NUCLEATION AND GROWTH OF A PASSIVE FILM ON AISI 420 MARTENSITIC STAINLESS STEEL UNDER POTENTIOSTATIC CONDITIONS*

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Abstract

The kinetics of the early stages of passive film formation on AISI 420 stainless steel in mixtures of 0.1M H_2SO_4 and 0.1M Na_2SO_4, with pH-values of 2.42, 2.85 and 3.33, were studied at different anodic potentials. The potentiostatic step method was used as an electrochemical technique in which the anodic current density was measured as a function of time. For analysis of the measured data, the theory of "topochemical reaction" was applied for the characterization of the exponent n in that part where the steepest current decay was observed. Through this theory, which includes the Erofeev equation $\xi = 1 - e^{-kt^n}$ (where $n = \sigma + a$), the number of conversion steps σ could be obtained, as well as the number of directions a in which the nuclei grow. It was found that this theory can be successfully applied to the passivation process of AISI 420 stainless steel.

Introduction

Passivation of chromium steels is of vital importance in the use of stainless steels in potentially aggressive media and this topic has naturally received much attention.[1-4] There is a general agreement in the literature that the excellent corrosion resistance of stainless steels in acidic solutions has its roots in the beneficial role of Cr additions in Fe-based alloys. In order for stainless steels to have this effect, the Cr content in the alloy must be greater than 12 at. %.[1,5,6]

Passivation of stainless steels in sulphuric acid is a widely studied subject in corrosion science. Although numerous studies have been reported on the properties of passive films that form on reactive metal surfaces in contact with oxidizing environments, we possess insufficient fundamental understanding of the mechanisms by which such films grow or break down. The studies have demonstrated that passive films on metals and alloys form as bilayers, consisting of a compact barrier layer, which is composed of a disordered crystalline phase growing into the metal, and an upper layer

which forms as precipitate from cations emerging from the base layer.[7] Alkire[8] described the passivation of Fe in aqueous solutions of H_2SO_4, using the potential step method in the following manner. In the first step, there is rapid metal dissolution under IR-limited constant current conditions, which causes an increase in the metal salt concentration near the corroding surface. Nucleation of an adherent salt film occurs on the surface, which then grows by continued precipitation from the supersaturated electrolyte and also by the continued anodic dissolution of the metal. Formation of the passive oxide layer occurs under the porous salt layer. The region of supersaturated electrolyte becomes dissipated and the salt film thereby attains a maximum thickness. The salt film begins to dissolve, eventually to disappear altogether, leaving only the passive oxide film on the metal surface. A number of authors[9-13] suggested that a primary salt film is a necessary precursor in the passivation of iron in sulphuric acid. In another study, Abakumova and Milyutin[14] suggested that the salt film creates conditions under which subsequent passivation by oxide films can occur.

Much information on the initial process of film growth on iron has been provided by Kruger and Calvert.[15] These authors found that film growth occurs in three stages. The first is controlled by diffusion of OH^- ions to the electrode surface. During the second stage, a number of complex processes occur, which cannot be characterised by any simple rate law. The third stage, i.e. that of steady-state growth, can be equally well described by either a logarithmic or an inverse logarithmic law. On the basis of the data obtained through electrochemical and ellipsometric investigations of passive films formed on iron in borate solutions Szklarska-Smialowska and Kozlowski[16] stated that development of passive films at constant anodic potential occurred in four stages. In his work, Griffin[17] suggested that the three steps might in principle represent elementary steps in the passivation of a pure metal. Namely, step 1 is the formation of a hydrated metal ad-ion, step 2 is the desorption of the ad-ion into the aqueous electrolyte phase, and the step 3 is a two-dimensional phase transition that produces a condensed oxide layer.

The goal of the present work was to examine the effect of pH on the kinetics of the early stages of passive film growth on AISI 420 stainless steel. The electrolytic

media used in this study were mixtures of 0.1 M H_2SO_4 + 0.1 M Na_2SO_4; (pH = 2.42, 2.85 and 3.31). These pH-values were chosen on the basis of previous investigations[18] showing that this steel corrodes more rapidly at pH-values lower than 2.85. Above 2.85, this type of steel has been shown to be more or less corrosion resistant. The potential step method was used as an electrochemical technique in which the anodic current density was measured as a function of time. Experimental data were collected at five passive potentials. For data analysis the theory of "topochemical reaction"[19] was applied for the characterization of the exponent *n* in that part where the steepest current decay was observed. Using this theory, which includes the Erofeev equation, $\xi = 1 - e^{-kt^n}$ (where $n = \sigma + a$), the number of conversion steps σ, as well as the number of directions *a* in which the nuclei grow can be determined. It was shown that the theory can be successfully applied to the passivation process of AISI 420 stainless steel.

