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The Growth of Oxide Films in High-Temperature Aqueous Environment

Part 1 - Growth Characteristics of Iron Oxide Films Generated in Dilute Lithium Hydroxide Solution at 300°C

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ABSTRACT

In the early stages of iron oxide growth on mild steel in pH 11 LiOH solution at 300°C, the oxide is largely oriented and grows at a rate and with a morphology dependent on the substrate grain orientation. After a certain film thickness is attained, however, the epitaxial oxide growing in the (001) Fe_3O_4//(001) α-Fe, [$1\bar{1}0$] Fe_3O_4//[100] α-Fe orientation degenerates, leaving in its place a much thinner, fine-grained, randomly oriented "base film" partially covered by large solution-grown Fe_3O_4 crystals. Experimental evidence indicates that the transformation is induced by stress generated within the epitaxial oxide as the film thickens.

The two-phased oxide structure which exists after completion of the epitaxial oxide degeneration persists through oxidation periods of at least 300 hours. Observations of its growth behavior lead to the postulation of a growth mechanism in which iron passes through the base film into solution, subsequently to precipitate forming the upper surface crystals. It is possible, using this hypothesis, to derive a theoretical rate law, which predicts that, in agreement with the experimentally determined corrosion rate data, the corrosion rate should decrease in a logarithmic fashion.

PROBLEM STATUS

This is a final report on this phase of the problem; work is continuing on other phases of the problem.

AUTHORIZATION

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THE GROWTH OF OXIDE FILMS IN HIGH-TEMPERATURE AQUEOUS ENVIRONMENT

Part 1 – GROWTH CHARACTERISTICS OF IRON OXIDE FILMS GENERATED IN DILUTE LITHIUM HYDROXIDE SOLUTION AT 300°C

John B. Moore, Jr.,* and Robert L. Jones

INTRODUCTION

With the advent of electron diffraction in the 1930's and, subsequently, electron microscopy in the 1940's came the capability to examine and analyze surface oxide films as thin as 100A or less; many studies have since been made of nucleation and growth processes in oxide films growing on metals and semiconductors. These studies have been of fundamental importance in the interpretation of thin-film oxidation kinetics, in the elucidation of the phenomenon of epitaxy, and in the general advancement of the field of thin-film physics. The greater proportion of these experiments by far has been concerned with the growth of oxide films in a *gaseous* environment, however, and only a very few have dealt with films forming on metals in high-temperature aqueous solution, despite the obvious technological importance of such films. It is noteworthy that uncertainty still exists as to even the gross mechanism of oxide-film formation under environments as found in the interior of steam-generating boilers (1). Since the serviceability of a boiler depends on the formation and maintenance of a protective surface oxide, a knowledge of the genesis of this film, and, ultimately, of the role which inhibitive or corrosive species or treatments play in the process, should be of considerable benefit in the problem of boiler corrosion prevention.

Research initiated by Potter (2) in England and Bloom (3) in the United States has shown that the morphology of iron oxide films generated on steel by attack of high-temperature NaOH solution apparently depends on the physical system employed. Static corrosion tests at these two laboratories using alkali solutions of similar composition and run at the same temperatures produce oxide films which are chemically the same (Fe_3O_4) but structurally different. The Potter films have been examined by electron microscopy (4,5) and scanning electron microscopy (6), as well as by standard metallographic techniques, and it has been established that they have two layers. The inner layer adjacent to the metal is composed of tiny crystallites which come together to form a regular, adherent layer of uniform thickness, which, although porous, is nonetheless protective. There is an irregular, poorly adhering, layer of much larger tetrahedral crystals above this; this outer layer is thought to be largely nonprotective. Bloom films, on the other hand, appear to be single layered and to consist of tightly bound, large Fe_3O_4 crystals with well-developed facets at the oxide/solution interface. These films are less porous and apparently more protective than Potter films. Previous morphological investigations of Bloom-type oxide films have been by metallographic cross section and light microscopy only, however, and the work reported here, which involves a time-sequence study by electron microscopy of the early stages of oxide-film growth under Bloom's conditions, was undertaken to provide additional information concerning the physical

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structure of this type film and to elucidate, as far as possible, the mechanism by which it is generated.

The question as to why one physical form of oxide film or the other should be preferred with a given system has been taken up by Marsh (7) and, more recently, by Castle and Mann (8). There have also been electron microscopical investigations of the growth of oxide films on stainless steel in high-temperature water (9,10), which are of interest in this general problem.

EXPERIMENTAL PROCEDURE

Most of the oxide films examined were formed on the interiors of sealed mild-steel capsules filled completely with pH 11 LiOH aqueous solution, following the technique devised by Bloom and Krulfeld (11), and heated at 300°C in a circulating-air oven. The periods of heating ranged from 30 minutes to 12 days. A few films were grown on the interior walls of small autoclaves, fabricated as described by Potter and Mann (2), using the same alkaline solution and temperature. Heating times in these experiments were generally less than 72 hours.

