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ELECTROCHEMICAL POLARIZATION STUDIES ON THE NATURE  
AND BREAKDOWN OF THE PASSIVE FILMS  
ON IRON AND STAINLESS STEEL

Intermittent galvanostatic and quasi-potentiostatic polarization measurements were carried out in  $\text{Na}_2\text{SO}_4$  solutions in the absence and presence of  $\text{Cl}^-$  ions and  $\text{H}_2\text{S}$  using iron and stainless steel electrodes. With consideration to the Fe- $\text{H}_2\text{O}$  binary and Fe-S- $\text{H}_2\text{O}$  ternary systems, and also the effects of pH and polarizing current density on the shape of the potential vs. time diagrams, conclusions were drawn concerning the corrosion products anticipated under the given conditions, and also the stability of the passive films. The differences in character of the passive films on iron and stainless steel are reflected primarily in their degree of protectiveness and their susceptibility to breakdown.

## INTRODUCTION

The purpose of this investigation was to show the differences in character and breakdown processes of passive films on iron and stainless steel.

Investigations have been carried out in aqueous  $\text{Na}_2\text{SO}_4$  solutions in the absence and presence of  $\text{Cl}^-$  ions and  $\text{H}_2\text{S}$  by means of intermittent galvanostatic and quasi-potentiostatic polarization methods.

The method of intermittent galvanostatic polarization was used first by Nagel, Ohse and Lange [1, 2] for the study of various metal-water binary systems. Theoretical aspects of the method have been discussed in detail by Lange and Göhr [3]. The method of intermittent galvanostatic polarization has also been used by Horváth, Hackl and Rauscher [4-6] for the study of metal-sulphur-water ter-

nary systems and of the effect of certain corrosion inhibitors on the anodic and cathodic processes.

By recording subsequent charging curves during periodic interruption of the polarizing current, potential vs. time diagrams can be obtained which in the period of current interruptions indicate more or less sharp "steady-state" arrests, comparable to the equilibrium potentials of the various electrode reactions, calculated on the basis of thermodynamic data. Further, from the differences between the "steady-state" potential and the polarization potential, and from the changes of these potentials with time, conclusions can be drawn on the establishment, protectiveness, maintenance or breakdown of the passivating film.

#### EXPERIMENTAL

Cylindrical electrodes were made of high-purity iron (Johnson-Matthey Ltd.) and of stainless steel prepared from alloying components of spectroscopic purity (composition: Cr 15, Ni 13, Mo 2). The stainless steel electrodes were abraded with silicon-carbide paper to a 600-grit finish, degreased with acetone, then pickled in 15%  $\text{HNO}_3$  and 5% HF solution at 353 K for 5 min, washed with a jet stream of tap water and rinsed in distilled water. The iron specimens were electropolished after mechanical polishing [7].

The stock solution was  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ , the pH of which was adjusted to the required value by addition of  $\text{H}_2\text{SO}_4$  or NaOH. Deaeration of the solutions was accomplished by bubbling purified  $\text{N}_2$  gas through the solutions. Saturation with  $\text{H}_2\text{S}$  was made by bubbling  $\text{H}_2\text{S}$  gas through the solutions, previously deaerated with nitrogen. In the experiments where the effect of NaCl and  $\text{H}_2\text{S}$  is examined, specimens were passivated in the  $\text{Na}_2\text{SO}_4$  solution and then the solution was replaced by the solution containing these substances from a container through a three way stopcock connected to the cell.

Experimental technique, cell and block scheme for intermittent galvanostatic polarization have been described in a previous paper [4].

All electrode potentials  $E_h$  given in the figures are referred to the normal hydrogen electrode.

## RESULTS AND DISCUSSION

For iron in strongly acidic solutions (pH 3) with the applied anodic polarizing current densities (maximum  $100 \text{ mA cm}^{-2}$ ) the potential arrest obtained in the period of current interruption did not even reach the value corresponding to the  $\text{Fe}/\text{Fe}_3\text{O}_4$  equilibrium, no passivation was observed (Fig. 1).

Experimental results indicate that the conditions are more favourable for the formation of iron oxides when either the polarizing current density or the pH of the solution is increased. In the potential vs. time diagram obtained with a  $1 \text{ mA cm}^{-2}$  polarizing current density at pH 4.5 (Fig. 2) the potential arrest suggests the possibility of the formation of a surface  $\text{Fe}_3\text{O}_4$  layer, which, however, provides no effective barrier against anodic dissolution. At pH 6.5, using a  $10 \text{ mA cm}^{-2}$  polarizing current (Fig. 3) passivation of iron can be observed. The progress of anodic passivation of iron is indicated in the potential vs. time diagram by a gradually increasing difference between the "steady-state" potential and the polarization potential. The electrode potential in the periods of current interruptions passing through the range corresponding to the  $\text{Fe}/\text{Fe}_3\text{O}_4$  equilibrium, shifts up to the

