THE ANODIC BEHAVIOR OF MAGNETITE AND ITS RELATION TO THE PASSIVITY OF IRON

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The relationship of the steady state rates of solution of passive iron and magnetite to the pH of the solution and also the nonsteady-state behavior of these electrodes with gradual changes in potential in the range of 0.9-1.4 V and with cutting-off of the polarization makes it possible to conclude that about the same nonstoichiometric passivated layer is formed on a magnetite anode as on an iron one and that the basic mechanism of their solution is electrochemical.

Close to the Flade potential, reducing solution of magnetite (Fe_3O_4), the same as for anodic solution of iron, is speeded up by a shift of the potential to the negative side [1-6]. At the opposite boundary of the passive zone anodic solution of magnetite also becomes more pronounced under certain conditions, but with an increase in potential [7].

In this article it is shown that a strong electrochemical similarity is found between magnetite and passive iron at medium potentials for the passive condition.

METHOD

Well-formed single crystals of natural magnetite with an apparent surface of 3.5-5 cm^2 were investigated. Platinum conductors 1 mm in diameter were pressed into holes bored in the crystals and protected from the solution by polyethylene insulators. Some of the tests were made with electrodes which had a working surface consisting of one face of the single crystal mounted in a glass tube with epoxy resin poured over it.

The data used in this report on the behavior of iron was obtained from electrodes of laminated strips of Armco iron using the earlier-described radioelectrochemical method [8, 9].

In the tests with magnetite the radiometric portion of the circuit was not used since with a unit radioactivity sufficient for quick measurements the total radioactivity of a compact single crystal of magnetite is too high for operation without the use of special means of protection. Therefore in the tests a choice was made of the area of potentials (0.9-1.4 V) where the only cationic products of the solution of magnetite are trivalent ions of iron [10] and where, consequently, the stationary current density closely correlates with the stationary rate of solution of magnetite according to the equation:

$$Fe_3O_4 + 8H^+ - e = 3Fe^{3+} + 4H_2O \qquad (1)$$

The solutions of double-distilled sulfuric acid in double-distilled water had purified nitrogen blown through them before and during the tests. The potentials were measured and are shown in the text with reference to a hydrogen electrode in the working solution. The test temperature was $25 \pm 0.1^\circ C$. The normal preparation of the magnetite electrode included holding at a potential of 0.5 V for an hour, which provides a comparatively mild reducing etch of the surface. The working face of the crystal covered with epoxy resin was ground before the test with fine corundum powder.

RESULTS

Steady-State Processes. After holding for 20-24 h at the specified potential the current density on the magnetite electrode is practically steady. In the range of 0.9-1.4 V at a given pH it does not depend

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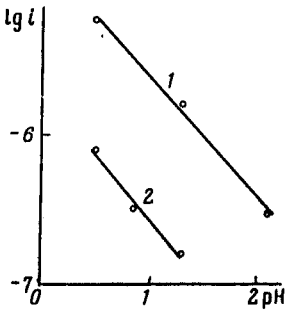

Fig. 1

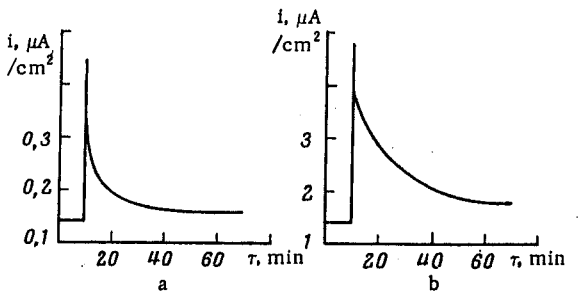

Fig. 2

Fig. 1. The relationship of the steady-state currents to the pH of the H_2SO_4 solution for a passive Fe electrode (1) and a magnetite electrode (2) (φ = 1.1 V).

