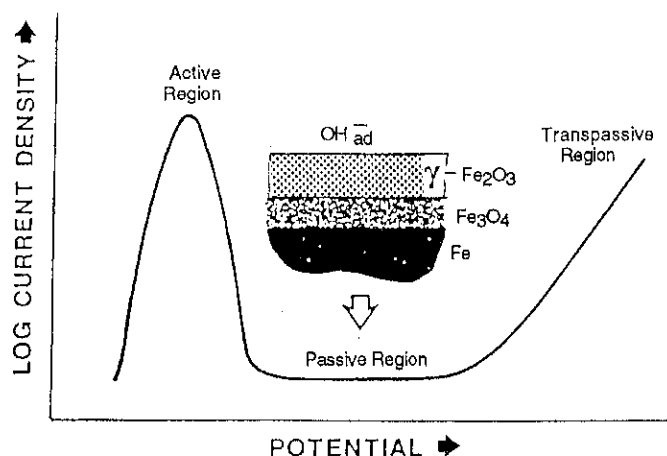
### NATURE OF THE PASSIVE FILM ON IRON

Iron and nickel are examples of metals that display an active-passive transition when anodically polarized in many aqueous solutions. Passivity is generally ascribed to the presence of a thin oxide film 1–4 nm thick that isolates the metal surface from the corrosive aqueous environment. The resistance of this anodic oxide film to dissolution is related to its physical and chemical nature, which determines the corrosion resistance of the metal. The other major factor influencing the rate of metallic corrosion is the aggressiveness of the aqueous environment, i.e., the pH, temperature, and anion content of the solution.

Iron can be passivated in aqueous solutions by the application of either a constant potential or a constant current. In both cases a certain minimum potential or current is required before passivation occurs and a finite time is required to attain the passive (i.e., very slow dissolution) state. Early work dealing with the electrochemistry of iron was done in acid solution, but over the last 30 years studies have been carried out mainly in neutral buffered solution. The major impetus for work on neutral solutions came from the research of Nagayama and Cohen [6] using a pH 8.4 sodium borate-boric acid buffer solution. In Figure 1, a schematic of the passivation curve for iron in this solution is shown. Starting with an oxide-free surface, the current first increases as the potential is increased, reaches a maximum, and then decreases again. There is a region (of over a volt) in which iron does not dissolve, or is passive, and then the current rises again due to oxygen evolution and/or transpassive metal dissolution. In the passive region iron is covered by a thin film of cubic oxide of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> type, which is probably formed by reactions such as



The film thickness increases with anodic potential to a limiting value approaching 5 nm. This is the same type of film that is formed by the reaction of clean iron with oxygen or dry air. The dissolution of iron by corrosion processes usually takes place



**Figure 1** Anodic polarization curve (determine potentiostatically) for iron exhibiting passivity.

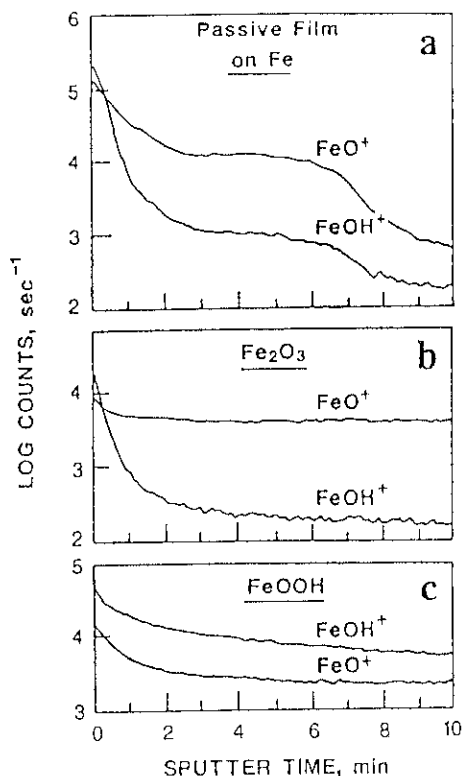
because of film breakdown and the rate of corrosion depends on the factors leading to film breakdown and repair.

The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> structure for the passive film presupposes that the film is formed by a heterogeneous reaction between iron and the solution, probably, as in the case of inhibitors, involving adsorption (of H<sub>2</sub>O or OH<sup>-</sup> ions), reaction, and thickening steps. Other compositions and structures have been proposed for the passive film, some involving the inclusion of hydrogen [7,8] or the presence of water [9]. In fact, the composition of the passive film on iron depends on the type of electrochemical treatment for forming the film and the nature of the solution in which it is formed. If iron is anodized in either a neutral solution without good buffer capacity or an acid solution, e.g., Na<sub>2</sub>SO<sub>4</sub> or H<sub>2</sub>SO<sub>4</sub>, respectively, the passivation process is very inefficient and most probably occurs with the participation of an FeSO<sub>4</sub>-type salt film, which eventually precipitates on the iron surface. This surface oxide film cannot be described as a "good" passive film and may contain incorporated species from the passivating solution. Indeed, there are suggestions that true passivity (i.e., anodic currents in the range of 1  $\mu$ A cm<sup>-2</sup>) cannot be achieved in solutions such as sulfate unless a prior oxide film exists on the surface and is not removed before anodic polarization is applied [10,11]. There may even be problems with passivation of iron in pH 8.4 borate buffer if the anodic treatment allows the dissolution of substantial amounts of Fe<sup>2+</sup>. In such a situation, the ferrous ion in solution may anodically deposit on the surface to give an outer  $\gamma$ -FeOOH layer. Sato and co-workers [12] suggest that such a film tends to arise in neutral solutions, and Seo et al. [13], using Auger spectroscopy, found incorporated boron in the oxide films formed in borate buffer solutions containing Fe<sup>2+</sup>. If the passivation of iron is carried out in pH 8.4 borate buffer using a potential step to anodic values well into the passive region, the surface oxide film forms with a current efficiency of essentially 100% [14] and can be described as a "true" passive film.

One of the most important developments over the past 20 years in the study of passivity has been the use and application of surface analytical techniques.

Techniques such as AES, XPS, and SIMS have been used with great advantage to obtain detailed information regarding the composition of thin passive oxide films on metals and alloys. However, these are *ex situ* techniques which involve removal of the sample from solution and installation into an ultrahigh-vacuum system. It has been suggested that the vacuum environment may cause dehydration of the passive film and remove bound water, which could play a vital role in conferring passivity. Because of this concern, many studies have been carried out using devices for transfer from solution to the vacuum system or have involved *in situ* measurements. Using a transfer device for Auger analysis, Bockris and co-workers [15] concluded that the passive film on iron is  $\text{Fe}(\text{OH})_2$  in a polymeric layered structure. In one of the earliest *in situ* structural investigations, O'Grady [16] used Mössbauer spectroscopy to examine both *in situ* and "dried" passive films at room and liquid helium temperatures. The *in situ* film was described as amorphous and polymeric, consisting of chains of iron atoms bonded together by dioxy and dihydroxy bridging bonds further linked by water to form a continuous film. However, the film was reported to change character on removal from the passivating medium and long-term drying to more closely resemble  $\gamma\text{-Fe}_2\text{O}_3$ . Eldridge and co-workers [17] performed experiments similar to those of O'Grady but were unable to reproduce his parameters. They confirmed that the film was primarily  $\text{Fe}^{3+}$  but could not rule out the possibility that it was microcrystalline. Eldridge and Hoffman [18] also reported that with the exception of those formed at very low passivating potentials, passive films do not seem to undergo significant local structural changes upon drying in the air. Graham and co-workers [19] used the more surface-sensitive electron back-scattering Mössbauer spectroscopy to examine *ex situ* passive films. They found Mössbauer parameters somewhat different from those of O'Grady's *in situ* film but close to those of his dried film and within the error limits of data obtained by Eldridge et al. for *in situ* films. Although low-temperature Mössbauer data resembled those for amorphous iron oxides or hydroxides, interpretation in terms of a small particle size crystalline oxide, probably similar to  $\gamma\text{-Fe}_2\text{O}_3$ , appears more plausible. Complementary XPS data for films formed in  $\text{Fe}^{2+}$ -free solutions supported the model obtained from the Mössbauer measurements that the films resemble  $\gamma\text{-Fe}_2\text{O}_3$ . The lack of hydroxyl ions within passive films has been confirmed by Mitchell and Graham [20] using SIMS. Figure 2 shows experimental SIMS data for a passive film together with "dry"  $\text{Fe}_2\text{O}_3$  and "wet"  $\text{FeOOH}$  standards. As seen in the figure, the profile for the passive film is very similar to that for the  $\text{Fe}_2\text{O}_3$  standard until the oxide-metal interface is reached after  $\sim 7$  min of sputtering (i.e., removal of the film by ion bombardment). The hydroxyl content within the film, calculated from the SIMS data, is zero ( $\pm 0.1\%$ ); a fraction of a monolayer of  $\text{OH}^-$  is adsorbed on the oxide surface. From these Mössbauer, XPS, and SIMS data, and also from reflection high-energy electron diffraction (RHEED) measurements, it can be concluded that the passive film on iron is a small particle size  $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ -type film without any incorporated  $\text{OH}^-$ . These data from modern surface-analytical techniques therefore confirm the structure proposed by earlier workers. Hydrogen may be incorporated in the outer layer of the cation-deficient oxide. In films as thin as these there is probably no phase boundary between  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  but a constant oxygen lattice with a varying ion concentration from the metal-oxide interface to the solution-oxide interface.

