

metal forms an electrical double layer, firmly attached to the metal and with its negative side outermost. The overall potential difference between metal and solution remains unchanged. Consequently, the appearance of an additional potential difference on the side of the solid phase should result in an equal fall in the potential difference (proportional to the amount of oxygen adsorbed) in the liquid phase, i.e. between the tin and the solution. A similar pattern of electrochemical passivation has been observed previously with iron¹⁰ and cobalt¹¹ electrodes in alkaline solutions.

In conclusion, it should be noted that both in the present investigation of the anodic passivation of tinplate in alkaline solution and in investigations of the anodic passivation of iron in sulphuric-acid solution, an inverse relation is observed between time of passivation and anodic-current density. The minimum current density I_0 determined graphically was 0.15 A/dm², and that of the constant $k = 0.30$.

SUMMARY

The investigation has shown the complete suitability of a rapid method of electrochemical passivation of tin in dilute solutions of sodium hydroxide. The time required for passivation of tinplate is diminished by lowering the temperature of the solution to 30° and the concentration of sodium hydroxide to 0.5–1.0%. Corrosion tests have shown that the stability of electrolytically passivated tinplate in media containing sulphur compounds is considerably higher than the corrosion resistance of tinplate passivated by chemical means.

THE BEHAVIOUR OF THE ELECTRODE POTENTIAL DURING THE PASSAGE OF AN ELECTRODE FROM THE PASSIVE TO THE ACTIVE CONDITION

Ya. M. Kolotyrkin

The behaviour of the electrode potential during transition from the passive to the active condition has attracted much attention in recent publications¹⁻⁹ on the mechanism of passivation and on the nature of the passive state of the iron electrode. It is now clearly established that the activation conditions and the behaviour of the electrode during the transition depend essentially on the presence or the absence of oxidising agents in the solution^{5,8}, on pH^{8,9}, and on the value of the initial potential⁹ at which the electrode is maintained before commencing the activation. In solutions of non-oxidising acids, such as sulphuric, the interruption of a polarising anodic current leads to a spontaneous displacement of the potential of a passive iron electrode towards negative values, until a value corresponding to an active metallic surface is attained^{7,9}. When this happens the change in potential is practically linear with time during an initial period, but it is followed by an arrest whose duration is longer the higher (more positive) the starting potential. After a certain time the potential suddenly jumps in the negative direction and reaches values corresponding to the active condition of the electrode. In solutions of fixed pH the arrest is always observed at the same potential, to which the German workers have given the name "flade potential".

They identify it with the passivation potential in view of the fact⁴ that the active condition is stable at potentials more negative than this value and the passive condition at more positive potentials.

In solutions of oxidising acids such as nitric acid no spontaneous activation of the iron electrode is observed when an anodic current is switched off^{5,9}. In these cases activation may be brought about either by polarising the electrode by means of an outside cathodic current or by placing an active (unpassivated) specimen in contact with the passivated one. However, activation by this procedure can only be achieved if the applied cathodic current exceeds a certain critical value: lower currents give rise to insignificant changes in potential towards negative values and fail to activate the electrode. By the same token, contact activation can take place only when the ratio of active to passive sample areas exceeds a certain critical value⁹ of the order of 10⁻⁴. Unless this condition is fulfilled contacting leads to the passivation of the active sample rather than to the activation of the passive. Even if the above conditions are observed activation cannot set in unless the electrode potential is shifted (by a cathodic current or by contacting an active specimen) to a definite value, not far from the "flade potential". If cathodic polarisation is interrupted, or contacting is discontinued, at more positive potentials, the electrode potential reverts to the initial value. If, however, the cathodic current or the contact are interrupted when the potential is somewhat more negative than the "flade potential" the activation of the electrode continues spontaneously.