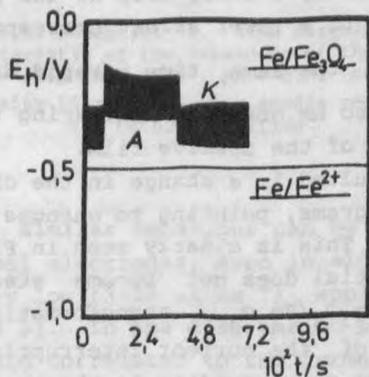


Fig. 1. Potential vs. time diagram for iron in  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  solution. pH = 1.3, current density  $1 \text{ mA cm}^{-2}$ . (The upper A and lower K line series were obtained by anodic and cathodic polarization, respectively)

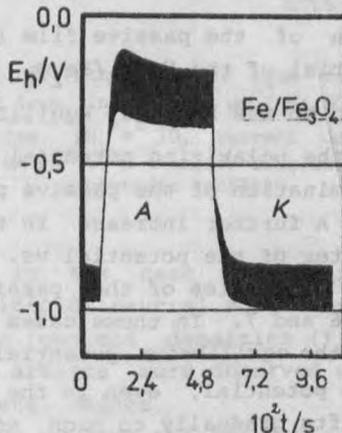
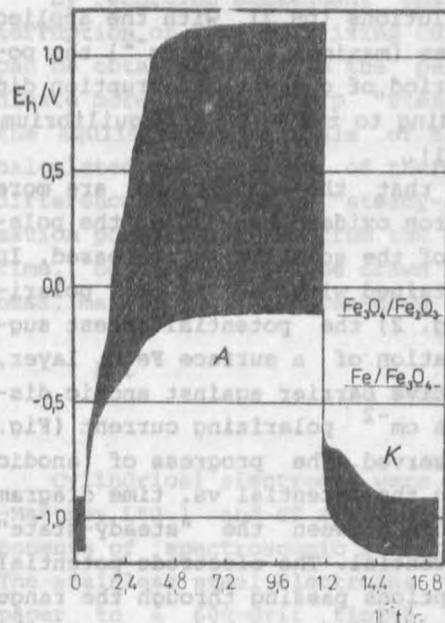


Fig. 2. Potential vs. time diagram with an anodic (A) and a cathodic (K) section for iron in  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  solution. pH = 4.5, current density  $1 \text{ mA cm}^{-2}$



equilibrium potential of the  $Fe_3O_4/Fe_2O_3$  transformation and in the passive state it drops at most to this level. The shape of this diagram is characteristic of the passivation behaviour of iron in  $Na_2SO_4$  solutions at pH values between 4 and 10. However, the passivation of iron in this pH range was not easily reproducible, spontaneous breakdown of the passive film occurred after various time intervals (Fig 4). The break-

Fig. 3. Potential vs. time diagram with an anodic (A) and a cathodic (K) section for iron in  $0.25 \text{ mol dm}^{-3} Na_2SO_4$  solution.  $pH = 6.5$ , current density  $10 \text{ mA cm}^{-2}$

down of the passive film is indicated by a sharp drop of the potential of the  $Fe_3O_4/Fe_2O_3$  formation to a lower arrest corresponding to the  $Fe/Fe_3O_4$  equilibrium. At the same time a rapid drop of the polarizing potential could also be observed indicating the elimination of the passive properties of the passive film.

A further increase in the pH resulted in a change in the character of the potential vs. time diagrams, pointing to changes in the properties of the passive film. This is clearly seen in Figs 5, 6 and 7. In these cases the potential does not become steady at the equilibrium potential of the  $Fe_3O_4/Fe_2O_3$  transformation, the potential, even in the periods of the current interruptions shifts gradually to high noble value corresponding to the transpassive region. More detailed analysis of these diagrams reveals further differences. At high pH values if the electrode is polarized with higher current density, the potential arrest corresponding to the formation of  $Fe_2O_3$  becomes indistinct, or does not appear at all.