The capsules were fashioned from mild-steel tubing of 0.020-inch wall thickness and 0.25-inch overall diameter, which was found, by analyses, to contain 0.09% C, 0.017% P, 0.032% S, 0.007% N, 0.57% Mn, 0.07% Si, 0.10% Cr, and 0.07% Ni. The autoclaves were made from 2-inch sections of 1-by-0.065-inch cold-rolled steel pipe closed at each end with 1-by-0.125-inch caps machined from bar stock. These steels contain 0.23% C, 0.015% P, 0.038% S, 0.004% N, 0.85% Mn, 0.21% Si, 0.05% Cr, and 0.05% Ni and 0.19% C, 0.004% P, 0.033% S, 0.004% N, 0.73% Mn, 0.01% Si, 0.06% Cr, and 0.05% Ni, respectively. The specimens were washed with hot detergent solution, degreased with trichloroethylene and vacuum annealed at 10^{-5} to 10^{-6} mm Hg and 875°C for 1 hour before being cooled and exposed to the atmosphere. This vacuum-anneal pretreatment produces a very thin film of Fe_3O_4, which often gives evidence of a high degree of orientation, on the metal surface (12). The annealed specimens were stored in a closed container over anhydrous $CaSO_4$.

The LiOH solutions were prepared with reagent-grade LiOH and triply distilled water. LiOH was chosen as the alkalizing agent in these experiments, because Bloom's work has led to the conclusion that LiOH has certain advantages over NaOH and KOH as a boiler water additive (13). Exploratory runs with pH 11 NaOH, however, produced oxide films indistinguishable in the electron microscope from those formed with LiOH solutions, indicating that, with the dilute concentrations and short-heating exposures employed here, the cation identity is probably not crucial to the film growth behavior observed.

Sections of oxide for electron microscopical examination were separated from the steel substrate by the iodine-methanol technique (14). When replicas were to be made, the platinum-preshadowed carbon replicas of the oxide surface were prepared before the oxide films were stripped from the metal. The composite replica-iron oxide film was then floated on aqueous 20% HF solution, which dissolved the oxide with no visible damage to the replica in just a few minutes.

Since we wished not only to follow the growth of the oxide film on the capsule wall but also to determine whether its growth morphology could be related to the oxidation kinetics of the corrosion reaction, corrosion rate data were taken for six capsules in the hydrogen-effusion apparatus built by Bloom (11). In this instrument, the corrosion rate is measured by monitoring the hydrogen which diffuses through the capsule wall, that hydrogen having originated in the reaction $3\ Fe + 4\ H_2O \rightarrow Fe_3O_4 + 4\ H_2$. The measurements were made at 300°C using PH 11 LiOH in capsules prepared from the same material and in the same manner as described above.

RESULTS

An examination of oxide films stripped from the three different steels, that is, from the capsule interiors and from the caps and walls of the autoclaves, indicates that the oxide morphology and growth pattern are qualitatively the same on all three surfaces, at least over the oxidation periods studied.

As the oxide film thickens, it becomes more coarsely crystalline, and characteristic morphologies develop on the different substrate grains as shown in Fig. 1. The oxide layer is often well oriented over the surface of an individual metal grain at this stage of film formation, and selected-area diffraction from these films will reveal numerous "single-crystal" diffraction patterns, of varying degrees of perfection, corresponding to several different oxide orientations. While the oxide in a given orientation does tend to exhibit a unique texture, as Fig. 1 indicates, these textures do not seem to develop equally well for all orientations, and the establishment of a relationship between a particular oxide morphology and selected-area diffraction pattern is difficult, except in one instance: oxide areas which have the distinctive morphology shown in the upper right corner of Fig. 1 always give electron-diffraction patterns corresponding to the (001) plane of the spinel crystal structure (Fig. 4a).

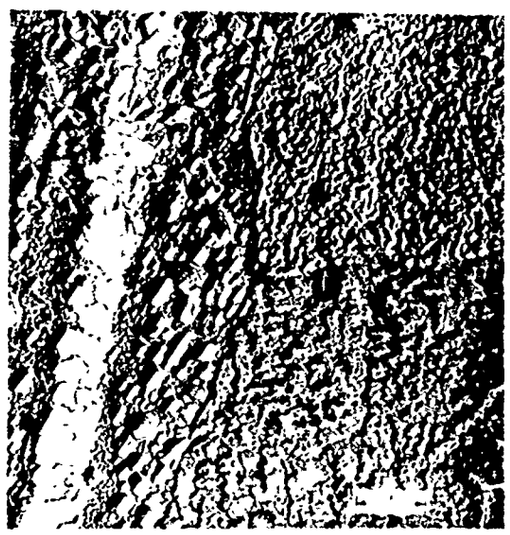
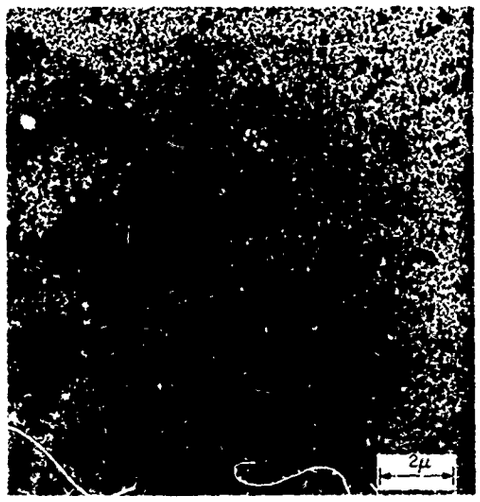