Fig. 2. Current–time curves obtained with a spasmodic increase in the potential of 100 mV (φ_1 = 0.9 V → φ_2 = 1.0 V): a) magnetite; b) Fe pas (0.1 N H_2SO_4).

on the potential, but is related to the concentration of hydrogen ions by the same exponential relationship as the steady current density of the passive iron (Fig. 1).

Comparing on the basis of Fig. 1 the rates of the steady-state processes at magnetite and iron electrodes it must be taken into account that in dissolving a gram ion of Fe^{3+} in the reaction

$$Fe_{met} - 3e = Fe^{3+} \qquad (2)$$

a charge nine times greater than in reaction (1) is expended.

Consequently, according to Fig. 1 the flow of cations from a unit of apparent surface of magnetite and iron must be almost the same in our experiments. However, the faces of the etched magnetite crystals were rough and covered with a lattice of microcracks so that it may be stated approximately that the true rate of anodic dissolution of the cationic sublattice of natural magnetite is somewhat lower than the rate of solution of passive iron.

Nonsteady-State Processes. The surge and subsequent gradually slowing down return of the current to the steady state found with a spasmodic increase in potential appear in magnetite about the same as in passive iron (Fig. 2).

With a spasmodic drop in potential (Fig. 3) the superficial similarity of the current–time curves is essentially lost.

In iron a surge of cationic current at the moment of switching is found only with large drops in potential and lasts only for a short time, about 0.1 sec. After this in weakly acid solutions ($\leq$0.1 N H_2SO_4) there is an interruption in the current at the low anode value which is longer with a lower acidity and solution temperature and with a higher drop in potential. During the period of the interruption both the solution current and the external current maintain values substantially lower than the steady-state values and the difference between these two currents, equivalent to the rate of cathodic removal of oxygen, remains practically constant.

In magnetite, with such drops in potential the cathode voltage of the nonsteady-state current lasts far longer, up to several dozen minutes, the amplitude and time of the cathode current increase with the value of the drop in potential, and the current–time curve has a completely flat shape. However, despite these differences individual portions of the current–time curves have obvious elements of similarity (Fig. 3): a) with sufficiently high drops the initial amplitude of the cathode current on the passive iron becomes almost the same as on the magnetite; b) the moment of the end of the delay in the growth of the anode current on the passive iron closely agrees with the moment of the change in the polarity of the external current on the magnetite (in Fig. 3 it is 26 min); c) the cathode charge passing by this time through the magnetite electrode Q_c = 0.32 mC/cm^2) is close to the difference between the full charge of the radiometrically determined iron ions dissolved during this time from the iron anode (Q_s = 0.54 mC/cm^2) and the simultaneous integral of the external anode current flowing through the iron electrode (Q_a = 0.20 mC/cm^2).

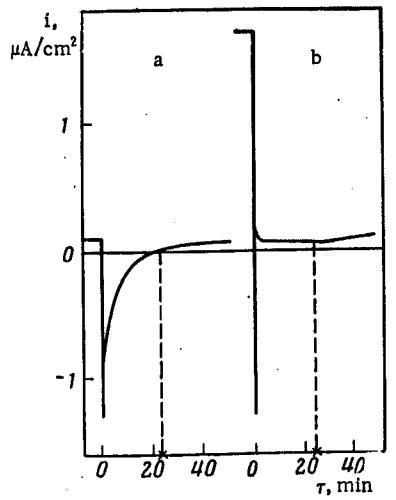

Fig. 3. Current–time curves obtained with a drop in potential of 500 mV ($\varphi_1 = 1.4$ V $\rightarrow \varphi_2 = 0.9$ V): a) magnetite; b) Fe_{pas}.

DISCUSSION OF RESULTS

The relationship of the mechanisms controlling the solution of iron and magnetite in the investigated area of potentials is not in doubt.

A number of the above-described factors indicate this, particularly: a) the steady-state solutions are comparable, independent of potential, but equally dependent upon pH rates (Fig. 1); b) the similarity of the current–time curves with increases in potential (Fig. 2); c) the similarity (in equivalent terms) of the quantities of oxidized metal which with a reduction in potential spontaneously (above the external current) are yielded to the solution from the surface of the passive iron and the quantities of oxygen which with the same change in potential are removed from the surface of the magnetite (Fig. 3).