Although there may indeed be no sharp boundary between  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ , the sandwich model does underscore the fact that there are significant differences

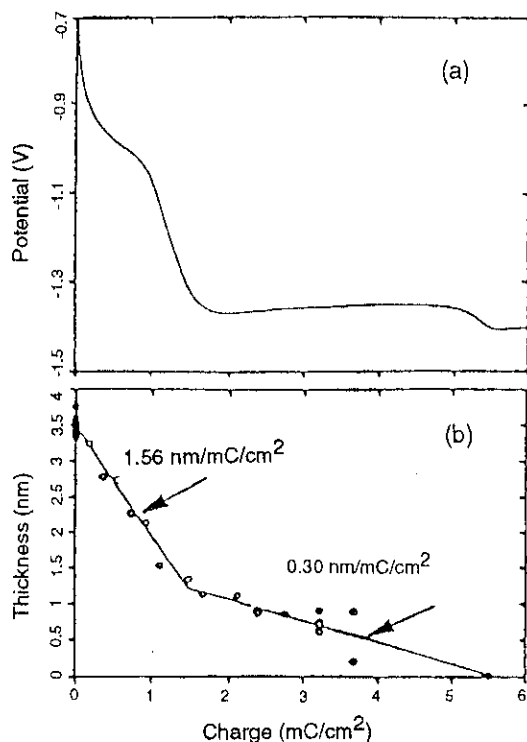


**Figure 2** Passivity of iron. SIMS profiles from (a) a passive oxide film formed in pH 8.4 borate buffer solution at 0.14 V (vs. Hg/Hg<sub>2</sub>SO<sub>4</sub>) for 1 h; (b) a “dry” sputter-deposited Fe<sub>2</sub>O<sub>3</sub> film; (c) a “wet” FeOOH film. Sputtering was by 1-keV xenon ions. (From Ref. 20.)

between the inner and outer layers. One of the important experimental results supporting the bilayer view is the two-stage cathodic reduction of the passive oxide film [6]. It has also been suggested [21] that the oxide film is a single-phase oxide and that the two cathodic reduction arrests discussed in the following are simply due to a two-stage reduction process, much like that seen with AgO or CuO. However, the experimental evidence in favor of the two-layer model is considerable, and the prevalent view at the present time favors the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> structure.

SIMS can be used to study in detail the cathodic reduction (i.e., removal) of passive films formed on iron in borate solutions enriched with <sup>18</sup>O [14]. Figure 3a shows the typical cathodic reduction profile with two arrests, the first likely due to the reduction of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and the second representing reduction of Fe<sub>3</sub>O<sub>4</sub> [6]. Figure 3b shows the oxide thickness as determined by SIMS as a function of cathodic reduction. Experimentally, samples were anodized in 10% <sup>18</sup>O-enriched solution and, after rinsing, were reduced to various extents in nonenriched solution. The break point in Figure 3b corresponds to the sharp drop in potential in the reduction curve and provides direct evidence for two different reduction mechanisms corresponding to the two arrests in the cathodic reduction profile. Comparison of the slopes in Figure 3b with calculated charge efficiencies for various reactions indicates

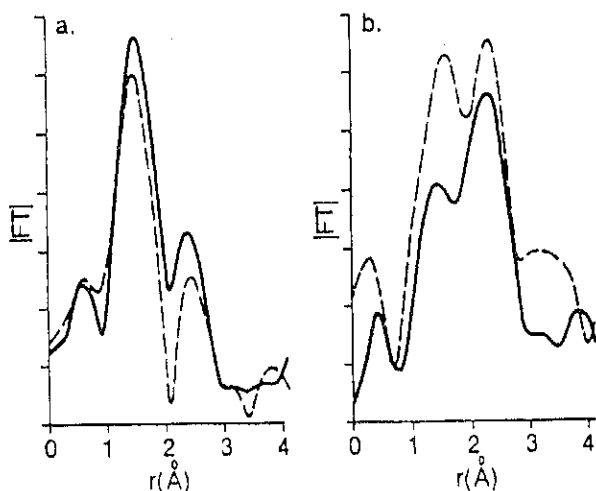




**Figure 3** Passivity of iron. (a) Cathodic reduction profile ( $10 \mu\text{A cm}^{-2}$ ) of a passive film formed in pH 8.4 borate buffer solution of 0.4 V (vs.  $\text{Hg/Hg}_2\text{SO}_4$ ) for 1 h. (b) Oxide thickness as determined from  $^{18}\text{O}$ /SIMS as a function of cathodic reduction; the slopes of the two lines are indicated. (From Ref. 14.)

that the first reduction represents  $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}^{2+}$  in solution (conversion rate,  $1.56 \text{ nm/mC/cm}^2$ ). The observed efficiency is not in agreement with reductions of  $\gamma\text{-FeOOH}$ , supporting the SIMS data discussed earlier indicating that the film contains no bound  $\text{OH}^-$ . The second reduction is most probably associated with  $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$  (metal), with a current efficiency  $\sim 60\%$ .

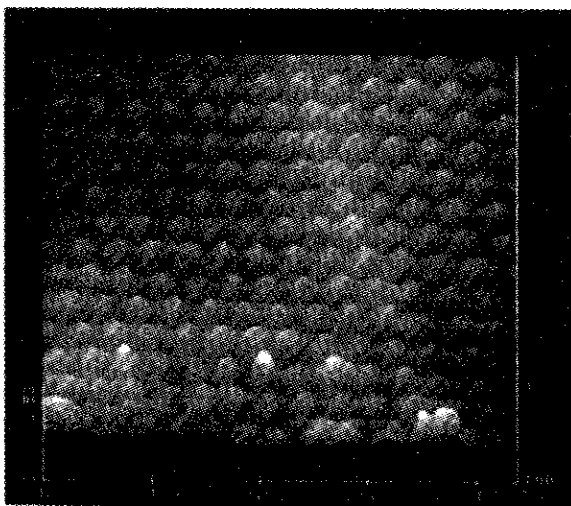
Additional support for the bilayer model comes from ring-disk experiments which indicate that reduction of the outer  $\gamma\text{-Fe}_2\text{O}_3$  layer generates  $\text{Fe}^{2+}$  in solution [22] and the in situ ellipsometric work of Ord and DeSmet [23], which identifies an outer, electrically limiting layer of  $\gamma\text{-Fe}_2\text{O}_3$  and an inner conducting layer of  $\text{Fe}_3\text{O}_4$ . An alternative model for the passive film is the chemiconductor model of Cahan and Chen [24], which suggests that the oxide is not a classical semiconductor but a highly doped film with  $\text{Fe}^{2+}$  and  $\text{Fe}^{4+}$  as defects; the stoichiometry of this film can vary over a wide, continuous range in response to changes in the electrode potential. It is evident that even with this model, the oxide film near the iron electrode contains  $\text{Fe}^{2+}$  and is therefore akin to  $\text{Fe}_3\text{O}_4$ . It is also interesting to note that the  $\text{Fe}^{4+}$  species discussed by Cahan and Chen is essentially equivalent to the  $\text{Fe}^{6+}$  defect species suggested by Nagayama and Cohen [6], each being a surface species which could influence film behavior such as breakdown. Schultze and co-workers [25,26]



**Figure 4** Passivity of iron. Magnitude of the Fourier transforms of EXAFS spectra for (a) ex situ and (b) in situ films. Nitrite-formed film results are given by the dashed lines and chromate formed film results by the solid lines. (From Ref. 30.)

have shown that the semiconductor model of the passive film can be used as a good approximation for the passive film in the steady state.

In a series of experiments designed to investigate directly the structure of oxide films on iron, Kruger et al. [27–31] employed the sophisticated technique known as EXAFS (extended X-ray absorption fine structure). The technique permitted spectra to be obtained for films in in situ conditions and for comparisons to be made with ex situ measurements (i.e., out of the electrolyte solution in the “dry” condition). It should be mentioned here that the majority of the films examined were not anodically formed but rather chemically prepared by exposure of iron to such passivating solutions as nitrite or chromate. Nevertheless, the results indicated very significant differences between the in situ and ex situ films, suggesting that “drying” of the films for ex situ examination does lead to major structural changes. Comparisons of ex situ and in situ films formed in nitrite and chromate are shown in Figure 4. The implication is that great care has to be taken when employing ex situ techniques, such as the ultrahigh-vacuum (UHV) spectroscopies or RHEED, because some films being studied may be structurally different from those present when the electrode is immersed in the electrolyte. In more recent research employing the spin-polarized neutron reflectivity technique, Krebs, Kruger, and co-workers [32,33] have studied in situ the passive film formed anodically on iron in the pH 8.4 borate buffer. The passive film was observed to be different from the air-formed film. If the passive film proves to be ferromagnetic, it would support an  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  bilayer model. However, as mentioned previously [19], there is some concern that what may appear as ferromagnetism in a bulk oxide would instead become superparamagnetism in a thin film. As pointed to by Krebs et al. [33], if this is the case for the passive film on iron, then it will be extremely difficult to apply a polarizing magnetic field strong enough to observe any changes in magnetic scattering density.



**Figure 5** Atomically resolved STM image recorded in air of the passive film on iron in pH 8.4 borate buffer at 1040 mV (NHE) for 15 min. (From Ref. 119.)