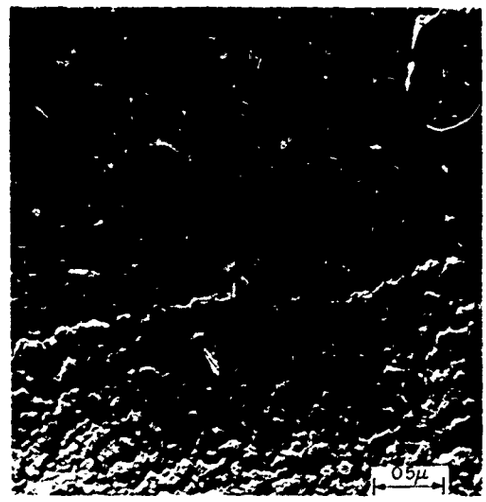
Fig. 1 - Oxide morphologies developed after 2 hours at 300°C, pH 11 LiOH

Electron diffraction alone is not sufficient to distinguish between Fe_3O_4 and γ-Fe_2O_3, or perhaps some cation-deficient intermediate, in these circumstances, but since this oxide exists and grows over several hours in an environment reported to produce Fe_3O_4, it is assumed to be Fe_3O_4 which originally existed on the metal substrate in the epitaxial orientation, (001) Fe_3O_4//(001) α-Fe, $[1\bar{1}0]$ Fe_3O_4//[100] α-Fe (15). Bloom, et al. (13), have found that $LiFe_5O_8$, which has a spinel structure very similar to Fe_3O_4 and γ-Fe_2O_3, can be generated in this system, albeit at somewhat higher LiOH concentrations; this third possibility was ruled out, however, when microanalyses of stripped oxide films failed to show the presence of lithium.

This easily identified (001)-oriented oxide, whatever its composition, makes an ideal specimen for following the course of oxide growth, and a study of these areas in oxide films generated with progressively increasing oxidation times — Figs. 2a through 2h



(a) 30 minutes

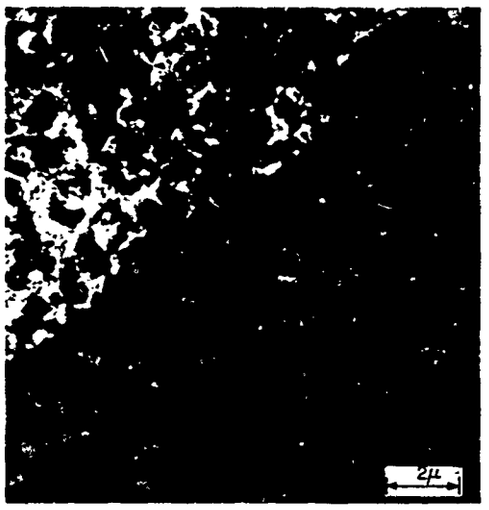


(b) 30 minutes (higher magnification of film)

(c) 2 hours

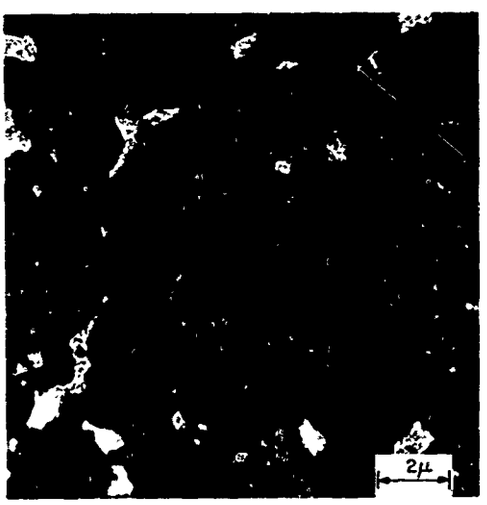
(d) 2 hours (higher magnification of film)

Fig. 2 - A time-sequence series of electron micrographs showing the iron oxide film at progressive stages of development. The left column shows the oxide after the indicated heating times at 300°C, pH 11 LiOH; the right column shows replicas of the oxide upper surface at corresponding times.



(e) 6 hours

(f) 6 hours



(g) 96 hours

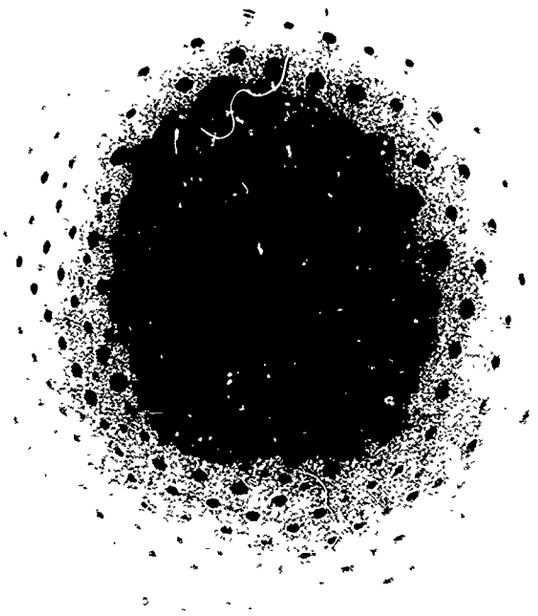
(h) 96 hours

Fig. 2 - A time-sequence series of electron micrographs showing the iron oxide film at progressive stages of development. The left column shows the oxide after the indicated heating times at 300°C, pH 11 LiOH; the right column shows replicas of the oxide upper surface at corresponding times (Continued).