In interpreting their results Bonhoeffer and his coworkers use a model, developed by them, according to which

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The Urals Institute of Metals

Received 23rd July 1958

Kirov Polytechnic Institute of the Urals, Sverdlovsk

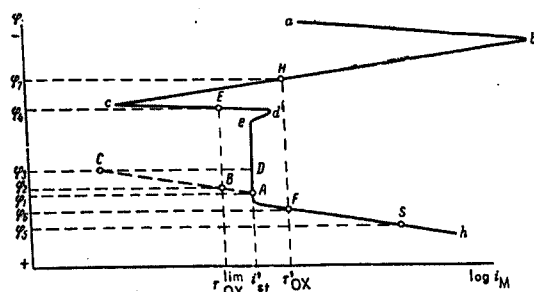


Fig. 1.

the passivation of a metal results from the formation of a thin layer of oxide on the surface. They point out that the appearance of such a film must change the nature of the corrosion process. The corrosion process which takes place at an active surface (ionisation of metal atoms and evolution of an equivalent quantity of hydrogen) is now precluded, and is replaced by the much slower dissolution of the oxide layer in the electrolyte⁸. These authors consider that the basic characteristic of passivity is a complete inhibition of the normal corrosion process by the presence between the iron and the electrolyte of a surface layer, able to conduct electrons, which now determines the electrochemical behaviour of the metal. It differs, in principle, from the retardation of corrosion by inhibitors, where we consider the slowing down of one or several of a number of coupled reactions which constitute the normal dissolution process.

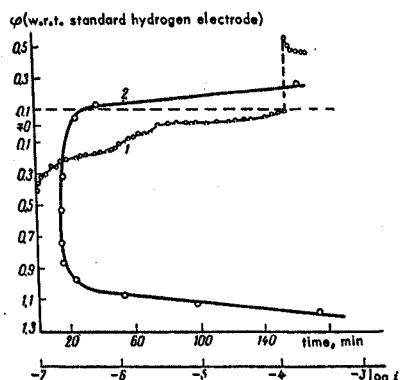


Fig. 2. 1) Potential change during self-activation of a chromium electrode in $N H_2SO_4$ at 50° ; 2) variation of the steady dissolution rate of chromium with potential under the same conditions.

On the basis of these considerations Bonhoeffer and his collaborators concluded that the cathodic current flowing during activation is consumed by the reduction of the oxide layer, whose thickness should correspond to the quantity of electricity required for activation⁸. Attempts were also made to clarify the nature of the "flade potential"^{5,9,10}, which was treated as a thermodynamic quantity corresponding to the formation of the passivating oxide on the iron surface. Such attempts, however, were unsuccessful.

Recent investigations in our laboratory have shown that the electrochemical behaviour of chromium, nickel and steel electrodes during anodic passivation in acid solutions of electrolytes is very similar to that of iron¹¹⁻¹³. The similarity lies mainly in the behaviour of the metallic surface over a wide range of polarisations corresponding to the passive state: the surface condition does not remain unchanged, but varies with the potential in a regular manner. From the results of this investigation we concluded, however, that the passivation of nickel, chromium, and stainless steel proceeds without the formation of an actual surface oxide: it results from the kinetic retardation of the anodic reaction following the change, with potential and with time, in the state of the electrode surface due to interaction with the oxygen of the water and the anions of the electrolyte, adsorbed on the surface. A definite condition of the metallic surface, characterised by a fixed overpotential for the anodic reaction, corresponds to each value of the potential lying in the passivation region. If the surface is maintained in a given condition its speed of dissolution will vary with potential according to the usual Tafel straight line, just as in the case of an active, unpassivated surface.