Experimental

Cylindrically-shaped specimens were made from a rod of martensitic stainless steel AISI 420 (composition in wt %: C, 0.21, S, 0.031, Si, 0.45, Cr, 13.3, Ni, 0.15, Cu, 0.47). The samples used for electrochemical experiments had a diameter of 16 mm and a thickness of 3 mm. The discs were first wet ground down to 600 grit silicon carbide paper, followed by polishing with 9μ and then with 3μ diamond paste to near mirror quality. The test solutions were mixtures of 0.1 M sulphuric acid (H_2SO_4) and 0.1 M sodium sulphate (Na_2SO_4), with pH-values of 2.42, 2.85 and 3.33, which were determined with a digital mV/pH meter.

For the corrosion study presented here, a Green cell, a potentiogalvanoscan (used as a potentiostat) and a personal computer were used (a diagram of the electrochemical cell was shown in a previous article[20]). The disc, with an exposed surface area of ≈ 1 cm^2 was fixed in a polytetrafluorethylene (PTFE) holder as the working electrode (WE) and the counter electrode was made of platinum. A saturated calomel electrode (SCE) was chosen as the reference electrode. Initially, the surface oxide layer was removed by applying four minutes of negative potential to the sample. After that WE was kept at open-circuit potential (OCP) to obtain a reproducible initial state. The potential step

measurements were performed in the region from OCP to suitable passive potentials. The experiments were made at a temperature of 30.0 ± 0.1 °C without deaeration of the electrolyte.

Theory

Under the heading of "topochemical reactions"[19] numerous processes can be included. The processes should include at least one solid substance among the reactants as well as among the products. First there are a large number of reactions of decomposition of solids; second, there are reactions between a solid and a gas, or alternatively, a liquid could be involved instead of a gas. All these reactions have one characteristic feature in common, i.e. the process proceeds at the interface between two solid phases, the reactant and the product.

For topochemical reactions the usual definition of the reaction rate is not suitable since the process takes place neither in the volume nor in the bulk of the substances but at the interface between the phases. It is for this reason that the reaction rate is defined as the change of the degree of conversion ξ over time t. Thus the reaction rate is given by $\dfrac{d\xi}{dt}$, where $\xi = (N_0 - N)/N_0$ if N_0 is the initial amount of reactant and N an instantaneous amount of the reactant.

There are no generally adopted theories of topochemical reactions and, accordingly, there are no topokinetic equations suitable for description of all the steps of a decomposition reaction. Therefore, we shall confine ourselves to the most reliable and most widely accepted concepts, the formation and growth of "reaction nuclei"- nuclei of the solid product.[19] Thus the kinetics of reaction depend primarily on the law of nucleation and on the law of growth of the nuclei. By using the law of nucleation at an increasing rate and the assumption that for the conversion of any one of the n_0 nuclei into an actively growing nucleus there are required σ consecutive steps with the rate constants $k_1, k_2...k_\sigma$, Erofeev derived the equation:

$$\xi = 1 - \exp\left(-\frac{8\pi n_0 k_1 k_2 ... k_\sigma}{(\sigma+3)!} k_g^3 t^{(\sigma+3)} \right)$$

or,

$$\xi = 1 - e^{-kt^n} \,.$$ (1)

The exponent $n = \sigma + 3$ and σ has the meaning of the elementary step in the transformation of a nucleus to an actively growing nucleus. In a more complete treatment $n = \sigma + a$, where σ is the number of steps and a depends on the number of directions in which the nuclei grow.

Results and discussion

To characterize the behaviour of an AISI 420 electrode in mixtures of 0.1M H_2SO_4 and 0.1M Na_2SO_4, with pH-values of 2.42, 2.85 and 3.33, the anodic current density was recorded as a function of time at various passive potentials of –0.1, 0.0, 0.1, 0.2, 0.3 V_{SCE}. Figure 1 shows the time dependence of current density at –0.1 V_{SCE}.
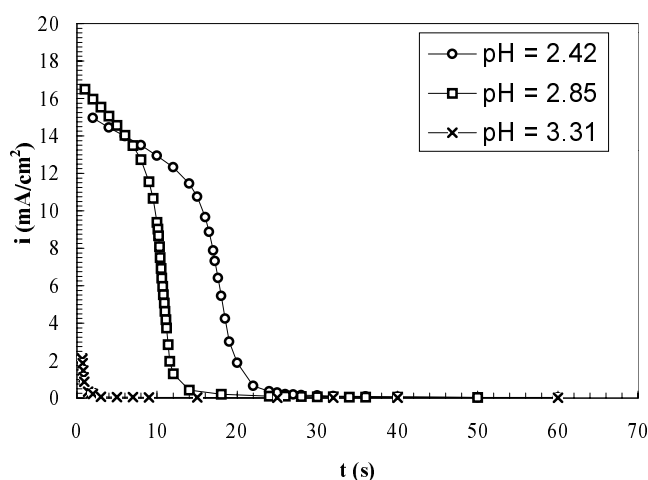