It is strange that at first glance this relationship of the mechanisms is inconsistent neither from the hypothesis of the chemical solution of the passivating film nor from the assumption that the film is magnetite or some other oxide of constant stoichiometric composition. Let us show that this is so.

In accordance with existing concepts and terminology the first refutable hypothesis leads to the subsequent one. The limiting phase of solution of the passive metal is the chemical solution of the passivating oxide. A precise and sufficient criterion of the chemical process is the absence in it of elemenary acts occurring with the participation of the mobile current carriers of the solid phase, vacancies or electrons, which are more mobile in this phase than with the normal interatomic distances for chemical reactions.

An absolutely necessary criterion for the chemical process is the absence of the above-mentioned mobile carriers if only in the general balance of the solution stage according to the total equation

$$MeO_x + 2xH^+ = Me^{2x+} + xH_2O \qquad (3)$$

in other words, the absence of changes in the average formal valence of the metal during the changeover from the oxide lattice to the solution.

To demonstrate that the investigated processes do not possess this criterion is possible using the example of magnetite electrodes, many portions of the behavior of which are more clearly defined than for iron ones.

If the limiting stage of solution, strictly speaking, of the oxide [Eq.(3)]occurs without a change in the valence of the iron but the process as a whole [Eq. (1)] includes an increase in its average valence from 8/3 to 3, then it is clear that transmission of the charge, the easy electrochemical stage of oxidation, must be accomplished either before or after the chemical stage and there are no other possibilities. Let us consider both of these sequences.

1. Let solution be the first change occurring in the original oxide, according to the formula

$$Fe_3O_4 + 8H^+ = Fe^{2+} + 2Fe^{3+} + 4H_2O \qquad (4)$$

Then the easy electrochemical stage

$$Fe^{2+} - e = Fe^{3+} \qquad (5)$$

must occur immediately in proportion to the appearance in the layer next to the electrode of each successive iron ion being dissolved, that is, it must occur under conditions of the maximum current of the reaction for the Fe^{2+} ions. But in this case moderate oscillations in potential cannot cause those changes in current which are noted in Figs. 2 and 3. Consequently, this does not occur.

2. On the other hand, suppose oxidation

$$2Fe_3O_4 + H_2O - e = 3Fe_2O_3 + 2H^+ \qquad (6)$$

precedes solution

$$Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O, \quad (7)$$

the limiting role of which is determined by the removal of the film of Fe_2O_3 inhibiting reaction (6).

According to this assumption, the equilibrium potential of (6) must be negative and the potential of any conceivable reaction for further anodic oxidation of Fe_2O_3 positive to the investigated area of potentials since in this area only Fe^{3+} ions are stable in solution [10] and they may be obtained nonelectrochemically only in dissolving a purely trivalent oxide. In such a case a drop in potential within the limits of this area may only temporarily, until corresponding thinning of the film, stop nonequilibrium formation of Fe_2O_3 according to Eq. (6) but may not cause any cathode currents.

Nonsteady-state cathode currents (Fig. 3) flowing through an actual magnetite electrode at the investigated drops in potential and independent of agitation or a change in the solution leads to reduction of the oxidizing component, which is accumulated at the surface of the electrode in greater quantity with a more positive potential prior to the drop. This indicates that stoichiometric Fe_2O_3 cannot in any case, in the investigated area of potentials, be assumed the only product of anodic oxidation occurring on the surface of the magnetite. Consequently, the kinetic method considered is improbable since of two or any other number of oxides of differing valence, even with a varying composition on the surface, it is impossible under the action of single H^+ ions to every time obtain only Fe^{3+} ions purely chemically without the participation of the mobile current carriers of the solid phase.

But if any variant including the limiting chemical stage in the kinetic method of the process leads to a basic contradiction between the method and the actual behavior of the anodically polarized magnetite, then it must be concluded that the very concept of the existence of a similar stage is incorrect.