We can thus conclude from these ideas and experimental results that the activation potential has no thermodynamic significance, and has an exclusively kinetic origin. To make the conclusion more convincing we shall examine in detail the behaviour of the electrode potential during the activation of a metallic surface. We must, of course, first consider the way in which the steady rate of dissolution varies with the potential. For a steel electrode in an acid solution the dependence may be expressed schematically by the curve $abcdefgh$ ¹² shown in Fig. 1*. In the first stage of passivation (section bc of the curve) the steady rate decreases exponentially as the potential becomes more positive. It is easy to see that this dependence, uncommon with anodic reactions, excludes the possibility of a self-sustained steady-state potential in this region of polarisations**. Thus if we consider that the rate of the cathodic reaction, which compensates for the transfer of metal into the solution in the form of ions during spontaneous dissolution, changes with potential according to an analogous law, we can easily see that the potential can assume a steady value only in the region of polarisations in which the steady rate of dissolution increases with the potential. As the Figure shows, this condition is satisfied only over the polarisation regions corresponding to the active state (section ab), to the re-passivation region (section fh), and to the narrow range of potentials labelled cd . The polarisation region in which the steady rate decreases with increasing potential (section bc) will be called the instability region

* Point f has been omitted in Fig. 1. It is given by the transition between the two linear portions of section eh .

** In the absence of redox side reactions able to maintain an exchange current larger than the steady rate of dissolution of the metal in the region of polarisation under discussion.

because it corresponds to the least stable potential of the corroding metal. As will be shown below, the presence of this region determines to a large extent the behaviour of the potential during self-activation of the metal.

Taking these results into consideration, we shall examine the behaviour of the potential of a passive electrode subsequent to the interruption of the anodic current.

According to our results for chromium electrodes, metal ions of different degrees of oxidation are formed on the metal surface, in relative amounts satisfying¹³ the oxidation-reduction equilibrium



throughout the time of polarisation of the metal in or near the re-passivation region (e.g. at potential φ_1). An exchange current $i_0 = \vec{i}_{ox} = \overleftarrow{i}_R$ will arise as a result of the oxidation-reduction process. In general this current must be included in the charge balance which gives rise to a potential stable with time

$$i_x = i_M + (i_{ox} - \overleftarrow{i}_R) \quad (2)$$

where i_x is the outer anodic current and i_M is the rate of dissolution of the metal in equivalent current units.

It is obvious that under stationary conditions, when $\vec{i}_{ox} = \overleftarrow{i}_R$, $i_M = i_x$. We shall further assume that the limiting reduction current of the oxidising component (shown dotted in Fig. 1) $\vec{i}_{ox}^{lim} < i_M$, and, consequently, that the potential of the polarised electrode is in every case determined by the kinetics of the dissolution reaction.

When the anodic current is switched off ($i_x = 0$) the balance of the charges entering and leaving the electrode is destroyed; this must lead to a shift of the potential towards more negative values and to the displacement of equilibrium (1) towards the right. We shall make the further assumption that this displacement results in the speed of reduction of the oxidising constituent reaching its limiting value $\vec{i}_{ox}^{lim}$ (indicated as τ_{ox}^{lim} in Fig. 1), whilst the speed of oxidation of the reducing constituent is decreased to $\overleftarrow{i}_R^1$.

If our views on the activation mechanism of passivation are accepted, and the slowness of corresponding processes is allowed for, it follows that a decrease in i_M , along curve AC, must also follow the interruption of the anodic current. It is obvious that the potential shift will persist until equality (3) is satisfied (point B):

$$i_M = \vec{i}_{ox}^{lim} - \overleftarrow{i}_R^1 \quad (3)$$

Under conditions such that it is possible to ignore $\overleftarrow{i}_R^1$ we can write

$$i_M = \vec{i}_{ox}^{lim} \quad (4)$$

The disturbance of this equality by the increased speed of dissolution, consequent upon the activation of the surface ($i_M \rightarrow i_{st}$)*, or by the decreased $\vec{i}_{ox}^{lim}$, consequent upon the loss of oxidising constituent from the solution, will be offset by the concomitant shift of the potential towards more

negative values. If the concentration of the oxidising constituent is kept constant the potential will change at a rate solely determined by the rate of activation of the surface. The activation of the surface and the potential change will be faster the larger the difference between $\vec{i}_{ox}^{lim}$ and i_{st} .