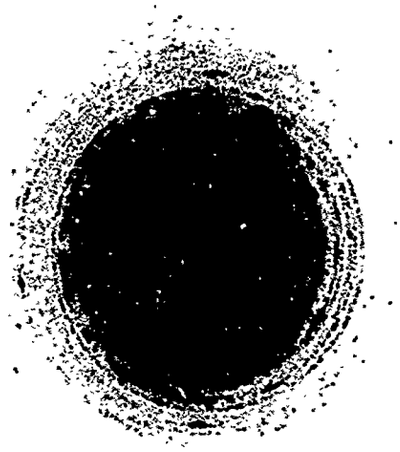
(Figs. 2b and 2d are at higher magnifications than the rest of the series to show better the fine structure of the oxide film) – reveals a most interesting phenomenon. The oxide in the (001) orientation evidently develops at a faster rate than the oxide in other orientations, because areas of (001)-oxide crystallites are detectable in films formed with as little as 30 minutes heating (Figs. 2a and 2b). It also grows in a different way, thickening in a uniform manner to form a compact, coherent layer, while the oxide in non-(001) orientations consists of a thin film and discrete, widely separated larger crystals, which appear to be considerably thicker than the film itself (Figs. 2c and 2d). The (001) epitaxial oxide continues to thicken with extended capsule heating and, as shown in Figs. 2e and 2f (6 hours heating), the boundary between the two oxide types becomes quite distinct. At about this point, however, one notices, in scanning across the oxide film, that the relative percentage of the surface area covered by the (001) oxide is definitely reduced, and more so than could be explained by fluctuations between individual specimens. Furthermore, if oxide films from longer heating periods are examined, the (001)-oxide morphology is found to be almost completely absent. These facts lead to the conclusion that after a certain limiting thickness is reached, the epitaxial (001) oxide must undergo a transformation, or perhaps more descriptively, a degeneration which removes it from the capsule surface. This conclusion is supported by the appearance of the residual (001) oxide in Fig. 2f and particularly in Fig. 3, where two areas of epitaxially oriented oxide are just being engulfed in the final stages of the transformation.

Fig. 3 - Two areas of epitaxial oxide (indicated by arrows) in the final stages of transformation after 6 hours at 300°C, pH 11 LiOH.

The manner in which this transformation occurs suggests that it is stress induced and that the process is initiated only after some minimum amount of stress has been generated within the epitaxial oxide, presumably as a result of the increase in oxide thickness. If selected-area diffraction patterns are taken just inside the boundary of a degenerating oxide region and then just outside of it, that is, on an area of the surface which had been previously covered by the oriented oxide, they (Figs. 4a and 4b, respectively) show that the transformation involves, in addition to a marked decrease in oxide thickness, a decided oriented-to-unoriented transition of the surface oxide. No quantitative value for the epitaxial oxide thickness requisite for the commencement of the transformation process can be given, but the process itself is observed to begin after 2 to 6 hours heating and to be largely completed after 24 hours at temperature.



(a) Epitaxial oxide areas



(b) Transformed oxide areas

Fig. 4 - Selected-area diffraction patterns

No other transformations of this nature were discovered when films from periods of heating longer than this were examined, the only visible change in the oxide morphology being a continually increasing coverage of the specimen surface by large, fully faceted crystals (Figs. 2g and 2h), which have been identified in previous work as Fe_3O_4. One noteworthy finding here, however, was that the thin oxide film next to the metal, the "base" film, which remains visible between the large crystals, apparently changes little or not at all in thickness as the oxidation periods become longer. This conclusion was reached by comparing the relative degree of electron transmittancy of base films formed with different heating times, as, for example, in Fig. 2e, where the time was 6 hours, and Fig. 2g, where it was 96 hours. While this technique is strictly applicable only to amorphous films, in instances such as this, where the films are composed of small, randomly oriented crystallites and the intensity losses due to diffraction are a direct function of film thickness, a good indication of relative film thickness can be obtained from a comparison of transmitted intensities, provided, of course, that the electron microscope settings are not changed between specimens.

Replicas of the base film (Fig. 2h) reveal that it has still another distinctive property. After extended periods at 300°C (over 50 hours), the individual crystallites at the upper surface of this film, which show definite crystallographic forms with shorter heating times, become rounded and pebblelike and occur only over a rather limited size range (approximately 300-500A). The appearance of the "equilibrium" base film is the same not only over the whole surface of a given specimen but also between specimens of different steel composition from both the autoclave and capsule systems, indicating that this pebblelike texture is characteristic of the base film.

Since the well-developed facets of the large upper crystals are strong indication that they are formed by precipitation from solution, presumably on top of the base film, several attempts were made to show that there is in fact a polycrystalline layer between these crystals and the metal substrate by mechanically dislodging the crystals in question to reveal the underlying stratum. These upper crystals adhere so tenaciously, however, that if a dislodging force is applied, as by burnishing the oxide film in situ on the capsule wall with the end of a wooden rod, they will shear across the main crystal body rather than be dislodged.