Consequently, the hypothesis connecting the passivity of iron with the protective action of the oxide film related to the magnetite or the products of its further oxidation may be correct only if it excludes the concept of the chemical solution of the oxide as the stage determining the rate of solution of the metal.

The second thing requiring proof is that the passivating layer cannot be magnetite or any other oxide of definite stoichiometric composition. Proof of this may be established by the fact that the number of individual stoichiometric oxides in the metal is limited and such a small number of discrete values of equilibrium potential corresponds to discrete changes of one to another.

If similar gradual transformations occur depending upon the degree of change of potential on the surface of the magnetite, then the nonsteady currents caused by drops in potential would change discretely both in relation to the original and to the final levels of potential.

However, in actuality, with a change in either of these levels these currents change completely smoothly, continuously, and as a first approximation are determined only by the value of the drop independently of the position of each of the levels individually.

The minimum drop in potential sufficient for the appearance of a cathode current on the magnetite is no more than several tens of millivolts over the whole investigated range of potentials. The original oxidation–reduction potential recorded at the moment of the end of polarization of the oxidized components which have accumulated on the surface layer of the electrode is always practically equal or very close to the polarization potential, as if the latter did not change smoothly. It being impossible with a discrete change in the composition of electrochemically active substances, this fact clearly indicates the smooth, or nonstoichiometric, change in the surface phase composition of the oxide electrode.

Existing data makes possible only preliminary conclusions, based primarily on indirect evidence, on the nature of the nonstoichiometric layer.

The negative charge transferable by a nonsteady-state cathode current after a drop in potential from 1.3 to 0.9 V ($3.2 \cdot 10^{-4}$ C/cm^2 of apparent surface) generally does not exceed the electrochemical capacitance of a single layer of atomic oxygen, but with a decrease in the amount of the drop the cathode charge removed from the electrode, as a rough estimate, drops linearly as the charge of the adsorption layer should drop in accordance with the Temkin adsorption isotherm.

Nonetheless, there is a combination of facts which makes it difficult to treat the nonstoichiometric surface layer only as a single layer of adsorbed oxygen with variable surface coverage. Let us list and attempt to explain some of these.

1. The very long time during which the cathode currents are maintained after a drop in potential (Fig. 3) and the even greater (hundreds of minutes) total length of the transition processes returning the current density to its steady-state anode value. In maintaining a steady rate of solution during this time it would be possible to dissolve a layer of oxide tens of Ångstroms thick.

2. The symbiotic and approximately proportional increase in the length of both of these portions of the transitional period with a decrease in the steady-state rate of solution of the magnetite as a result of the decrease in the acidity of the solution.

3. The smoothness of the transition from negative nonsteady-state currents to positive ones (Fig. 3) and the absence at this or any other point of the current–time curve, up to the time it is no longer steady-state, of any bends which would be expected with the transition of the decisive role in determining the external current from certain individual processes to others.

These facts allow us to present the following more reliable picture of the transition processes with different changes in potential.

The solution of the surface layers of the oxide lattice lasts throughout the whole transitional period and this means that all this time the external (cathodic or anodic) current is determined by the algebraic difference between the charge of the iron ions subjected to hydration and the charge of the H^+ ions being consumed in the conjugate bonding of the oxygen of the oxide in the water.

Obviously, a smooth change in this difference with a transition through the zero point indicates not so much a change in the rate of solution of the lattice in general as a suitable change in the numerical relationship of the combined atoms of metal being dissolved and the oxygen. And since this change, in addition to being smooth, occurs parallel with solution of some limited number of layers of the lattice, it would be difficult to reject the idea of a direct causal relationship between these processes and to explain the change in the current only by the gradual and randomly coincident consumption of the adsorbed oxygen, which by the moment of the drop in potential is found above the already being dissolved outer layers of the lattice. Most likely the changes referred to reflect the actual reduction in the steady-state degree of oxidation occurring on the anodically polarized magnetite depending upon the degree of transition from more positive polarization potentials to less positive ones.