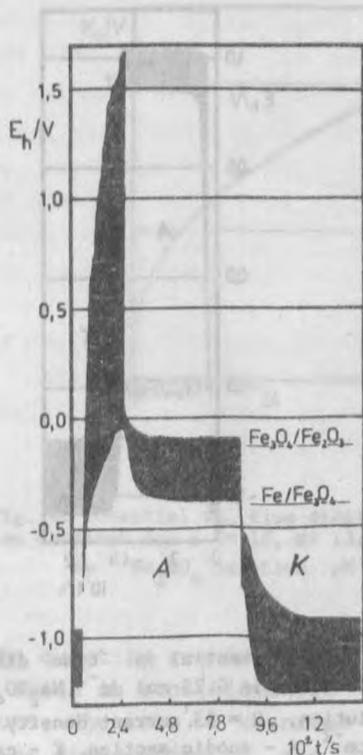


Fig. 4. Potential vs. time diagram characteristic of the breakdown of the passive film on iron. pH = 6.5, current density  $16 \text{ mA cm}^{-2}$ . A - anodic section, K - cathodic section

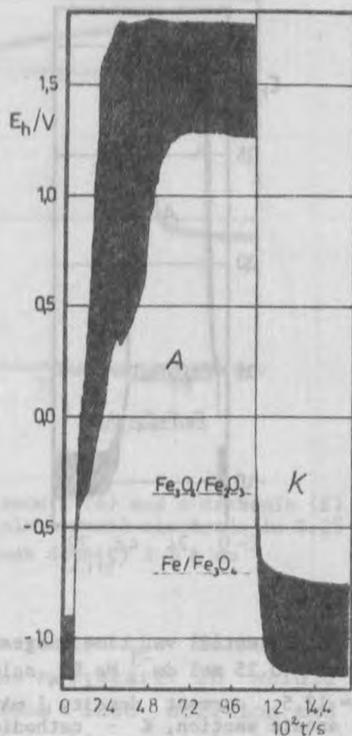


Fig. 5. Potential vs. time diagram for iron in  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  solution. pH = 10, current density  $10 \text{ mA cm}^{-2}$ . A - anodic section, K - cathodic section

Similar behaviour can be observed in the case of stainless steel electrodes, even in slightly acidic or neutral solutions, at very low ( $3\text{--}30 \mu\text{A cm}^{-2}$ ) applied anodic current densities (Figs 8 and 9). In the diagrams no potential arrests were observed which could be correlated to the formation of metal oxides.

It is to be noted, that in the case of iron the changes in the character of the diagrams, consequently the changes in the properties of the layer with the pH of the solution are continuous.

The electrochemical behaviour of iron and stainless steel during anodic polarization depends on several parameters, e.g. on the rate by which the metal ions leave the metal lattice to enter

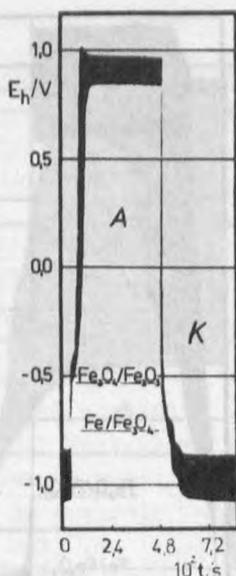


Fig. 6. Potential vs. time diagram for iron in  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  solution.  $\text{pH} = 12.5$ , current density  $1 \text{ mA cm}^{-2}$ . A - anodic section, K - cathodic section

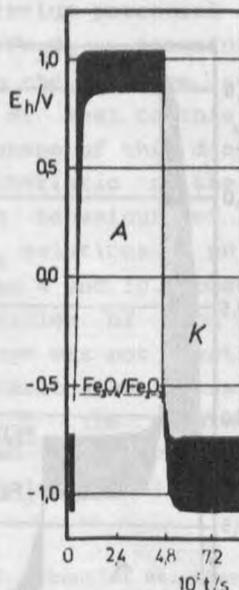


Fig. 7. Potential vs. time diagram for iron in  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  solution.  $\text{pH} = 13$ , current density  $3 \text{ mA cm}^{-2}$ . A - anodic section, K - cathodic section

the solution, the rate of oxygen chemisorption, the relation of the strengths of metal-metal bond and metal-oxygen chemisorption bond. Consequently, the processes leading to anodic dissolution or to passivation of the metal, are rather complicated. Thus, it is suggested a somewhat simplified picture to explain the observed phenomena.

During anodic polarization, on shifting the electrode potential towards more noble values, the quantity of adsorbed oxygen ( $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{OH}$ ) on the metal surface increases, as also does the strength of chemisorptional interaction. At the same time, metal ions leave the metal lattice at a rate depending on the nature and quality of the metal, the hydration energy of the metal ions, the electrode potential and the pH. When, at a definite value of the electrode potential, the quantity of the chemisorbed oxygen in the surface metal-oxygen chemisorption complex becomes nearly equal