The points in Fig. 5 represent the arithmetic mean of corrosion rate data from five capsules (one capsule of the original six leaked). The individual curves all have the same general form, and at 190 hours they are all within ±5% of the mean value shown. A logarithmic curve can be fitted to these averaged data points with good precision using the empirical method of Champion and Whyte (16). This fit may not be quite as meaningful as Fig. 5 would lead one to believe, however, because the derived logarithmic equation indicates an oxide-film thickness of approximately 1500A at $t = 0$, a value most likely too high by a factor of five or more. On the other hand, it is known that the hydrogen-effusion technique employed here tends to give high results at short corrosion times, because a certain amount of gas is desorbed from the capsule's exterior as it comes to temperature (11).

DISCUSSION

Two distinct aspects of oxide-film growth in high-temperature LiOH solution have been revealed, which will be discussed separately for clarity. These concern the degeneration of the epitaxially oriented (001) iron oxide, an event occurring in the earlier stages of film formation, and the two-phased, double-layered structural configuration which the oxide film assumes as this process is completed.

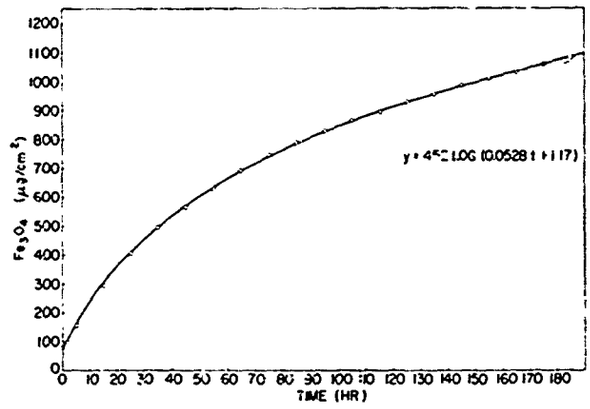


Fig. 5 - Oxidation of low-carbon steel in pH 11 LiOH at 300°C

Mechanism of Epitaxial Oxide Transformation

In considering possible mechanisms for the epitaxial oxide degeneration, note needs be made of the recent experiments of Grauer and Feitknecht (17). They found that the protectiveness of air-formed oxide films on iron (these were strongly oriented) against attack by chromate solution increased with film thickness up to a certain point but then decreased drastically. This loss of protective ability was attributed to the appearance of pores or fissures in the oxide film. They observed further that corrosive attack then proceeded in such a way that sections of the original oxide were undermined and displaced from the specimen surface, leaving in their place a very thin, randomly oriented, passive Fe_3O_4 film.

A sufficient number of our observations run parallel to those of Grauer and Feitknecht to suggest that we may be observing two different manifestations of one basic phenomenon. We see, for example, electron diffraction patterns (Fig. 6) very much like the one published by these authors to show the degree of orientation existing in their air-grown films when we examine areas of crystallite nucleation (Fig. 2a) in films grown in our capsules during short (30 minutes) heating exposures. These patterns are of some interest themselves, for while they resemble the (001) projection of the spinel reciprocal lattice, they cannot be indexed on this basis because of the presence of additional, anomalous diffraction spots, particularly those corresponding to the (311) planes of the spinel lattice. Reports of similar diffraction patterns from oxide films on iron or steel have been made previously, and several hypotheses as to the origin of the (311) spots have been advanced (18-21). The one point of agreement seems to be that these patterns are associated with the process of nucleation of oriented oxide crystals on the specimen surface. For our own part, we observe that as the areas of oriented oxide thicken with extended heating, they cease to show this type of pattern and yield instead the simple (001) spinel pattern (Fig. 4a).

Drawing from this background, we envision the following chronological sequence for the growth and subsequent transformation of epitaxial (001) iron oxide in the Bloom capsule system. A vacuum-anneal pretreatment, such as the specimen tubing receives, tends to produce an oriented Fe_3O_4 film on the iron surface (12); this effect would be especially strong for (001) Fe grains where the favorable epitaxial orientation (001) Fe_3O_4//(001) α-Fe, $[1\bar{1}0]$ Fe_3O_4//[100] α-Fe is possible. When the capsules are filled with LiOH solution, some Fe_3O_4 may dissolve (22), but since the volume of the capsule is

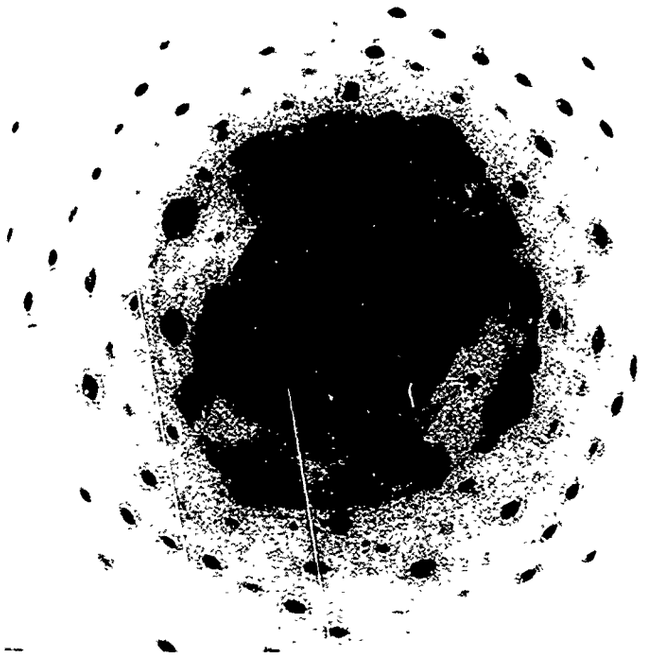


Fig. 6 - Selected-area diffraction pattern from an area of nucleating crystallites in an iron oxide film after 30 minutes at 300°C, pH 11 LiOH