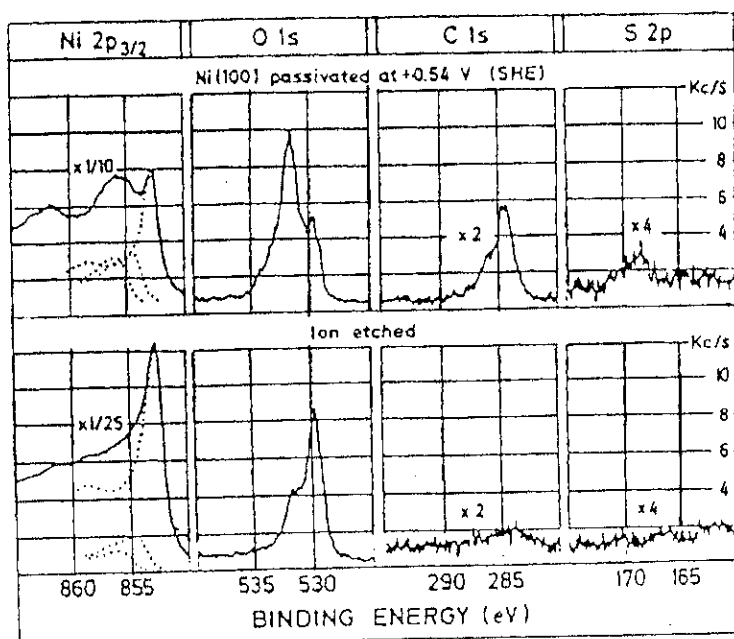
More recent studies have used in situ and ex situ scanning tunneling microscopy (STM) [119] X-ray scattering [120,121] to study the passive film formed on iron in borate buffer solution. Ex situ STM examination in air (Fig. 5) showed long-range crystalline order on the film surface with the same triangular lattice of spacing  $0.30 \pm 0.01$  nm appearing on all the crystallites studied. In situ STM at intermediate potentials after passivation at high potentials showed the same lattice on a large number of areas. The structure is consistent with a  $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$  structure of the passive film and the results refute the suggestion of a highly disordered or amorphous passive film. X-ray scattering data [120,121] of the passive film are consistent with a spinel oxide ( $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , or related structure) and inconsistent with other crystalline bulk oxides, hydroxides, or oxyhydroxides. However, the data demonstrate that neither  $\text{Fe}_3\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$ , nor any combination of these phases can adequately describe the experimental data. The model proposed [120,121] assumes a uniform distribution of vacancies and interstitials and the best-fit structure has a stoichiometry of  $\text{Fe}_{1.9 \pm 0.2}\text{O}_3$ , which indicates that most of the Fe cations are in the  $\text{Fe}^{3+}$  state. In the proposed structure, the octahedral vacancies are randomly distributed but occupy specific sites in  $\gamma\text{-Fe}_2\text{O}_3$  and are absent in  $\text{Fe}_3\text{O}_4$ ; in  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  the tetrahedral sites are fully occupied and there are no octahedral interstitials.

#### NATURE OF THE PASSIVE FILM ON NICKEL

The situation with nickel is quite different from that for iron, passivity being readily achieved in a wide variety of solutions over a large range of pH [34]. In the case of nickel, there is not the necessity to have a highly buffered neutral solution in order to achieve good passivity, and this may be due to the fact that the potential for anodic deposition of an  $\text{NiOOH}$  film is fairly high [35]. For example, nickel passivates much more readily than iron in unbuffered pH 3.0  $\text{Na}_2\text{SO}_4$  [34]. Iron is much more sen-

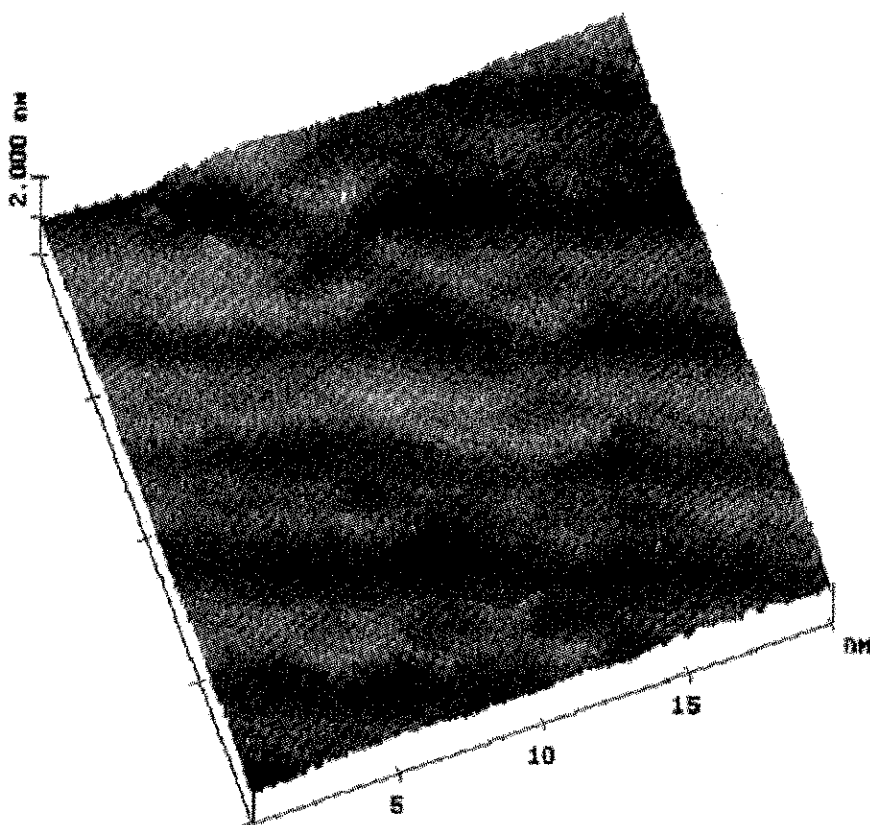
sitive to the conditions of passivation than nickel, and good passivity can be achieved with iron only under rather specific conditions. The fundamental reason for this difference is most probably associated with differences in the nature of the passive oxide film present on each metal.

As with iron, a considerable amount of works has been performed on nickel to investigate the nature of the passive oxide film. The exact composition of this film is still under discussion, but there is general agreement that its thickness is between 0.9 and 1.2 nm [35,36] and that anodic potential does not have a strong influence on thickness. In contrast, with iron and oxide film thickness varies from 1.5 to 4.5 nm depending on the electrode potential. The two most prevalent views of the passive film on nickel are that it is either entirely NiO with a small amount of nonstoichiometry giving rise to  $\text{Ni}^{3+}$  and cation vacancies [37] or that it consists of an inner layer of NiO and an outer hydrous layer of  $\text{Ni}(\text{OH})_2$  [38]. In the latter view, the film structure is similar to that observed when value metals (e.g., aluminum and tantalum) are anodized in acid solution. (A review of the subject is given in Ref. 39.) Evidence in support of the two-layer model comes mainly from XPS investigations [38,40,41]. Figure 6 shows XPS data of Marcus et al. [38]. The O 1s region for the passive film shows two fairly well-resolved peaks at 529.8 eV and 531.6 eV with a shoulder at higher binding energy. These two peaks correspond to the positions of oxygen in NiO and  $\text{Ni}(\text{OH})_2$ . (The shoulder is assigned to sulfate.) There may, however, be other interpretations of these XPS data as suggested by Roberts and co-workers [42], who point out that  $\text{Ni}^{3+}$  defects can give rise to spectral features very similar to those of  $\text{Ni}(\text{OH})_2$ . Another view is that the NiO film has some adsorbed hydroxyl ions on the



**Figure 6** Passivity of nickel. XPS spectra of a nickel(100) electrode after passivation in 0.1 N  $\text{H}_2\text{SO}_4$  at 0.54 V (vs. SHE) for 30 min. (row 1); row 2 shows spectra obtained after ion etching (0.5 keV, 1 min,  $P_{\text{Ar}} = 4 \times 10^{-5}$  torr). (From Ref. 38.)

surface and this gives rise to the observed spectral features [43]. Even the proponents of  $\text{Ni}(\text{OH})_2$  suggest that it is present not as the bulk hydroxide with a hexagonal lattice but rather as some modification to the  $\text{NiO}$  structure. The highly crystalline structure of the passive film formed on nickel in 0.05 M  $\text{H}_2\text{SO}_4$  solution has been characterized by ex situ and in situ STM studies of Maurice, Talah and Marcus [44,122–124]. The crystalline lattice observed on an atomic scale is shown in Figure 7. The surface structure is characterized by the presence of steps and kinks (Fig. 7a) and point defects possibly related to vacancies (a divacancy is imaged in Fig. 7b). The lattice parameter is consistent with that of (111) $\text{NiO}$  as the inner component of the passive film and the (0001) orientation of  $\beta\text{-Ni}(\text{OH})_2$  as the outer component of the passive film, which is  $\sim$  one monolayer thick. The formation of a stepped crystalline structure consistent with (111) $\text{NiO}$  and (0001)  $\beta\text{-Ni}(\text{OH})_2$  has been confirmed in situ for  $\text{Ni}(111)$  passivated in pH 3 acid solutions [125,126]. It is clear that the passive film is composed almost entirely of  $\text{Ni}^{2+}$  cations, in contrast to the situation with iron, where one finds  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and possibly even  $\text{Fe}^{4+}$  and/or  $\text{Fe}^{6+}$ . The



**Figure 7** Ex situ STM topographic images of the passive film formed on  $\text{Ni}(111)$  in 0.05 M  $\text{H}_2\text{SO}_4$  at +750 mV/SHE. The left image (a) above shows the stepped crystalline structure ( $V_t = +0.135$  V,  $I_t = 0.8$  nA,  $\Delta Z = 0.6$  nm). The right image (b) shows the lattice recorded on the terraces ( $V_t = +0.111$  V,  $I_t = 0.5$  nA,  $\Delta Z = 0.6$  nm). The hexagonal cell and two point defects are marked. (From Ref. 124.)