When the potential φ_4 is reached (point E) the steady dissolution rate becomes equal to the rate of reduction of the oxidising constituent. Further displacement of the potential may only be brought about by decreasing $\vec{i}_{ox}^{lim}$. We can readily see, however, that such a displacement of the potential must unavoidably lead, in this case, to a decrease in the quantity i_{st} as required by section cd of the polarisation curve. It follows that potential changes in this region should be the slowest, and may be mistaken for arrests in the potential-time curve.

This slow change may continue only until the potential reaches a value corresponding to point C**. At still more negative potentials the value of i_{st} will once again be greater than $\vec{i}_{ox}^{lim}$.

In so far as the further increase in the difference between these values must be very rapid, the subsequent change in potential must take place at an increasingly fast rate and activation will come about, as it were, autocatalytically***.

As can be seen in Fig. 2, we have observed a potential behaviour of the above kind during the self-activation of a chromium electrode in $N H_2SO_4$ at 50° ****. As was to be expected, the onset of the fast change in potential almost exactly coincided with the lower limit of the instability region.

The results of this experiment also conclusively demonstrate that the activation potential does not coincide with the passivation potential. In the system studied the difference amounts to nearly 0.3 V.

The maximum quantity of oxidising agent which suffers reduction at the self-activating chromium electrode may be evaluated for this system. We shall assume that the capacity of the electrical double layer of the passivated chromium electrode has the normal value of $20 \mu F cm^{-2}$. We must then impart to the electrode a charge of $20 \times 10^{-6} C cm^{-2}$ for a potential shift of about 1 V, such as accompanies the passage from the passive to the active state. As was shown above, changes in the electrical surface charge may only take place, in the absence of external polarisation, via dissolution of the passivated metal, whose rate cannot exceed

* Obviously, any fluctuation in the value of $\vec{i}_{ox}^{lim}$ due to changes in diffusion conditions, will lower the rate of decrease of the potential.

** The so-called arrests in published φ -time curves never correspond to an absolutely constant potential. The potential continuously, though slowly, changes towards more negative values^{8,10}. In some cases¹⁶ appreciable fluctuations of the potential with time are observed, probably owing to time-dependent changes in the diffusion conditions of the oxidising constituent.

*** No activation of the electrode will be observed if the background concentration of oxidant in the solution is sufficient for the velocity of its reduction to exceed the velocity of dissolution of the metal at the potential of point C.

**** The experiments were carried out by V. M. Knyazheva.

* i_{st} refers to the rate of steady dissolution of the metal at a given potential, determined by the potentiostatic curve *abcdefgh*; i_{st}^1 refers to the rate of steady dissolution corresponding to the (constant current) section *ef* of the same curve (Fig. 1).

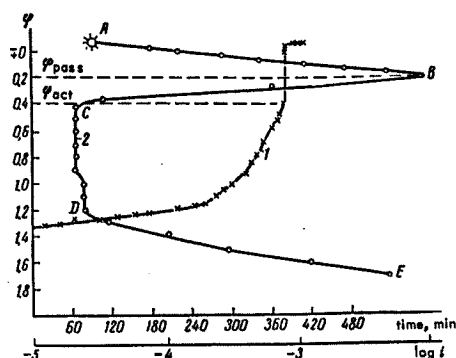


Fig. 3. 1) Potential change during the self-activation of a nickel electrode in $N H_2SO_4$; 2) variation of the steady dissolution rate of nickel with potential under the same conditions.

the stationary value (i_{st}) determined by the potentiostatic curve. According to our results this value, for chromium in $N H_2SO_4$, is equivalent to a current density of approximately $2 \times 10^{-7} A cm^{-2}$.