small, the dissolution probably does not go to completion. With the commencement of heating, the residual film, still oriented, begins to develop further; both the rate and morphology of this development depends on the substrate grain orientation (Fig. 1). The growth rate of (001) iron oxide is apparently higher than that of iron oxide in other orientations (Fig. 2d), and a compact, coherent, and relatively thick layer of oxide soon builds up in this orientation. Stress mounts within this oxide layer as its thickness increases until finally the film fails, producing pores and fissures that permit the LiOH solution access to the underlying metal. Corrosive attack occurs then at the stressed metal/oxide interface so as to cause the oriented oxide to be replaced by a much thinner, finely crystalline, randomly oriented iron oxide film in a manner analogous to that reported by Grauer and Feitknecht. The displaced oxide dissolves, either at the time of displacement or later, since it is in a sealed capsule at high temperature, and then precipitates as secondary crystals on the underlying randomly oriented base film.

While the postulated stress-induced fissures could appear at random sites, e.g., above occlusions in the epitaxial oxide film, our experimental evidence is that attack usually initiates at the outer perimeter of a (001) epitaxial oxide area and proceeds inward. This is explainable if one assumes that the oxide grows thickest just above the substrate grain boundary and that fissures would, therefore, be more likely to appear first in this region. The inward march of the transformation reaction results finally in a total engulfment, or "swallowing up," of the oriented oxide as shown in Fig. 3.

Our electron micrographs also show that an encircling ring of larger crystals, which are apparently reprecipitated Fe_3O_4, is always present about a degenerating (001) oxide region. These secondary crystals arise presumably because the solution in this vicinity is heavily saturated with iron ion species, either from dissolution of the original oxide

or fresh corrosive attack on the exposed metal surface, and the freshly formed base film just beyond the epitaxial oxide boundary represents the nearest stable site for nucleation and crystal growth from solution. As the degenerating oxide recedes across the specimen surface, more or less continuous segments of the encircling ring should be left behind, since these crystals are nonmobile; indeed, strands of surface crystals which may be evidence of such a phenomenon are often found, as in the lower portion of Fig. 2e and at the right side of Fig. 3, near the epitaxial oxide boundary. These residual crystal strands might be better delineated and more abundant except that they are initiated in a supersaturated environment under nonequilibrium conditions and, hence, likely to be subject to further recrystallization themselves.

Development of Two-Phased Oxide Film

The overall appearance of the two-phased film which develops with degeneration of the epitaxial oxide and the manner in which the base film comes to be more and more covered by large Fe_3O_4 crystals as the corrosion reaction progresses strongly suggest that iron passes through the base film and into solution, subsequently to precipitate on the base-film surface. This mechanism for the formation of oxide films on iron in high-temperature aqueous media has, in fact, been proposed by Castle and Mann (8), who showed that by varying the factors which control the degree of saturation immediately at the corroding surface, one could apparently grow either Bloom films (no stirring – high saturation) or Potter-Mann films (stirring or iron-ion sink – low saturation). If this theory is correct, the large surface crystals, formed by precipitation on a randomly oriented film, should themselves be randomly oriented; our electron micrographs reveal, however, that in certain areas the facets of the individual crystals are well aligned (Fig. 2h). There is no reason to expect crystals precipitating from solution onto a truly polycrystalline, randomly oriented substrate to nucleate and grow with a three-dimensional orientation, and the alignment displayed by these crystals needs explanation if the dissolution-precipitation mechanism is to be considered valid.

A similar type of orientation has been found by Field and Holmes (4) for Potter-Mann films, and they have published a metallographic cross-section micrograph of the oxide film (their Fig. 10) which clearly shows that, in this case, a polycrystalline layer exists between the metal grain and the oriented upper oxide crystal. In a discussion of this phenomenon, these authors pointed out that it seemed to be related to the fact that the specimen had been annealed, since oriented upper crystals occurred only with annealed surfaces and never with abraded surfaces.

A review of our electron micrographs brings forth two possibilities for the origin of the aligned surface crystals observed in our oxide films, neither of which would necessarily preclude the idea that the two-phased film grows primarily through the dissolution-precipitation mechanism. The areas of crystal alignment are apparently associated with underlying metal grains, since we find instances of abrupt change in the direction of alignment across lines which probably represent the substrate grain boundaries, and different growth patterns are observed, depending on whether the metal grain is (001) or non-(001) oriented.