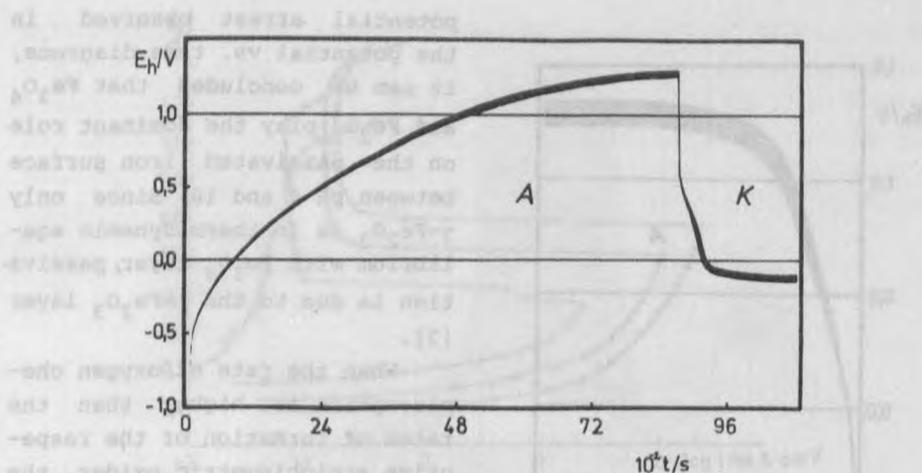
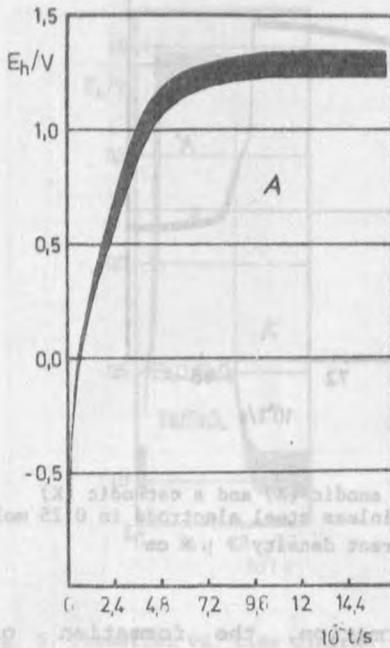


Fig. 8. Potential vs. time diagram with an anodic (A) and a cathodic (K) section obtained for a Cr 15, Ni 13, Mo 2 stainless steel electrode in 0.25 mol  $\text{dm}^{-3}$   $\text{Na}_2\text{SO}_4$  solution. pH = 6.5, current density  $3 \mu\text{A cm}^{-2}$

to the quantity required for  $\text{Fe}_3\text{O}_4$  formation, the formation of this oxide in stoichiometric proportions may start. In acidic solutions, the rate of transfer of  $\text{Fe}^{2+}$  ions into solution and the rate of dissolution of the lower valency oxide are relatively high, and thus a further increase in the ratio of oxygen is not possible. Increase of the pH of the solution results in a decrease of the dissolution of the oxide, and also makes the conditions more favourable for the chemisorption of oxygen from  $\text{OH}^-$  ions. This promotes the formation of  $\text{Fe}_2\text{O}_3$ . However, if several factors affecting changes in the structure and solubility of the oxide layer and in the surface concentration of  $\text{Fe}^{2+}$  ions and thus favour the formation of  $\text{Fe}_3\text{O}_4$ , or if the epitaxy of the oxide layer is not perfect, local breakdown of the passive film occurs. From this respect it has to be taken into consideration the physical state of the metal surface, the rate of thickening of the oxide layer, the decrease of pH at the solid/electrolyte interface, the autoreductive oxide dissolution taking place in the presence of  $\text{Fe}^{2+}$  ions [8-10].

These considerations suggest that the passivation and depassivation phenomena in the case of iron can be attributed to various factors having opposite effects. With consideration to the



potential arrest observed in the potential vs. time diagrams, it can be concluded that  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  play the dominant role on the passivated iron surface between pH 4 and 10. Since only  $\gamma\text{-Fe}_2\text{O}_3$  is in thermodynamic equilibrium with  $\text{Fe}_3\text{O}_4$  layer, passivation is due to the  $\gamma\text{-Fe}_2\text{O}_3$  layer [3].

When the rate of oxygen chemisorption is higher than the rates of formation of the respective stoichiometric oxides, the

Fig. 9. Potential vs. time diagram with an anodic (A) section obtained, for Cr 15, Ni 13, Mo 2 stainless steel electrode in  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  solution. pH = 6.5, current density  $30 \mu\text{A cm}^{-2}$

enrichment of the surface complex in oxygen is continuous and the oxidation state of the metal gradually increases. This is reflected by the gradual shift of the electrode potential to high noble values in the period of current interruptions. The hypothesis according to which iron can be present in higher oxidation states is supposed by the experimental results of Nagayama and Cohen [9].

In the case of stainless steel the presence of alloying elements considerably retards the metal ions from leading the metal lattice. Thus, oxides of definite stoichiometric composition do not form in the course of anodic passivation. It is assumed that the electrochemical behaviour observed in the case of stainless steel can be explained by the formation of chemisorption film, in agreement with the hypothesis of Uhlig [11], Kolotyrkin [12] and other authors.