In the absence of oxidising agents the time required for the self-activation of the electrode, given by the expression $2 \times 10^{-7} t = 20 \times 10^{-6}$, should be about 1.7 min. In our experiments 2.5 h (9×10^3 sec) were required. Obviously, this is possible only if the actual self-discharge current of the double layer has the value

$$i = i_{st} - \vec{i}_{ox} = \frac{20 \times 10^{-6}}{9 \times 10^3} = 2.2 \times 10^{-9} A cm^{-2}.$$

From this relationship we find that the rate of reduction of the oxidising constituent could not have exceeded an equivalent current density of $1.978 \times 10^{-7} A cm^{-2}$, and the maximum quantity of oxidant which could have been expended in the activation of the electrode under our experimental conditions could not have exceeded 1.9×10^{-8} equivalent (calculated for $1 cm^2$ of electrode surface). In this connection we must note that if $i_{st} < 10^{-9} A cm^{-2}$ even a background concentration of oxidant in the initial solution as low (according to Vetter⁹) as $10^{-9} N$ can profoundly influence the rate of potential decay during self-activation of the electrode.

When the behaviour of the potential during activation is observed in solutions of varying pH it is essential to bear in mind that the variation with potential of the steady rate of dissolution changes considerably if the pH is changed. Thus, in the case of chromium¹¹ the change from acid to neutral solutions caused the complete disappearance of the instability region. According to our model the change in potential during activation should show no discontinuity in this case.

To explain the slower rates of potential decay in neutral and alkaline solutions we must note that increases in pH are accompanied by a significant decrease in i_{st} . Thus, for example, Weil and Bonhoeffer's data⁸ for the iron electrode give an almost 35-fold decrease in i_{st} (from 7×10^{-6} to $2 \times 10^{-7} A cm^{-2}$) for a change from pH = 0 to pH = 6. According to Bonhoeffer⁹ the steady dissolution rate can reach even lower values ($\sim 1 \times 10^{-9} A cm^{-2}$) in alkaline solutions. Such a decrease in i_{st} may well be the fundamental cause of the increased duration of the potential

drop, mentioned above, which is observed on changing from acid to neutral and alkaline solutions. It is therefore unnecessary to assume an increased supply of oxidising constituent or an increased thickness of the passivating film with increase in pH.

It is obviously essential, when studying the kinetics of the potential decay in solutions of varying pH, to consider also the diffusion characteristics of the oxidising constituent. In the case of acid solutions, in which the corrosion products of iron, chromium, and stainless steel are easily soluble, the oxidising constituent of the dissolution products is distributed throughout the solution, and its reduction rate may be determined by diffusion. In alkaline or neutral solutions the solubility of the corrosion products is not large, and they can settle on the surface of the metal. The supply of oxidant may thus be concentrated in the sludge, and this may facilitate the access of the compound to the surface of the electrode*.

Making use of the same model we shall examine the phenomena which must accompany the potentiostatic activation of an electrode. It is easy to see that if we pass quickly from ϕ_1 to ϕ_3 the rate of dissolution of the metal must decrease to a value corresponding to point C. Since in this case $i_M \ll \vec{i}_{ox}^{lim}$ the electrode must be polarised by a cathodic current $\vec{i}_x$, compensating for the difference between the rates of the anodic and the cathodic reactions, in order to keep the potential at just that value:

$$\vec{i}_x = \vec{i}_{ox}^{lim} - i_M. \quad (5)$$

After some time the metallic surface must become depassivated since it will strive to assume the stable condition for the given potential; this will make i_M grow to its limiting value i_{st} (point D) and will change the value and the sign of the polarising current. This conclusion is in full agreement with Weil and Bonhoeffer's observations on the potentiostatic activation of the iron electrode⁸.

An essentially different behaviour of the potential should be observed if the limiting rate of reduction of the oxidising constituent exceeds the steady rate of dissolution of the metal in a polarisation region where the latter rate remains constant. This state of affairs can obviously obtain after prolonged polarisation of the metal in the re-passivation, or in the oxygen-overpotential, region, and also in solutions of oxidising acids. In the first two cases the metal surface may be the site, respectively, of the accumulation of a significant concentration of ions in a higher oxidation state or of oxygen accumulation.