Many of the tiny crystallites which make up the early, very thin oxide films on non-(001) grains (upper half of Fig. 2b) are aligned, presumably by epitaxial forces. While these oxide films may, therefore, be considered to be partially epitaxially oriented, the areas of orientation are small and separated from one another, and apparently sufficient stress does not develop, in subsequent thickening of the oxide film, to cause a disorienting transformation in this grouping of oriented crystals. If it happens that the crystal alignment is such that planes giving preferred growth from solution are favorably oriented, then this set of crystals can act as nuclei for the development of aligned secondary crystals; moreover, since precipitation from solution under these circumstances

represe. a low-stress mode of crystal growth, the precipitated secondary crystals may grow to appreciable size while still maintaining their alignment. It appears then that aligned secondary crystals occur on non-(001) grains because the nucleation sites, rather than being randomly situated, are actually oriented themselves from the very beginning of the growth process.

The initial oxide growth process on (001) substrate grains, on the other hand, is such that stress is produced within the oxide film, and a transformation takes place that removes the original oxide, replacing it with a new polycrystalline and randomly oriented film. Can oriented growth of precipitated crystals occur on this surface? There is experimental evidence to indicate that it can. In Fig. 2e, for example, a number of the smaller surface crystals appearing on the freshly formed base film show a simple crystallographic form and a range of size which suggests that they are most likely newly nucleated and growing secondary crystals. Furthermore, the edges of many of these crystals are aligned, providing a clear indication that oriented growth is taking place here. The implications of this finding are uncertain. It may be simply that the transformation does not remove every vestige of orientation in the (001) oxide layer and that some crystallites of the great number constituting the base film remain in register with the substrate and hence with each other. This idea is supported by an examination of the base-film diffraction pattern (Fig. 4b), which reveals a slight tendency to residual preferred orientation. Or, it may represent still another instance where an oriented species is observed to nucleate in a previously amorphous or randomly oriented surface film: such observations are not uncommon in gaseous oxidation experiments, having been reported by, among others, Gulbransen for iron oxide films (23) and Ba 'ett for aluminum oxide films (24). Whatever the source of these oriented crystallites, it may be expected that, although they may grow initially by recrystallization within the oxide film, they will eventually switch over to growth from solution and thus lead to the generation of large oriented upper crystals on (001) metal grains.

While these hypotheses may rationalize the presence of oriented secondary crystals in the films studied here, it is not obvious that the same arguments could be applied to explain the appearance of the oriented upper surface crystals found by Field and Holmes (4), where the polycrystalline layer between surface crystal and substrate is fully 5 microns thick. How the surface crystals maintain orientation with the substrate through an intervening layer of such thickness remains a crucial, but unresolved, question in the development of theories of oxide-film formation in high-temperature aqueous solution.

Although none of our conclusions are contingent upon a knowledge of the film structure under the large secondary crystals, it has been tacitly implied in these discussions that as the crystal being formed from solution grows laterally over the base film, the crystallites of this film are not incorporated into the body of the larger crystal, i.e., that a polycrystalline phase remains between the precipitated crystal and the metal below. There is as yet no experimental proof of this; the assumption is made through analogy with the work of the Potter and Mann group, who have observed that the upper surface crystals never incorporate the inner polycrystalline layer. Extensions of the upper crystal down into the polycrystalline region are sometimes found, however (4), and it may be that the adherence displayed by the secondary crystals in our capsule system results from a mechanical locking-in effect that such extensions would provide.

Significance of Evolved Oxide Structure

Two noteworthy characteristic properties are displayed by the base film once the two-phased structure is fully established: its upper surface takes on a distinctive pebblelike texture, and the film itself comes to a certain limiting thickness beyond which it will not grow. These properties are invariant, as far as can be seen, over the surfaces of the several different specimens examined, and it appears therefore that they are

independent of such factors as substrate grain orientation, minor variations in alloy composition, and slight differences in surface pretreatment. Work with anodically passivated metals has shown that noncrystallographic oxide growth such as this occurs when the rate-determining step is diffusion through the passivating oxide film (25). Moreover, it may be noted that while the base-film qualities seem unusual at first sight, they are just those that would be expected for an oxide film being simultaneously generated at the oxide/metal interface and dissolved at the oxide/solution interface. The film then would come to a limiting thickness as the rates of the two competing reactions become equal, and its outer surface, which is being continually renewed, would develop a morphology determined predominantly by the dissolution process. Oxide formation at the oxide/metal interface would initially be the faster reaction, but as the oxide film thickens, this reaction, controlled by solid-state diffusion of reactants to or from that interface, would slow until its rate just equals that of the dissolution reaction at the oxide surface.

This hypothesis concerning the generation of the base film, which has been developed from observations of the growth behavior of the oxide, turns out to be quite similar to a mechanism of formation for passive oxide films advanced by Vetter (26); he explains the small but constant corrosion current which "passive" films exhibit by proposing that there is dissolution of the passive film and that the rate of the anodic formation of the passive oxide and of its dissolution becomes equal at some given (and constant) film thickness. This, and the fact that the passive oxide films isolated by Grauer and Feitknecht (17) show essentially the same characteristics as our base film (they also being finely crystalline, randomly oriented films which remain at apparently constant thickness and show no substrate-grain-orientation dependence) gives reason to believe that what we have described phenomenologically as the base film may actually be a high-temperature passive oxide film.