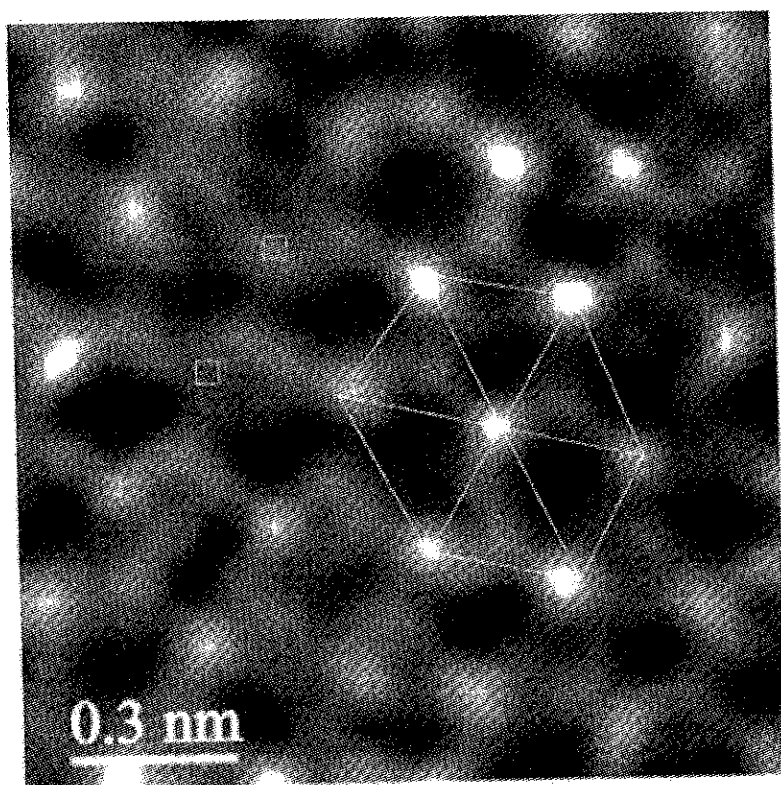


Figure 7b

passive oxide film on nickel, once formed, cannot easily be removed by either cathodic treatment or chemical dissolution; indeed, one usually has to revert to electro-polishing to get back again to the bare nickel surface [45]. This is in sharp contrast to the situation with iron, where the passive film is readily removed, and again points to differences in oxide stoichiometry (and possibly structure) playing a major role.

### KINETICS OF OXIDE FILM GROWTH

The growth of passive oxide films has been extensively studied on metals such as iron and nickel. Ideally, an electrolyte giving 100% current efficiency for oxide growth is used and the decay of current with time is monitored after the potential has been adjusted to a constant value (i.e., the electrode is under potentiostatic control). After some initial few milliseconds, the anodic current is usually observed to decrease in a manner which gives rise to a linear  $\log i$ - $\log t$  plot (see, e.g., Fig. 11). The results can be understood in terms of a logarithmic growth of the oxide with time and a corresponding exponential decrease of the current with film thickness ( $d_{\text{ox}}$ ), i.e.,

$$d_{\text{ox}} \propto \log t$$

$$i \propto \exp - d_{\text{ox}}$$

or

$$d_{\text{ox}} \propto \log i$$

This means that each 10-fold increase in time results in the same increase in film thickness, say by an amount  $\Delta x$ , and that each increase by this amount  $\Delta x$  is capable of decreasing the rate of further growth by a factor of 10. As seen above, when oxide growth is governed by the direct logarithmic law, the slope of the  $\log i$ - $\log t$  plot will be  $-1$ . Another commonly observed growth law, the inverse logarithmic law, is based on the early work of Cabrera and Mott [46], which is considered in more detail in the chapter on thin oxide film formation. Cabrera and Mott suggested that growth occurs by a high-field conduction of metal ions through the oxide film and that the activation barrier is at the metal-oxide interface. This should be especially true when the film is very thin (nm thickness range) so that ion movement through the film is not the rate-determining step. Both the direct and inverse logarithmic laws give very similar kinetic results and it is extremely difficult to distinguish between them. Although the situation with oxide film growth in the early stages is a very complex topic, there seems to be more or less general agreement that the first-formed phase is a chemisorbed oxygen layer. At certain sites on the electrode surface this two-dimensional phase begins to convert to a three-dimensional phase oxide, which spreads across the entire surface. This is the so-called nucleation-lateral growth mechanism for oxide formation. The oxide continues to grow (i.e., thicken) as long as its rate of formation exceeds its rate of dissolution. It should be noted that not only the nature of the metal and the applied electrode potential but also the nature of the surrounding electrolyte are important in determining the kinetics of oxide growth.

### PASSIVE FILM STABILITY

In the case of iron, as mentioned earlier, only films formed at very low passivating potentials thicken to  $\sim 1.7$  nm upon air exposure. Oxide films on nickel are stable over the entire passive potential range and are not affected by air exposure, at least in terms of the amount of oxygen in the oxide film and its origin. This resistance to air exposure of passive films formed on iron and nickel makes their examination by ex situ techniques much more valid and the subsequent results more meaningful. Detailed work in the case of nickel, using the open-circuit potential decay technique, shows that the passive oxide film is most likely resistant to any transformation upon both air exposure and ultrahigh-vacuum pumping [47]. It needs to be emphasized, however, that the pH of the formation electrolyte can have a strong influence on ex situ analysis. This arises because upon breaking the electrical circuit prior to exposing the electrode to air, the oxide film is in contact with the electrolyte, which, if it is too aggressive, can dissolve at least some of the film. For this reason, it is not a simple matter to obtain reliable ex situ results when acid solutions (i.e.,  $\text{pH} \leq 2.0$ ) are used. In this context, the safest solution when working with both iron and nickel is pH 8.4 borate buffer, in which the rate of oxide chemical dissolution is extremely low.

SIMS has also been used to study the air stability of oxide films formed on Fe-Cr alloys in  $\text{H}_2^{18}\text{O}$ -enriched solutions [48,49]. At first glance, the results are somewhat surprising and suggest that the oxides are less stable to air exposure than those formed on nickel and iron. Indeed, the extent of this air instability increases

significantly in going from Fe-6Cr to Fe-26Cr; i.e., more chromium in the alloy translates to more change upon air exposure. These results are discussed further in the sections on passive films on alloys.

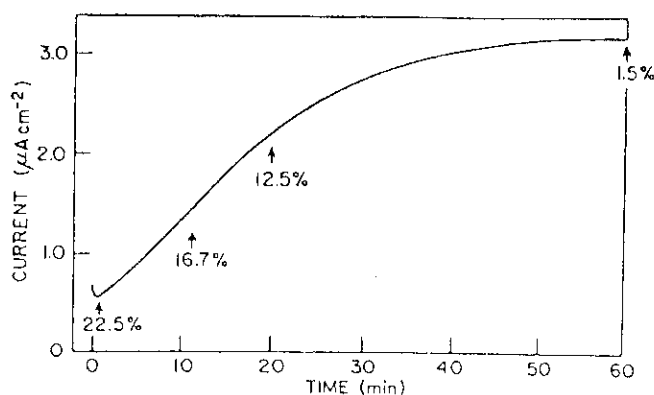
### BREAKDOWN OF PASSIVE FILMS ON IRON AND NICKEL

For iron, the consensus view is that the  $\gamma\text{-Fe}_2\text{O}_3$  layer is responsible for passivity [14,23,50] while the  $\text{Fe}_3\text{O}_4$  provides the basis for formation of the higher oxidation state but does not directly contribute toward the lowering of the anodic dissolution currents. The most probable reason that iron is more difficult to passivate (and is more sensitive to the passivating conditions) than nickel is that with iron it is not possible to go directly to the passivating species  $\gamma\text{-Fe}_2\text{O}_3$ . Instead, a lower oxidation state film of  $\text{Fe}_3\text{O}_4$  is required, and this film is highly susceptible to chemical dissolution. Until the conditions are established whereby the  $\text{Fe}_3\text{O}_4$  phase can exist on the surface for a reasonable period of time, the  $\gamma\text{-Fe}_2\text{O}_3$  layer will not form and active-type iron dissolution will continue. Indeed, it is generally accepted that the active dissolution of iron occurs via an oxide intermediate [51], possibly  $\text{Fe}(\text{OH})_{\text{ads}}$  or  $\text{Fe}(\text{OH})_2$  as reviewed by Brusic [52], which is not a three-dimensional oxide phase. At a sufficiently high anodic potential (which depends on solution composition and pH), the conversion of this oxide intermediate into a true three-dimensional passive oxide is favored over its dissolution. A similar model for active dissolution applies to nickel, the oxide intermediate being  $\text{Ni}(\text{OH})_{\text{ads}}$  or  $\text{Ni}(\text{OH})_2$ . Nickel, however, is different from iron in that the passivating species—an  $\text{Ni}^{2+}$  oxide considered to be  $\text{NiO}$  with possibly some  $\text{Ni}(\text{OH})_2$  at the outer surface—does not require any intervening oxidation state in order to exist. This means that passivity can be established, in a wide variety of solutions, without the need for large amounts of metal dissolution and subsequent salt film formation.