Therefore, not denying in principle either the existence or the possibility of the kinetic role of the single layer adsorbed oxygen, it is possible to assume that the surface nonstoichiometric layer occurring on the oxide electrode as a result of anodic polarization traps more than one elementary layer of the crystalline lattice and is characterized by a relatively smooth change in composition across the thickness, which in turn depends upon the potential.

The electrochemical character of the limiting act of solution of an oxide anode has already been explained logically by the fact that this act, as was shown above, is not nonelectrochemical. To present in the form of such an act the whole process, expressed by an equation of type (1), is impossible even on the basis of a very general consideration of the practical impossibility of accomplishing the elementary act with simultaneous participation of so large a quantity of independent particles. In practice any similar plan is disproven by close to 0.5 the apparent order of the total reaction for H^+ ions (Fig. 1).

In addition, acknowledgement of the nonstoichiometric nature of the surface layer and the smooth changes in its make-up also call for definite conclusions about the character of the elementary acts at the border with the solution. A nonstoichiometric nature may not be the property of an individual molecule. This is a property of the whole lattice, the appearance of which is impossible if at least one of the components is not capable of entering or leaving the lattice independently of the other. But in the solution of a two component lattice it is impossible to acknowledge that one component might leave independently without acknowledging the independence of the second.

As already mentioned [2, 6] these ionization transitions

$$[O]_{lat.} + 2H^+ \rightarrow H_2O(-2[e]) \quad (8)$$

$$[Fe]_{lat.} \rightarrow Fe^{3+}(+3[e]) \quad (9)$$

by their nature are so independent that for a given surface condition it is possible for them to react separately to a change in electrical potential, but at the same time they are linked by the overall material and electrical balance and, in conformance with the Gibbs–Duhem relationship, must influence one another through the change in the surface condition placing in a mutual relationship their steady-state rates.

Precisely these transitions must be considered as the electrochemical stages which are the basis of the solution process and determine its kinetics.

All of this has a very direct relationship to the solution of passive iron. As soon as the metal is covered by an oxide film its further behavior is to a decisive degree dictated by the properties of the oxide surface. The difference is determined only by the fact that on the metal electrode under the oxide film there is a metallic lattice which is a continuous source of cations migrating through the film. Therefore reaction (8) in the form of a directional electrochemical transformation is found on the passive iron only in the nonsteady-state periods: from left to right after a sudden increase in potential and in the opposite direction after a drop.

In the steady-state condition the only directional transition at the film–solution boundary is reaction (9), which does not require compulsory conjugate removal of the oxygen since the cationic vacancies occurring may be eliminated as the result of migration through the film.

This, finally, does not mean that in solution of the metal movement of the surface oxygen into the solution is a generally impossible act. Such acts undoubtedly do occur, but being compensated by the transitions encountered, they may occur in addition to the process of solution and create an independent exchange current maintaining the surface activity of the oxygen at a level close to equilibrium. The understanding that, in comparison with cations, oxygen passes through the oxide–solution boundary practically reversibly has been brought out earlier [6, 10]. Now there is clear confirmation of the closeness of the steady-state rates of solution of oxide and passive iron, the impossibility of which in measuring the solution of oxide by reaction (8) is obvious.*

CONCLUSIONS

1. The close similarity of the anode behavior of magnetite and passive iron shows that they both dissolve electrochemically.

2. It may be assumed that the sublayer of magnetite on the surface of the passive iron serves only as a base and a material for creating a completely passivated nonstoichiometric layer, the thickness and surface oxygen content of which changes smoothly with potential and the properties of which determine the delay in the anode output of cations to the solution both on the iron and on the magnetite electrodes.

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* Full equality of the rates should not be expected since on the metal the surface nonstoichiometric layer is subjected to far greater rearrangement as a result of migration than on the oxide and consequently must possess a large nonequilibrium excess of free energy.