Suppose, for example, that prolonged polarisation of the electrode at potential ϕ_3 gives rise to a surface concentration of oxidant sufficient to attain its limiting reduction rate $\vec{i}_{ox}^{lim}$. Interrupting the anodic current must lead directly, in this case, to a negative shift in potential to somewhere near ϕ_6 (point F) where conditions satisfying Eqn. (3) will obtain. However, the dissolution rate in Eqn. (3) appropriate to this case has a steady value corresponding to the initial re-passivation region. Under these conditions the potential

* It is essential, however, to bear in mind that the formation of this sludge, just like the formation of the loose crystalline deposit of iron sulphate on an iron surface during the first stage of passivation in sulphuric acid, is only a concomitant phenomenon and is not responsible for the passivation of the surface¹⁷.

cannot undergo the further negative shift connected with the activation of the surface. As long as these conditions obtain potential changes can only be induced by a decreased rate of reduction of the oxidant due to a decreased concentration of oxidant in the layer of solution adjacent to the electrode, or by a superimposed cathodic polarisation.

We have realized* this particular condition whilst activating a nickel electrode. The variation of the steady dissolution rate with potential in $N H_2SO_4$ for this electrode is given by curve 2 of Fig. 3. It can be seen that i_{st} is approximately $3 \times 10^{-5} A cm^{-2}$. Hence the self-activation of passivated nickel in pure acid solution can take place so fast as to make the measurement of the kinetics of the corresponding potential change impossible by ordinary techniques. However, in the presence of a significant concentration of foreign oxidant (Ce^{4+}) the activation of the electrode after switching off the anodic current is no longer fast: the electrode potential in this case assumes a stable value near 1.33 V.

As the concentration of the oxidant is decreased (for instance, by partial reduction at an auxiliary platinum electrode) the nickel potential moves towards more negative values, fairly slowly at first but more rapidly afterwards (curve 1, Fig. 3). It is important to note that in this case, too, the onset of the sudden change in potential coincides exactly with the lower limit of the instability region.

Inspection of Fig. 1 also shows that when $i_{st} \ll i_{OX}^{lim}$ a superimposed cathodic polarisation can activate the metal only if the potential of the latter is shifted to a value somewhat more negative than φ_r , such that i_{st} exceeds i_{OX}^{lim} . Obviously, discontinuing the imposed polarisation at this potential will not arrest the further activation of the electrode which can now proceed spontaneously. By the same token, the interruption of the cathodic current at potentials more positive than φ_r must be followed by a shift of the stationary potential towards its initial value.

The results of the analysis presented, and our experimental data, conclusively show that the behaviour of the electrode potential during the passage of a metallic surface from the passive to the active condition can be fully explained on the basis of kinetic considerations and of a proper description of the variation with potential of the steady rate of dissolution of the passivated metal.

As has already been shown for the steel electrode¹² this variation can in turn be understood by considering the effect of two stages of passivation or adsorption-chemical interaction of the constituents of the solution, and in particular, the effect of the interaction between the oxygen of the water and the metallic surface. We can postulate that in the first stage of passivation oxygen adsorption takes place at the most active centres of the metallic surface, leading to a very considerable retardation of the anodic reaction and giving rise to the appearance of the "instability region".

SUMMARY

The behaviour of the electrode potential of a metal in an electrolyte solution during changes in the surface condition from the passive to the active state is examined. The rate

of the observed potential shift towards more negative values is completely determined by the magnitude of the self-discharge current arising from the difference between the velocities of dissolution of the passivated metal and of reduction of the oxidising constituent of the system. In the absence of foreign oxidants any products of metal dissolution finding their way into the solution as ions in their higher valency states can fulfil the function of oxidising constituents.

It has been shown that if the previously established potential dependence of the dissolution rate of the passive metal is taken into consideration the time-arrests observed in the potential decay curves, at potentials not far from the activation potential, are of a purely kinetic nature and have no thermodynamic significance (in contrast to the assumption of the German workers for the case of iron). For chromium and nickel in sulphuric-acid solutions it has also been shown that the activation potentials are appreciably more positive than the passivation potentials.

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* The experiments were carried out by N. Ya. Bune.