The above considerations are in agreement with the results of potentiostatic polarization (Fig. 10). Passivation of iron becomes

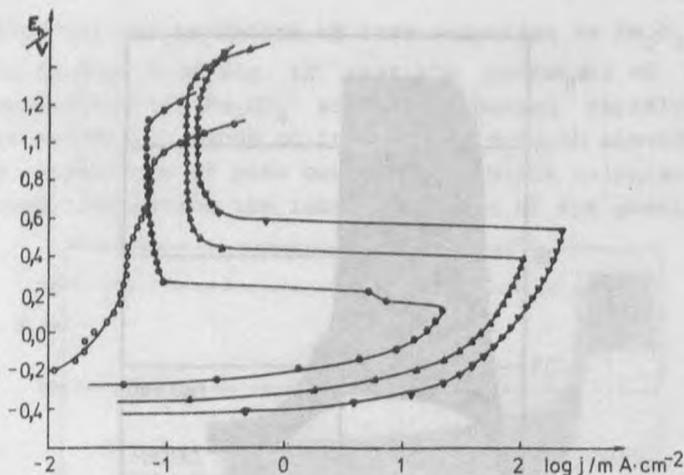


Fig. 10. Potentiostatic polarization curves obtained with an iron electrode in  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  solution. Scanning rate:  $25 \text{ mV/min}$ .

▼ - pH = 1.3, Δ - pH = 4.0, ● - pH = 9.8, ○ - pH = 13.0

easier with increasing pH: the passivation potential shifts towards less noble values and the corresponding critical current density of passivation decreases. There is no active section in

the curve measured in solution of pH 13. Similar behaviour was observed for stainless steel in neutral  $\text{Na}_2\text{SO}_4$  solutions. These are the cases where no potential arrests can be observed in the potential vs. time diagrams.

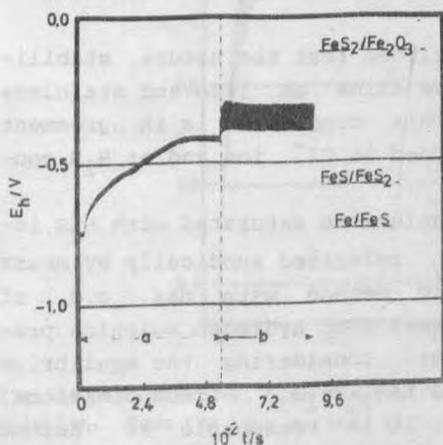


Fig. 11. Potential vs. time diagram obtained by intermittent galvanostatic anodic polarization for iron in  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  solution saturated with  $\text{H}_2\text{S}$ . Polarizing current density: a -  $1 \text{ mA cm}^{-2}$ , b -  $10 \text{ mA cm}^{-2}$ .

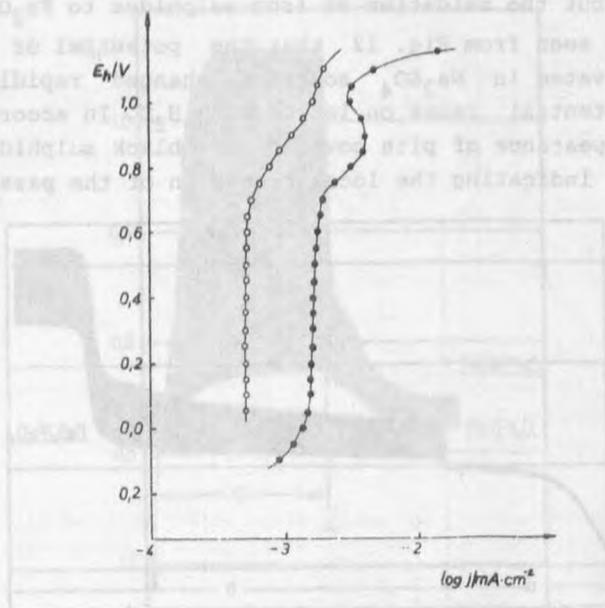


Fig. 15. Potentiostatic polarization curves obtained for stainless steel with 20 mV potential steps in 5 min. O -  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  ● -  $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  saturated with  $\text{H}_2\text{S}$

In contrast to iron, the electrode potential of stainless steel in the  $\text{H}_2\text{S}$  containing solution shifted to the passive potential range when applying a relatively low anodic current density, such as  $75 \mu\text{A cm}^{-2}$  (b range in Fig. 13). The first potential arrest in the diagram is correlated to the formation of sulphides of alloying elements, which increase the overvoltage of anodic process and thus the oxidation of metal sulphides occurs during anodic polarization. A potential arrest corresponding to second potential arrest was also observed when  $\text{H}_2\text{S}$  was introduced into the  $\text{Na}_2\text{SO}_4$  solution in which the stainless steel electrode has been passivated at cd. of  $50 \mu\text{A cm}^{-2}$  (Fig. 14). At this potential the electrode was passive without any indication of localized corrosion. This is also supported by the electrode potential-current curves measured with quasi-potentiostatic polarization method (Fig. 15).