Although the passive oxide film on nickel is very thin ( $\sim 1$  nm), it can be highly resistant to breakdown by either chemical dissolution or cathodic reduction and can suppress the anodic dissolution current to very low values. In spite of the fact that there is little variation in the thickness of the oxide with film formation conditions, the resistance of the film to breakdown can vary over many orders of magnitude [53]. This can be explained in terms of the "defect" character of the film and the influence of conditions of film formation on the density of film defects. Indeed, the highly defective nature of the thin ( $< 1$  nm) air-formed  $\text{NiO}$  film makes it possible to remove this particular film easily [54]. The nature of the defects is not really known but may well be related to  $\text{Ni}^{3+}$  and corresponding cation vacancies. The thickness of anodic oxides on nickel can be increased above 1.2 nm by galvanostatic polarization in borate buffer [55], with the thickness increasing with time and eventually reaching values in excess of 200 nm. The oxide film in this case consists of an inner compact layer of  $\sim 1$  nm  $\text{NiO}$  with the thick outer porous part being  $\beta\text{-NiOOH}$ . The considerable increase in oxide film thickness does little or nothing to increase resistance to breakdown, as evidenced by the much faster film growth with increasing thickness [35]. Although there may be some exceptions, it is frequently found that the thicker the oxide, the less protective it is. In fact, it has been suggested that increasing the oxide film thickness beyond the normal passive film value is detrimental to its resistance to breakdown [56].



The origin of passive currents has been the subject of considerable discussion, the obvious question being whether low passive currents always indicate a high degree of resistance to oxide film breakdown. Research on the passivation of nickel has resulted in considerable advances in our understanding of this area, especially with the use of  $^{18}\text{O}$ /SIMS to identify changes which occur in the oxide film [57]. Figure 8 shows the results obtained when nickel previously passivated in a borate solution containing 23%  $^{18}\text{O}$  is exposed to a pH 1.0  $\text{Na}_2\text{SO}_4$  solution containing no added  $^{18}\text{O}$ . The percentage of  $^{18}\text{O}$  decreases with time, suggesting that there are breakdown and repair events occurring within the oxide which lead to its eventual complete re-formation in the non- $^{18}\text{O}$  electrolyte. In Figure 8, the rate of the current increase in the  $\text{Na}_2\text{SO}_4$  electrolyte is a direct function of the conditions of prior anodization in the borate solution; the rate of current increase is lower at longer times and higher anodic potentials. The reorganization of the film to a new steady state in the more acid solution is therefore dependent on the defect character of the oxide. One important observation in this work [57] was the almost total absence of the influence of chloride ion ( $\text{Cl}^-$ ) in the acid solution on the kinetics of film reorganization, suggesting that  $\text{Cl}^-$  in solution was not, at least in this particular case, facilitating chemical dissolution of the oxide film. The conclusion was that the defect character of the  $\text{NiO}$  film, in conjunction with the aggressiveness of the solution, established the current which flows in the passive region. Consequently, for constant solution aggressiveness, the passive current is a monitor of the defect character of the film. The situation with iron is somewhat different in that the current efficiency for passive film formation in pH 8.4 borate buffer is essentially 100%, meaning that all of the anodic charge is used to thicken the film [6]. In this case, the passive current is a measure of the rate of film formation, not iron dissolution. For nickel, even in pH 8.4 borate buffer, the current efficiency for film formation is  $\leq 20\%$ , indicating that a great deal of the anodic charge is associated with dissolution. Therefore, for nickel, the anodic current is a good measure of the resistance of the system to corrosion.



**Figure 8** Passivity of nickel. Increase of anodic current with time for nickel prepassivated in pH 7.65 borate buffer solution (23%  $^{18}\text{O}$ ) at 0.4 V (vs.  $\text{Hg}/\text{Hg}_2\text{SO}_4$ ) for 5 min and then transferred to a pH 1.0  $\text{Na}_2\text{SO}_4$  (100%  $^{16}\text{O}$ ) solution for continued polarization at 0.4 V. Also shown is the percentage of  $^{18}\text{O}$  detected in the oxide film by SIMS at various times of exposure to the pH 1.0  $\text{Na}_2\text{SO}_4$  solution. (From Ref. 57.)

In discussions of passivity and its breakdown, the influence of solution anions is usually considered only with reference to aggressive species like chloride ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), and fluoride ( $\text{F}^-$ ). Some important papers, however, have concentrated on the influence of nonaggressive anions on metal passivity [11,58,59] and the importance of these species in the passivation process. For iron, while it is clear that solution pH plays a critical role in passivation, it is also apparent that the nature of the anion can determine the growth and development of the surface oxide film. For example, the anodic activity of iron is found to be much lower in borate than acetate solution at the same pH of 7.4. This suggests that the solution anion species in borate are highly beneficial for iron passivation, in agreement with a number of papers which have proposed the direct (inhibitive) participation of borate buffer anion species in iron oxidation [60,61]. The choice of borate as the "ideal" solution for passivating iron is therefore no mere accident but the selection of a solution with good inhibitive ability. The participation of solution anion species in the dissolution and passivation is clearly illustrated in experiments at constant pH (7.4) but with a widely varying acetate concentration [58,62]. The fact that the anodic activity depends on acetate concentration suggests the direct participation of acetate anions in the anodic processes. In this research area, a series of papers by Kolotyrkin and co-workers [63–65] has given considerable insight into the formation of charge transfer complexes at the iron surface and the involvement of these complexes in the passivation process. It is evident from the foregoing that solution anions can influence the current efficiency for passive oxide film formation on iron and can therefore dictate whether or not localized pitting corrosion will occur in halide-containing solutions (see, e.g., Refs. 66 and 67). These effects are much more subtle than the frequently encountered salt film development in nonbuffered solutions of sulfate or perchlorate but are certainly no less important. A major problem in this area of research is the inability to have a solution anion species with simultaneously good buffer capacity and absence of interaction with the iron anode surface; indeed, by their very definition, good buffers consist of anions with strong complexing ability. Because of this, the role of buffer capacity (through solution pH) and inhibiting adsorption ability are next to impossible to separate. Such a separation becomes important in the area of pitting corrosion, since both large changes in local solution pH and competitive adsorption of aggressive anions such as  $\text{Cl}^-$  are occurring.

A great many papers have been written about the important role that solution anions play in corrosion and passivation, especially of iron. An excellent chapter was published some years ago by Hensler in *Encyclopedia of Electrochemistry of the Elements* [68]. Examples of other, more recent publications are articles by Sato [69] and Kuznetsov and Valuev [70]. The concept of solution anions interacting with the electrode surface and forming surface-ligand complexes, as well as influencing the potential distribution at the surface, is being developed. It is becoming apparent that in order to understand the mechanism of passivation and its breakdown, it is necessary to understand both the electrode and the electrolyte solution and the interaction between these two components of the corrosion process.

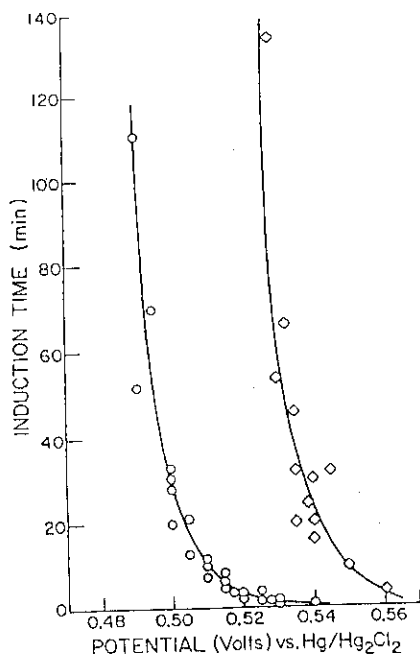
The strong influence of nonhalide anions on the passivation of iron is illustrated by experiments in which borate was added to sulfate solution. In pure sulfate, passivation occurs only after formation of a salt film, which requires the passage of considerable anodic charge. In borate solution, as mentioned earlier, the passive film forms with essentially 100% current efficiency. the addition of borate to sulfate

results in a gradual decrease in the anodic passivation charge, and with a 20% borate addition the charge decreases to its minimum. The beneficial influence of borate is believed to be due to its ability to facilitate the nucleation of surface oxide [71] as well as controlling the surface pH during the potential step anodization. The fact that one does not require 100% borate in order to have a fairly efficient passive film growth has important implications for its use as a corrosion inhibitor.

In the case of nickel, the nature of the electrolyte does not play as major a role as it does with iron and slat films do not appear to play any role in the passivation process. Nevertheless, solution anions still exert some influence on nickel passivation [72]. Any discussion of the involvement of halide ions, such as  $\text{Cl}^-$ , in the passivation process must take into account the rather distinct differences in the passivation behavior of iron and nickel. It has been observed that  $\text{Cl}^-$  in solution has little or no influence on the anodic passivation of iron in pH 8.4 borate buffer [73], but the same is also true for nickel in borate solution. On the other hand, the passivation of nickel in pH 8.4  $\text{Na}_2\text{SO}_4$  is definitely influenced by the presence of  $\text{Cl}^-$  in solution [74], the anodic charge increasing with increasing  $[\text{Cl}^-]$ . The gradual addition of borate to a  $\text{Cl}^-$ -containing sulfate solution is found to decrease the anodic passivation charge such that when  $\sim 10\%$  borate is present,  $\text{Cl}^-$  no longer has much influence on passivation.