There remains to be considered whether or not the oxide-film morphology which has been revealed in this work can be correlated with the kinetic rate data taken during the formation of the film. We see first, from the smoothness of the curve in Fig. 5, that the degeneration of (001) epitaxial oxide either does not entail evolution of appreciable quantities of hydrogen or takes place over such a small percentage of the specimen surface area that its effect on the overall corrosion rate is negligible. Secondly, we note that the curve is logarithmic. Logarithmic reaction-rate curves for the water-iron corrosion system have several times in the past been associated with the blocking of pores in the oxide film, so it is of interest to see if evidences of a pore-blocking mechanism can be found here. No pores are visible in our electron micrographs, but this, of course, does not preclude the existence of pores smaller than the limit of resolution of the electron microscope (which may be as high as 50A with these specimens) or of pores which follow a tortuous and nondirect route through the film. We can assume though that if there are pores in our oxide films, they are most likely in the base film. There is, however, no indication of any change in this film such as would suggest that pores are being blocked as the reaction progresses; i.e., the base film does not become thicker nor does it become more or less finely crystalline. The one change that is observed during this period is that the base film is being increasingly covered with thick, adherent Fe_3O_4 secondary crystals. Since these crystals are, from every indication, protective, this all goes to suggest that the smooth decrease of the corrosion rate with time occurs not because pores are being blocked within the base film but because more and more of this reactive film is being covered by shielding Fe_3O_4 crystals.

The passing of cations through an oxide film to precipitate as discrete crystals at the solution/oxide interface is formally equivalent to the passing of cationic vacancies in the opposite direction through the film to congregate as cavities at the oxide/metal interface. Furthermore, in both cases, the oxidizing species is forbidden access to the underlying metal at the site of the cavity or crystal, and the effective surface area capable of continuing the corrosion reaction is thus reduced. It is possible therefore to adopt the derivation made for the new logarithmic law which is obeyed when cavities occur at the

metal/oxide interface (27), making allowance for the fact that the oxide base film here remains at constant thickness, and show that the logarithmic nature of the corrosion rates observed in these studies can be accounted for in terms of the covering of an underlying oxide film by precipitating crystals and that the oxide growth morphology and kinetic rate data are, in this sense, mutually consistent.

SUMMARY

In the growth of oxide films on annealed polycrystalline mild steel in high-temperature pH 11 LiOH solution, the initial films tend to be epitaxially related to the substrate grains and to develop characteristic morphologies on the various grain orientations. The (001) oxide morphology is particularly distinctive, and it has been possible to follow the growth and subsequent degeneration of this epitaxial species in detail. The degeneration of the (001) oxide begins only after a certain oxide thickness is attained, a fact suggesting that the transformation results from stress generated within the epitaxial oxide as its thickness increases.

The oxide film that exists after the epitaxial oxide has been transformed appears to consist of two layers — a thin, finely crystalline, randomly oriented base film and, above that, an incomplete layer of much larger, thicker crystals, which are presumably solution-grown Fe_3O_4. The upper surface of the base film shows a pebblelike texture that is very uniform from point to point on the specimen. This surface is apparently made up of rounded crystallites, which are somehow held to a very restricted size range (300-500A). Furthermore, it appears that the base film comes to and remains at some limiting thickness as the corrosion reaction proceeds. Both of these observations have been interpreted as indicating that the base film is being simultaneously formed at the oxide/metal interface and dissolved at the solution/oxide interface, the film's upper surface texture resulting from the dissolution process and its limiting thickness coming about as the rates of the competing reactions become equal.

All indications are that, once this stage is reached, further film growth occurs by the passage of iron ions through the base film into solution to subsequently precipitate as large Fe_3O_4 surface crystals, and the only change detected in the oxide-film structure after this is a continually increasing coverage of the base film by the upper crystal layer. Our corrosion rate data reveal a logarithmic decrease in the oxidation rate over this same time period, which suggests that the precipitated crystals are protective and that the corrosion rate decreases as more crystals come down and the remaining area of exposed base film is reduced. This hypothesis is supported by the fact that one can, using the physical model proposed here, derive a theoretical rate equation which indicates that the corrosion rate curve should indeed be logarithmic.

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13. ABSTRACT

In the early stages of iron oxide growth on mild steel in pH 11 LiOH solution at 300°C, the oxide is largely oriented and grows at a rate and with a morphology dependent on the substrate grain orientation. After a certain film thickness is attained, however, the epitaxial oxide growing in the (001) Fe_3O_4//(001) α-Fe, [$1\bar{1}0$] Fe_3O_4//[100] α-Fe orientation degenerates, leaving in its place a much thinner, fine-grained, randomly oriented "base film" partially covered by large solution-grown Fe_3O_4 crystals. Experimental evidence indicates that the transformation is induced by stress generated within the epitaxial oxide as the film thickens.

The two-phased oxide structure which exists after completion of the epitaxial oxide degeneration persists through oxidation periods of at least 300 hours. Observations of its growth behavior lead to the postulation of a growth mechanism in which iron passes through the base film into solution, subsequently to precipitate forming the upper surface crystals. It is possible, using this hypothesis, to derive a theoretical rate law, which predicts that, in agreement with the experimentally determined corrosion rate data, the corrosion rate should decrease in a logarithmic fashion.

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