Considering these results and comparing the potential vs. time diagrams obtained in the presence and absence of  $\text{H}_2\text{S}$ , it can

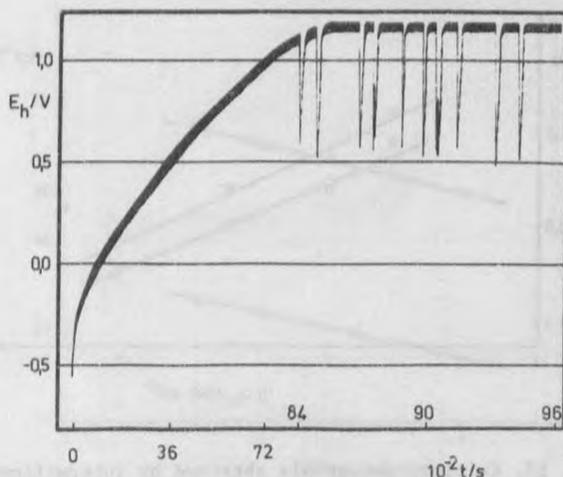


Fig. 16. Potential vs. time diagram obtained by intermittent galvanostatic anodic polarization for stainless steel in  $0.25 \text{ mol dm}^{-3}$  NaCl solution. Polarizing current density:  $3 \mu\text{A cm}^{-2}$

be concluded that the presence of  $\text{H}_2\text{S}$  considerably changes the passivation characteristics of stainless steel, i.e. the composition and structure of the passive film. It is supposed that on the surface of the stainless steel electrode passivated in the presence of  $\text{H}_2\text{S}$ , the oxidation products of metal sulphides are also present. This layer, however, is less protective than that of the chemisorbed film formed primarily in the absence of  $\text{H}_2\text{S}$ .

For iron in NaCl solutions, no passivation took place during anodic polarization with intermittent galvanostatic method. Further, immediate breakdown of passivity was observed for iron previously passivated in  $\text{Na}_2\text{SO}_4$  solution, after the introduction of chloride-containing electrolyte. These phenomena and the potential vs. time diagrams are similar to those observed with  $\text{H}_2\text{S}$ .

On stainless steel - in contrast to iron - periodic breakdown and repair of the passive film occurred during anodic polarization in NaCl solutions. A potential vs. time diagram, characteristic of this behaviour, is shown in Fig. 16. It can be seen, that the electrode potential shifts gradually towards the positive direction - like in  $\text{Na}_2\text{SO}_4$  solutions - when, however, the electrode potential approaches the range, characteristic of the passive state,

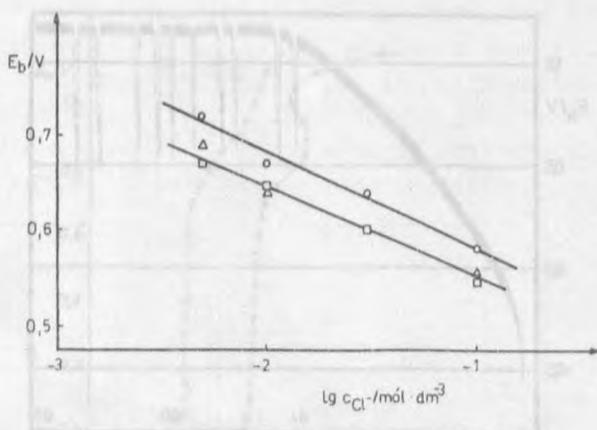


Fig. 17. Critical potentials obtained by intermittent galvanostatic polarization ( $\Delta$ ), galvanostatic polarization without current interruption (O) and quasi-potentiostatic method ( $\square$ ) as a function of  $Cl^-$  concentration

a sharp drop towards the negative direction will follow. This potential drop corresponds to the local breakdown of the passive film. After falling down, the electrode potential rises relatively rapidly again to the previously attained positive value. This phenomenon occurs repeatedly. The mean value of the minima of potential fluctuations provide a new range, which is characteristic of the susceptibility of stainless steel to pitting corrosion.

The critical potential for pitting corrosion was also determined by galvanostatic method without current interruptions and by quasi-potentiostatic polarization with a sweep rate of 20 mV/5 min. The critical potentials obtained by the three different methods as a function of  $Cl^-$  concentration are shown in Fig. 17. It is seen that the minima of potential fluctuations observed by intermittent galvanostatic method and considered as "repassivation potentials" are nearly equal to the "breakdown potentials" measured by quasi-potentiostatic method. It can also be established that tenfold increase in chloride concentration renders the breakdown potential 0.095 V more negative. This shift is in good agreement with the results of Leckie and Uhlig [13] obtained for Cr-Ni stainless steel. (The more positive breakdown potential here are due to the 2% Mo content of the steel).