## ROLE OF CHLORIDE ION IN PASSIVE FILM BREAKDOWN

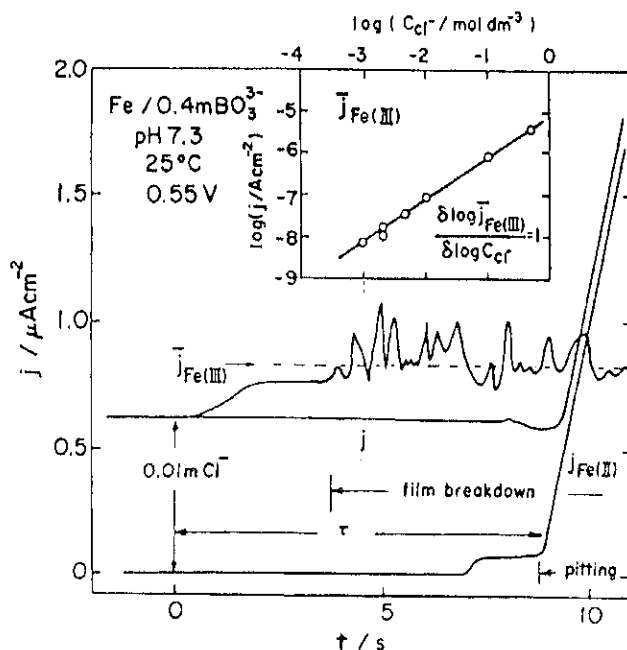
Although it has been well known for many decades that  $\text{Cl}^-$  gives rise to local pitting corrosion of metals and alloys, the precise role of  $\text{Cl}^-$  in achieving pitting is not well understood. For example, it is still not clear whether  $\text{Cl}^-$  causes the initial local breakdown of the passive oxide film or simply interferes with the repassivation process after the film has broken down locally because of chemical dissolution [75–77]. In analyzing data on  $\text{Cl}^-$ -induced pitting, it is important to determine whether the passive oxide film was formed in a  $\text{Cl}^-$ -containing solution or the  $\text{Cl}^-$  was added only after passivity was established in the absence of  $\text{Cl}^-$ . The first type of experiment is much easier than the second in terms of reproducibility of results and the time needed for pitting to occur (usually called the induction time). One of the favored models to explain the initiation of pitting corrosion involves the incorporation of  $\text{Cl}^-$  into the oxide lattice and its possible diffusion to the metal-oxide interface to initiate local breakdown events [78–80]. To check this possibility, a considerable amount of research has been performed in an attempt to detect the presence of  $\text{Cl}^-$  in passive oxide films on iron and nickel. The best chance of getting  $\text{Cl}^-$  into the oxide lattice should be to form the film potentiostatically in a reasonably concentrated  $\text{Cl}^-$  solution (e.g., 0.25 M) under conditions where significant pitting has not begun so as not to simply detect a chloride-containing corrosion salt film which exists in well-developed pits [81]. In  $\text{Cl}^-$ -containing borate solution, there is no indication of any  $\text{Cl}^-$  in the anodic film on iron [82], perhaps in agreement with the fact that  $\text{Cl}^-$  has no influence on the passivation charge [73]. On the other hand, nickel passivated in a  $\text{Cl}^-$ -containing sulfate solution is found to contain a considerable amount of incorporated  $\text{Cl}^-$ , the actual amount depending on the  $[\text{Cl}^-]$  in solution and the anodic potential [83]. This incorporated  $\text{Cl}^-$  makes the passive oxide film on nickel more defective, decreasing its resistance to open-circuit chemical dissolution [84]. It might



**Figure 9** Passivity of nickel. Induction time for pitting vs. potential of anodization for nickel samples pretreated at 0.3 V in pH 4.0 Na<sub>2</sub>SO<sub>4</sub> either with (◇) or without (○) 1 M Cl<sup>-</sup> in solution, and pitted in a 0.08 M Cl<sup>-</sup> solution. (From Ref. 84.)

be expected that this incorporated Cl<sup>-</sup> would also increase the susceptibility of nickel to pitting, but this is not the case. In a series of carefully performed experiments, the resistance to pitting (based on the pitting potential) was actually much higher in the case in which the passive film on nickel contained Cl<sup>-</sup> [84]. This is shown in Figure 9, which illustrates the results obtained when nickel prepassivated in either a Cl<sup>-</sup>-free or a Cl<sup>-</sup>-containing solution is exposed to a different Cl<sup>-</sup>-containing solution to measure the induction time to pitting. The sample prepassivated in the Cl<sup>-</sup>-containing solution (and with  $\geq 5$  at % Cl<sup>-</sup> incorporated in the oxide lattice [83]) requires much higher anodic potentials for pitting to occur. Whatever the reason for this result, it certainly suggests that the Cl<sup>-</sup> incorporation into the passive oxide film on nickel is not the reason for pit initiation.

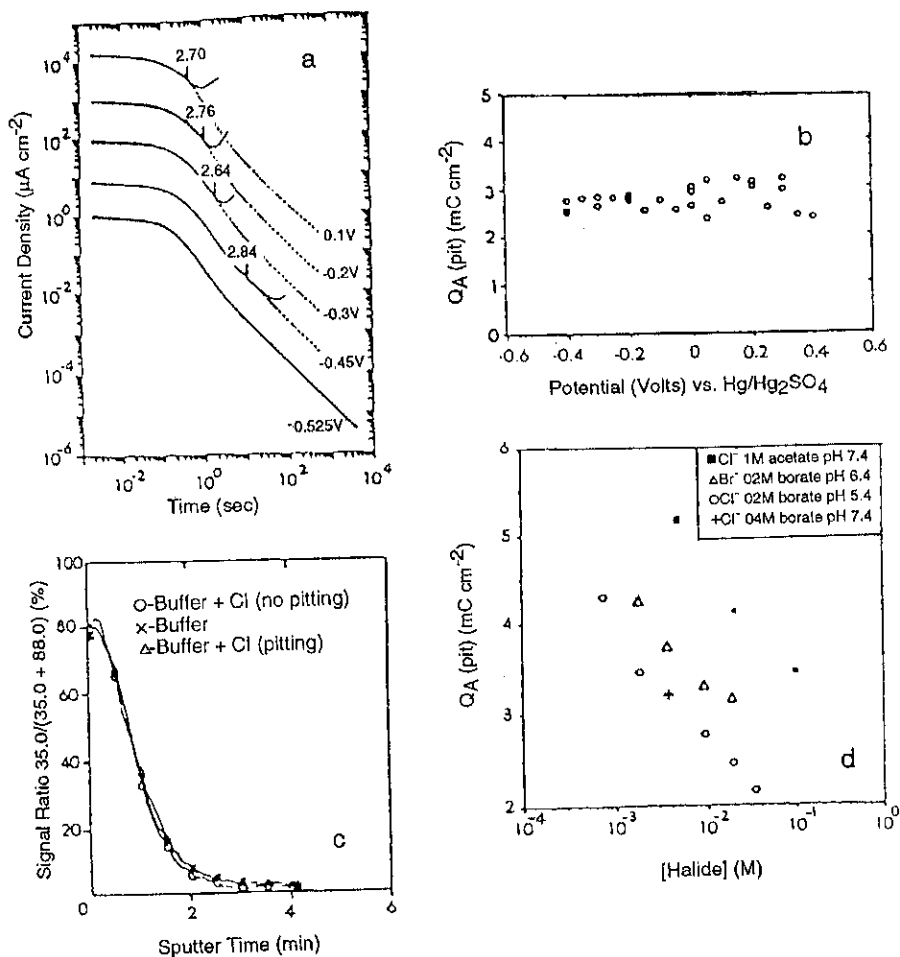
Research by Heusler and Fischer on Cl<sup>-</sup>-induced pitting of prepassivated iron [85] and Fe-6Cr [86] in borate buffer solution suggested an interesting model for pit initiation. A rotating ring-disk electrode system was used to monitor the production of Fe<sup>2+</sup> and Fe<sup>3+</sup> after the addition of Cl<sup>-</sup> to the borate solution. During the induction time before pitting began, the current associated with Fe<sup>3+</sup> appeared to increase while that for Fe<sup>2+</sup> production (as well as the total current) remained constant (the result is illustrated in Fig. 10). This was taken to indicate that Cl<sup>-</sup> ions caused "local" currentless dissolution of the oxide, i.e., local film thinning, by adsorbing on the surface and interfering with film repair. When this had proceeded sufficiently, bare metal was locally exposed and pitting began, with a corresponding large increase in the current associated with Fe<sup>2+</sup> production. It should be noted



**Figure 10** Passivity of iron. Charges in total anodic current  $j$ , iron(III) ion dissolution current  $j_{\text{Fe(III)}}$  (passive film dissolution current), and iron II  $j_{\text{Fe(II)}}$  (pitting dissolution current) for passive iron in borate solution as function of time after introduction of chloride ions. (From Ref. 85.)

from Figure 10 that the induction time is very short ( $<10$  s) and the current associated with  $\text{Fe}^{3+}$  production (measured by applying a cathodic potential to the ring) is very noisy. These ideas have been further expanded by Heusler and colleagues (see, e.g., Refs. 87–89) by using electrochemical noise analysis to study the random pitting process. Although the ideas developed are intriguing, it should be noted that these important ring-disk experiments have not, to the best of our knowledge, been repeated by other researchers. Strehblow et al. [90] attempted to repeat the experiments but could not detect any  $\text{Fe}^{3+}$ . Independent confirmation of the result would be helpful in resolving important aspects of passivity.