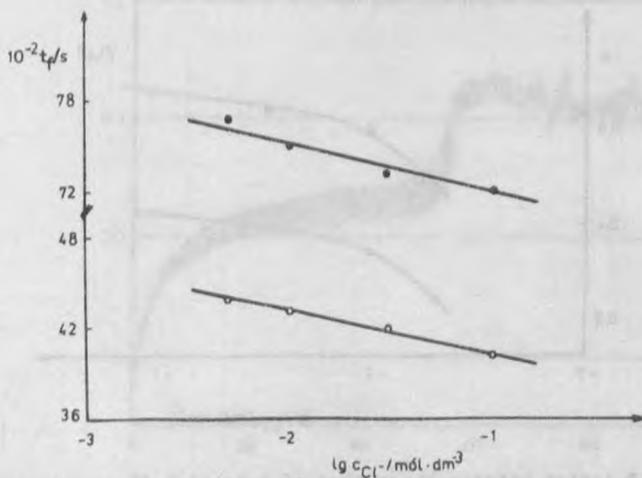


Fig. 18. Relation between the periods of time until the first breakdown and chloride concentration. O - by intermittent galvanostatic polarization  
● - galvanostatic polarization without current interruption

In galvanostatic experiments, without current interruptions, the mean value of the minima of potential fluctuations corresponding to the same chloride concentration is 30 mV more positive.

From the potential vs. time diagrams the period of time from the start of anodic polarization and the frequency of potential fluctuations can also be determined. The period of time measured from the start of anodic polarization till the first breakdown decreases slightly with increasing  $\text{Cl}^-$  concentration. Without current interruptions, however, this period is remarkably shorter (Fig. 18). The number of potential fluctuations per minute increases with increasing chloride concentration (Fig. 19). This increase, nevertheless, has a diminishing tendency and without current interruptions the number of fluctuations is almost twofold.

Experimental results obtained for stainless steel in chloride media can be interpreted on the basis of the chemisorption theory of passivity, considering the competitive adsorption of chloride ions and oxygen originating from  $\text{H}_2\text{O}$  and  $\text{OH}^-$ . Oxygen has normally higher affinity than  $\text{Cl}^-$  for adsorption sites on a stainless steel surface [13]. Since the shape of the initial section of potential vs. time diagrams obtained for  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  so-

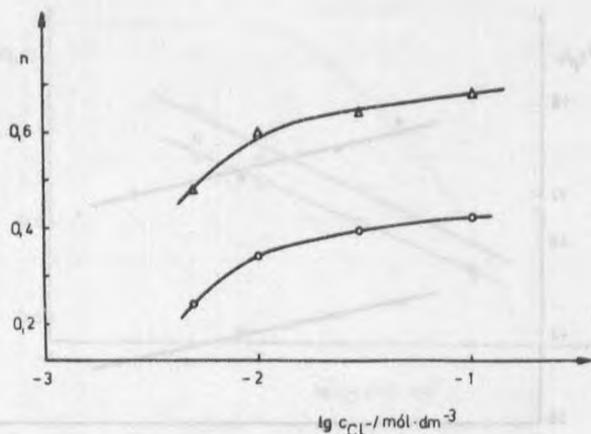


Fig. 19. Relation between the number of potential fluctuations per unit of time and  $\text{Cl}^-$  concentration determined from intermittent galvanostatic (O) and galvanostatic ( $\Delta$ ) potential vs. time diagrams

lutions are quite similar, furthermore the time measured till the first breakdown decreases only slightly with increasing  $\text{Cl}^-$  concentration, it can be concluded that  $\text{Cl}^-$  ions initially do not disturb oxygen chemisorption leading to passivation. Shifting the electrode potential towards more noble values, the amount of adsorbed  $\text{Cl}^-$  ions increases [14] and the metal-chloride chemisorption bond is getting stronger [15]. If these parameters reach critical values at certain weak sites on the surface, pit nucleation and subsequent local breakdown of the passive film may occur. In the course of anodic polarization without current interruption, the electrode potential shifts more rapidly towards the transpassive region, thus the critical chloride concentration and bond strength are reached sooner and the period of time before the first breakdown is remarkably shorter. As a result of the intensive local dissolution of the steel, the electrode potential drops rapidly towards the negative direction with simultaneous desorption of  $\text{Cl}^-$  ions. However, the potential changes only to a definite, nearly constant value depending on the bulk concentration of  $\text{Cl}^-$  ions and the composition of the steel. Then the oxygen chemisorption again becomes prevailing, resulting in passivation. It may be supposed that at this potential a critical chloride/oxygen ratio and a nearly stationary state exist. This

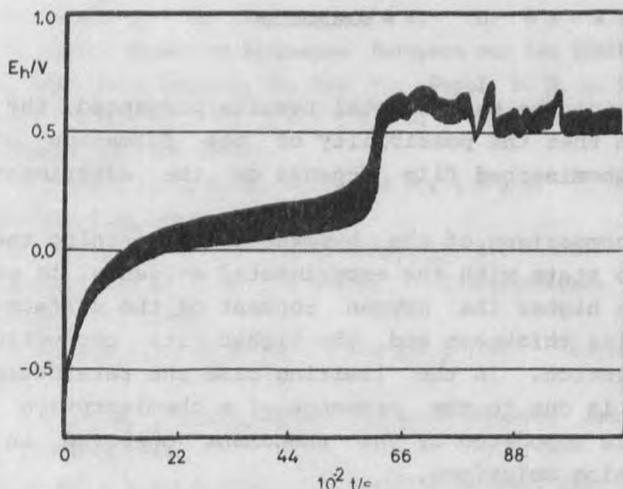


Fig. 20. Potential vs. time diagram for stainless steel in  $0.1 \text{ mol dm}^{-3} \text{ NaCl}$  solution saturated with  $\text{H}_2\text{S}$ . Polarizing current density:  $50 \mu \text{ A cm}^{-2}$

state can be attained using intermittent galvanostatic polarization or quasi-potentiostatic polarization, but can not be attained without current interruption. In the latter case the critical potential is more positive. The changes in the experimentally determined parameters with  $\text{Cl}^-$  concentration can also be explained by the aid of the above assumption based on the competitive adsorption theory.

If  $\text{H}_2\text{S}$  and  $\text{Cl}^-$  ions coexist, all those phenomena, characteristic of these corrosive agents, can be observed with some modifications. Using intermittent galvanostatic method, the potential of stainless steel electrode passes over the potential range characteristic of the formation of metal sulphides. Stable passivity, however, is not possible at higher positive potentials, due to the presence of  $\text{Cl}^-$  ions. Potential fluctuations are less sharp and after a relatively short period of time pits continue to grow without repassivation (Fig. 20).

## CONCLUSION

Considering the experimental results presented, the conclusion can be drawn that the possibility of the formation of a phase oxide or a chemisorbed film depends on the experimental conditions.

From a comparison of the hypothesis concerning the formation of a passive state with the experimental evidence, it can be assumed that the higher the oxygen content of the surface layer, the smaller is its thickness and the higher its protection against metal dissolution. In the limiting case the retardation of metal dissolution is due to the presence of a chemisorption film. This conclusion is supported by the phenomena observed in  $H_2S$  and/or  $Cl^-$  containing solutions.

On introducing  $H_2S$  or chloride into a  $Na_2SO_4$  solution, the passivity of iron previously established in the solution immediately breaks down. For stainless steel, however, corrosion with  $H_2S$  can easily be prevented by anodically polarizing the specimen to the potential range where metal sulphides are oxidized to oxides. In  $NaCl$  solution, stainless steel showed repeated breakdown and repair of the passive film during the intermittent galvanostatic polarization. This is explained as a result of the competitive adsorption of oxygen and  $Cl^-$  ions. When both  $H_2S$  and  $Cl^-$  ions were present, pitting corrosion proceeded without repassivation. The stainless steel surface passivated in the absence of  $H_2S$  are more protective than those contaminated with oxidation products of metal sulphides which may be formed during anodic polarization in the presence of  $H_2S$ .

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BADANIA NATURY ELEKTROCHEMICZNEJ POLARYZACJI  
I PĘKNIĘĆ PASYWNYCH WARSTW NA ŻELAZIE I STALI NIERDZEWNEJ

Zastosowano metodę galwanostatyczną z przerywanym impulsem prądowym i metodę quasi-potencjostatyczną do polaryzacji elektrod żelaznej i stalowej (Cr 15, Ni 13, Mo 2) w wodnych roztworach  $\text{Na}_2\text{SO}_4$  z udziałem i bez udziału jonów  $\text{Cl}^-$  oraz  $\text{H}_2\text{S}$ . Podano dla układów Fe-H<sub>2</sub>O Fe-S-H<sub>2</sub>O wpływ pH i gęstości prądu polaryzacji na przebieg diagramów potencjał-czas. Omówiono otrzymane produkty korozji oraz stabilność warstwy pasywnej. Zróżnicowanie charakteru warstw pasywnych na żelazie i na stali wskazuje na ich własności ochronne i odporność na pękanie.