There are strong suggestions from other experiments that  $\text{Cl}^-$  does not alter the passive film on iron during the induction time prior to pitting [91]. Indeed, it has been observed that once a “good” passive film on iron has been formed (e.g., in the pH 8.4 borate buffer solution),  $\text{Cl}^-$  will not cause pit initiation even at high potentials in the passive region [73,92]. In this situation pitting would have to await disruption of the film by mechanical, chemical (e.g., due to a change in solution pH), or electrochemical (e.g., due to transpassive dissolution at very high anodic potentials) means. In this latter work [73,92,93], an interesting model for pit initiation on iron was proposed. Pit initiation was found to be associated with a particular stage in the development of the passive film, corresponding to a specific film thickness, which was dependent on the halide concentration ( $\text{Cl}^-$  or  $\text{Br}^-$ ) but not on the anodic



**Figure 11** Breakdown of passive films on iron. (a) Current transients for various potentials in the passive region. The solid curves are for iron in solution containing  $9.45 \times 10^{-3} \text{ M NaCl}$  in borate buffer and the dashed curves are for iron in pure borate buffer. The current density scale refers to the top curve, at 0.1 V. For clarity, at lower potentials the curves have been displaced by factors of 10. The arrows show the points at which the curves can be seen to diverge, with the number referring to the integrated anodic charge, in  $\text{mC cm}^{-2}$ , which has passed to this point. (b) This anodic charge passed [ $Q_A(\text{pit})$ ] before pitting occurred in  $9.45 \times 10^{-3} \text{ M NaCl}$  as a function of anodizing potential. (c) SIMS [ $\text{Cl}^-/(\text{Cl}^- + \text{Fe}^{16}\text{O}_2)$ ] signal depth profiles for films on iron in  $\text{Cl}^-$ -free and  $\text{Cl}^-$ -containing borate buffer solutions. The data have been truncated at the oxide-metal interface. (d) Average values of  $Q_A(\text{pit})$  as a function of halide concentration in various buffer solutions. (From Ref. 93.)

potential. This critical stage of development was characterized by the amount of anodic charge which had passed prior to pitting.

Figure 11a shows some potentiostatic current transients for iron in solutions with and without  $\text{Cl}^-$ . Below the pitting potential, the two curves are coincident. Above the pitting potential, after a certain anodization time, the two curves are seen to deviate.

The charge passed to this point of deviation is defined as  $Q_A$  (pit). As seen Figure 11b,  $Q_A$  (pit) remains relatively constant with potential even though the induction time for pitting decreases as the potential increases. SIMS has been used to monitor the thickness and halide content of the film during growth [91]. During the induction time to pitting, the film was found to grow at the same rate in halide-containing and halide-free solutions. Figure 11c illustrates the  $\text{Cl}^-$  concentration in passive films formed in  $\text{Cl}^-$ -containing and  $\text{Cl}^-$ -free borate buffer under various conditions as determined by SIMS.  $\text{Cl}^-$  was present only on the surface of the samples, and its concentration did not depend on the presence of  $\text{Cl}^-$  in the solution and whether pitting had or had not occurred. These results suggest that pitting is associated with a particular combination of film thickness and halide concentration. This is illustrated in Figure 11d, which shows average values of  $Q_A$  (pit), obtained for a variety of buffer solutions and halide ion concentrations. Clearly,  $Q_A$  (pit) depends on the halide concentration, is independent of solution pH (between 7.4 and 8.4), and is strongly dependent on the identity of the solution species, both the nature of the halide ion ( $\text{Cl}^-$  or  $\text{Br}^-$ ) and that of the supporting buffer (borate or acetate). A larger value of  $Q_A$  (pit) is associated with less aggressive solution, so  $\text{Cl}^-$  is seen to be more aggressive than  $\text{Br}^-$ , and 1 M acetate inhibits pitting compared with 0.4 M borate. While these experiments suggest that pit initiation is associated with the development of a particular thickness of oxide film, the exact reason for pitting susceptibility at a specific oxide film thickness is not clear but appears to be related to the formation of some sort of surface complex between the still developing oxide film and the halide ions in solution.

There are many different explanations for pit initiation, but there seems at least to be general agreement that locally high  $\text{Cl}^-$  concentrations and low solution pH values strongly favor the process [81,94,95]. One of the major problems over the years has been to distinguish between pit initiation and propagation, i.e., to determine if there is a difference between the factors which keep the pitting process going and those which started pitting in the first place. The electrolyte conditions inside well-developed pits have been investigated by a number of workers (see, e.g., Ref. 96), all of whom found a high  $[\text{Cl}^-]$  and low pH. On the other hand, the initiation process is much more difficult to study because the pits are extremely small [97] and the state is transitory. A technique known as noise analysis has been used by several groups to study pit initiation [98], but the results are still open to different interpretations. There are also suggestions that the pitting process is not deterministic (i.e., with a constant induction time for constant electrochemical conditions) but rather random and amenable to stochastic (statistical) theory [99]. The ideas elaborated in Chapter 10 would explain the scatter of results and difficulty in achieving reproducibility when doing pitting experiments. The other point of view is that pitting is deterministic but at the same time very sensitive to many experimental parameters such that reproducibility is not easy to achieve. Although considerable effort and advances have been made in the stochastic approach to pitting, it has so far not made the mechanism of the pit initiation process much clearer.

## PASSIVE FILMS ON IRON AND NICKEL ALLOYS

As indicated earlier, a clear understanding of the nature, role, and stability of the passive oxide film on pure iron and nickel is not easy to achieve. The difficulties are

even more pronounced in the case of alloys, in which more than one metallic component is involved. The most important simple alloy is probably Fe-Cr, and this system has been investigated extensively for more than 50 years. The reason for the interest is straightforward: the addition of chromium to iron improves the corrosion resistance of the latter. This improvement is most probably due to changes in the nature of the passive oxide film because of the presence of chromium in the film. The resistance to corrosion tends to increase with chromium content in the alloy, with abrupt improvement occurring at  $\sim 12\%$  chromium [100]. This result has been correlated with the increasing tendency of the oxide film to become more disordered (i.e., less crystalline) as the chromium content of the alloy increases [101], the suggestion being that an amorphous (or vitreous) oxide [102] is more resistant to breakdown than a crystalline one [103]. Besides these important changes in the oxide film structure, there are also changes in the composition and thickness of the film when chromium is present [104]. The oxide tends to be thinner and more chromium rich as the chromium content of the alloy increases [105]; the thickness of the passive oxide films is  $\sim 1.7$  nm, in contrast to values of up to 5 nm for pure iron. With chromium in the alloy (especially  $\geq 12\%$ ), the nature of the passivation solution is not nearly as important as it is in the case of iron. Indeed, it is more appropriate to work in aggressive (acid) solutions if one wants to remove the prior air-formed oxide film on, e.g., the electropolished alloy [106]. The explanation given above for the lack of corrosion resistance of iron was the nature of the passive oxide film and the necessity to form a prior  $\text{Fe}_3\text{O}_4$ -type oxide which is very susceptible to dissolution. With the addition of more than 12% chromium to the alloy, the mechanism and/or stages of passive oxide film formation change and the initially formed is stable even in very strong acid solution; i.e., there is no requirement for the formation of a salt layer to assist passivation.

Chromium is known to have a strong tendency to form oxyhydroxide compounds, and the presence of chromium in the passive film on Fe-Cr alloys is thought to ensure a somewhat hydrated structure for the oxide [107]. In fact, there have been suggestions that "bound water" is present in the film, and this helps to facilitate film repair after film breakdown [108] and thus helps Fe-Cr alloys to resist pitting corrosion. The bound water model is still, however, not generally accepted and remains the subject of some speculation.

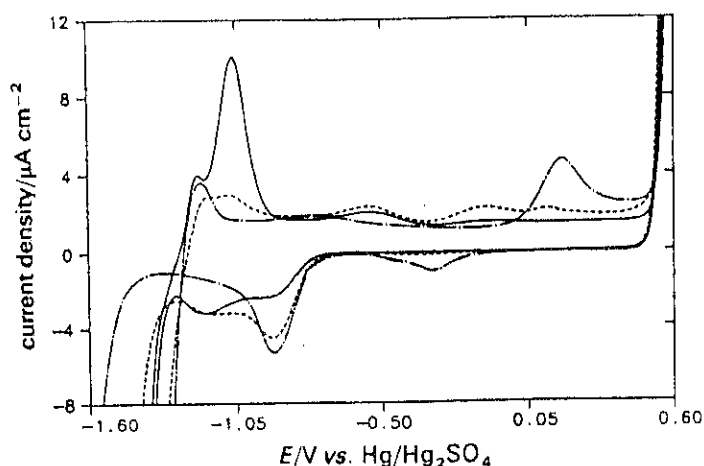
The  $^{18}\text{O}$ /SIMS work mentioned earlier on various Fe-Cr alloys [48,49] indicated that the more chromium in the alloy, the more likely it is that changes will occur on air exposure, with Fe-26Cr alloys being less resistant to change than Fe-6Cr alloys. This instability of the passive film on alloys with a high chromium content was taken to be an inherent property of the film, possibly associated with the presence of exchangeable hydroxyl species. This instability, however, gives the films the flexibility to respond to changing environmental conditions and may explain the increased resistance of the alloys to pitting Kruger [102], who suggested that the bond and structural flexibility of the oxide films on high chromium content alloys makes them more resistant to breakdown and therefore the system more resistant to corrosion. Fe-26Cr alloys tend to be very resistant to pitting corrosion, in fact so much so that special conditions are required to initiate pits [109]. Also, the oxide films are very resistant to removal and even the air-formed film on Fe-26Cr requires a strong etching treatment in an acid solution for its complete removal, as observed by Frankenthal [106] and others [49]. The oxide film on Fe-Cr alloys in the passive



potential region consists mainly of  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , and some  $\text{Fe}^{2+}$  [110], but at higher anodic potentials in the transpassive region some of the  $\text{Cr}^{3+}$  is converted to  $\text{Cr}^{6+}$ , which is highly soluble [111]. For this reason, transpassive dissolution can lead to significant amounts of dissolution of the oxide film on Fe-Cr alloys and hence corrosion.

More recently, in situ XANES (X-ray absorption near edge spectroscopy) [127] and STM [128,129] have been used to study the composition and structure of oxides on Fe-Cr alloys. The XANES work [127] on a range of Fe-Cr alloys in pH 4.5 acetate buffer showed that at  $-1.2$  V, the nonreducible oxide/hydroxide (remnants of the air-formed film) consists entirely of  $\text{Cr}^{3+}$  and resembles  $\text{Cr}(\text{OH})_3$  more than  $\text{Cr}_2\text{O}_3$ . Upon stepping the potential to  $-0.3$  V, additional alloy is oxidized but significant amounts of the oxidized iron dissolve as  $\text{Fe}^{3+}$ . Upon stepping the potential from  $-1.2$  to  $+0.2$  V, a significant amount of alloy oxidizes, in an Fe:Cr ratio identical to that of the alloy, accompanied by little dissolution of iron. This results in a passive film  $+0.2$  V with a composition less rich in chromium than at  $-0.3$  V. The transpassive film formed at  $+0.8$  V is also enriched in chromium, primarily as  $\text{Cr}^{3+}$  but with a small amount of  $\text{Cr}^{6+}$ . Ex situ STM [128] of passive films formed on Fe-Cr alloys (15–25 at % Cr) in sulfuric acid solution shows more crystallinity in the oxide at lower chromium contents, but alloys with 18 and 21 at % Cr show time-dependent recrystallization. The films formed on 25 at % Cr alloys are normally disordered. The results are interpreted in terms of the structural stability of a  $\text{Cr}_2\text{O}_3$  or  $\text{CrOOH}$  gel formed by oxygen bridging of chromium atoms as they are exposed by rapid selective dissolution of iron. When the gel is sufficiently mobile, it can crystallize on a low-index plane of the metal surface. The STM images of the crystalline surfaces are interpreted as [111] projections of the chromium oxide or hydroxide structure. Ex situ STM of passive films formed on Fe-22Cr(110) single-crystal surfaces [129] shows a coalescence of the oxide nuclei and a crystallization of the inner  $\text{Cr}_2\text{O}_3$  layer in epitaxy with the substrate. The epitaxial relationship is  $\alpha\text{-Cr}_2\text{O}_3$  (0001)//Fe-22Cr(110). Aging under polarization is beneficial to the stability of the passive film in air and prevents the dehydration reaction of the hydroxide coupled to an oxidation reaction of iron observed on freshly passivated surfaces. Comparison with a similar study of passivated Cr(110) surfaces [130] indicates that the presence of iron plays a role in the coalescence and crystallization process occurring during aging of the passivated alloy surface under polarization. The crystallization of oxide on (100)Fe-18Cr-13Ni single-crystal surfaces [131] proceeds faster than on Fe-22Cr(110) because the rate is modified by the presence of nickel in the alloy. Nickel is enriched in the metallic phase underneath the film and slows down the formation of  $\text{Cr}_2\text{O}_3$  in the inner part of the film. This favors a more complete process of crystallization. Aging under polarization is again beneficial to the further stabilization of the passive film in air.

The electrochemical behavior of two Cr-containing alloys is compared with that of pure iron in Figure 12. In each case, the electropolished sample was cathodically reduced at  $-2.4$  V prior to initiation of the anodic sweep. In the case of iron, the usual prepeak is observed at  $-1.2$  V followed by an active dissolution peak at  $-1.06$  V. The subsequent passive region extends up to the point at which oxygen evolution commences. The cathodic sweep displays two reduction waves, which, as described earlier, correspond to the two stages normally observed during galvanostatic reduction of the passive film. For the Fe-6Cr alloy, the active dissolution peak



**Figure 12** Cyclic voltammograms for iron, Fe-6Cr and Fe-26Cr at  $0.5 \text{ mV s}^{-1}$  in pH 8.4 borate buffer. (—) Fe; (---) Fe-6Cr; (-·-) Fe-26Cr. (From Ref. 49.)

is much smaller and there is some indication of transpassivity at 0.12 V. In the case of Fe-26Cr, there is no active dissolution peak, only the prepeak which is observed with pure iron. Also, a strong transpassive dissolution peak is present at 0.17 V; on the cathodic sweep, a corresponding reduction wave is observed at  $-0.31 \text{ V}$ . Although this latter peak doubtless corresponds to the reduction of  $\text{Cr}^{6+}$  in the oxide film, the reaction is not quantitative because the anodic peak charge is substantially larger than the cathodic one. The most probable explanation for this is that during the scan of the anodic transpassive region, a significant amount of the generated  $\text{Cr}^{6+}$  dissolves into the electrolyte and is therefore not available in the oxide film for reduction during the next cathodic scan. The use of single anodic and cathodic scans, such as those shown in Figure 12, provides a great deal of information about the dissolution and passivation processes of metals and alloys. Considerable care, however, has to be taken in order to avoid artifacts and, even when these are avoided, interpretation of the results is not always simple. In comparison, current-time transients resulting from potential-step experiments do not reveal the same major differences between Fe, Fe-6Cr, and Fe-26Cr [49], except perhaps at longer times of passivation and then only in a rather subtle manner. Indeed, in those experiments in borate buffer the anodic currents at longer anodization times are actually higher with more chromium in the alloy. This initially unexpected result shows just how difficult it is to understand Fe-Cr passivation comprehensively. It also indicates that more than one electrochemical approach should be employed when studying these systems if one wishes to avoid the mistake of making sweeping general statements which are not necessarily correct. The subject of austenitic stainless steel passivation will be discussed in detail in a following chapter.

Although less work has been done on the passivation of other binary alloys, many interesting observations have been made and a few selected examples will be considered. In the case of Ni-Fe alloys of varying composition, alloy dissolution results in surface enrichment with nickel (as a consequence of the preferential dissolution of iron) and the formation of a passive film composed of an inner layer of

NiO and an outer layer of nickel and iron hydroxides [112,113]. Because sulfur is frequently found in steel, Marcus and Olefjord [112] also investigated the role of sulfur in the passivation of Ni-Fe alloys. They found that sulfur is enriched on the surface during alloy dissolution and may concentrate to sufficiently high coverage to block passivation completely. An alloy addition which increases the pitting resistance of steels is molybdenum [114–116]; however, the role of molybdenum is still under discussion. Research has been carried out on the binary Ni-Mo system [117] in an attempt to better understand the role of molybdenum in suppressing corrosion. XPS work on Ni-6 at % molybdenum showed surface enrichment of molybdenum during alloy dissolution and enrichment of molybdenum in the passive film from 6% up to 10%. While nickel is still present as  $\text{Ni}^{2+}$ , molybdenum is present in the  $\text{Mo}^{6+}$  oxidation state [118]. It is interesting to note that the presence of molybdenum in the passive oxide film on the Ni-6% MO alloy was found to make the film more defective in comparison with NiO, with higher anodic currents in the passive potential region [118]. This might initially seem surprising considering that the presence of molybdenum in an alloy tends to increase the resistance to pitting corrosion. It should be remembered, however, that a similar trend was observed when  $\text{Cl}^-$  was incorporated in the passive film on nickel; i.e., the film is more defective so far as general dissolution is concerned but more resistant to localized pitting corrosion. The results again point to the observation that what is an oxide defect toward general chemical dissolution may not be a defect for  $\text{Cl}^-$ -induced pitting. Indeed, as far as pitting is concerned, it may be better to have many oxide defects of a certain type rather than just a few of the ones which give rise to pitting corrosion. The surface enrichment of molybdenum is believed to facilitate the passivation process, e.g., by decreasing the active dissolution current; however, the passive oxide film thus formed is not as perfect as it would ordinarily be. Since there will be less active-type dissolution when the film breaks down, the current efficiency for repair will be higher. This will mean that less  $\text{Cl}^-$  migrates into the local breakdown area, and there is therefore a smaller probability of sustained breakdown, i.e., pitting corrosion. This research on alloys illustrates how important it is to distinguish between different types of defects in oxide films and their different susceptibilities to breakdown leading to pitting corrosion.

## CONCLUSIONS

Very thin oxide films (1–4 nm) have been shown to have a profound influence on the corrosion rates of metals and alloys. Differences in the composition and stoichiometry of these films from metal to metal can lead to very large differences in their stability and efficiency of growth, as has been demonstrated for iron and nickel. Solution anions, even the nonhalide types, can play a major role in passive film growth and breakdown. The anions usually encountered in buffer solutions (e.g., borate) appear to have a beneficial (inhibitive) influence on oxide film growth over and above their ability to stabilize the solution pH. Consequently, when discussing oxide films on metals and alloys, it is necessary to consider the nature of both the oxide film and the solution in which the film is formed, as well as the electrochemical conditions of film formation. The precise role of halide ions such as  $\text{Cl}^-$  is still unclear, aside from the fact that they give rise to severe localized (i.e., pitting) corrosion. Their influence on oxide film growth, development, and breakdown is not a simple matter.

The role of alloying elements in the passivation process has been briefly discussed. Alloying additions such as chromium and molybdenum can substantially influence the structure and composition of the passive oxide film and thereby the process of passivation. The alloys discussed have been of the fairly simple binary type, where it is easier to analyze the surface oxide films by surface analytical techniques and to understand the results. This treatise provides a basis for the following discussion of stainless steels, where the number of alloy additions is increased as is the complexity of the passivation process.

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