Figure 1: Current density as a function of time under potentiostatic control at
E= - 0.1 V_{SCE} for AISI 420 stainless steel in mixtures of 0.1 M H_2SO_4 + 0.1 M Na_2SO_4; pH = 2.42, 2.85, 3.31.

The curves in Fig. 1 display much higher values of the initial current density i_{init} (t = 0), at pH = 2.42 and at pH = 2.85 than at pH = 3.31 and a different decrease of current density to the passive value. Similar behaviour was observed at other passive potentials.

The theory described briefly above was used for interpretation of the experimentally obtained results. The decay rate of anodic current density was explained in terms of the rate of nucleation and oxide film growth by the modified Erofeev equation:

$$\log\left(\ln\left(\frac{i_{init}}{i}\right)\right) = \log k + n \log t ,\tag{2}$$

by substituting into equation (1) the initial i_{init} and instantaneous currents i for the amount of reactants. This modification is based on the supposition that the concentrations of reactants are proportional to the current densities. The dependence of $\log\left(\ln\left(\frac{i_{init}}{i}\right)\right)$ versus logarithm of the reaction time is shown in Figures 2-4.
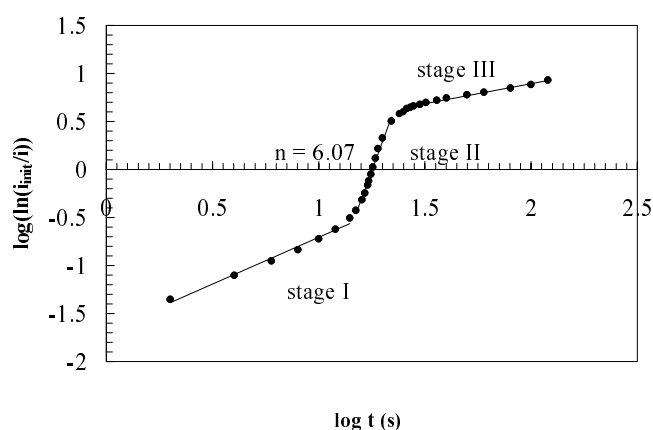

Figure 2: Double logarithmic plot of the ratio of i_{init}/i vs. logarithm of time under potentiostatic control at E = -0.1 V$_{SCE}$ for AISI 420 stainless steel in 0.1 M H$_2$SO$_4$ + 0.1 M Na$_2$SO$_4$; pH = 2.42.
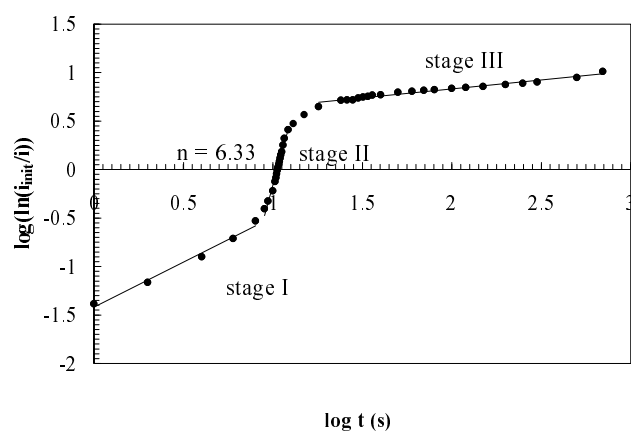
Figure 3: Double logarithmic plot of the ratio of i_{init}/i vs. logarithm of time under potentiostatic control at E = -0.1 V_{SCE} for AISI 420 stainless steel in 0.1 M H_2SO_4 + 0.1 M Na_2SO_4; pH = 2.85.

Figure 4: Double logarithmic plot of the ratio of i_{init}/i vs. logarithm of time under potentiostatic control at E = -0.1 V_{SCE} for AISI 420 stainless steel in 0.1 M H_2SO_4 + 0.1 M Na_2SO_4; pH = 3.31.
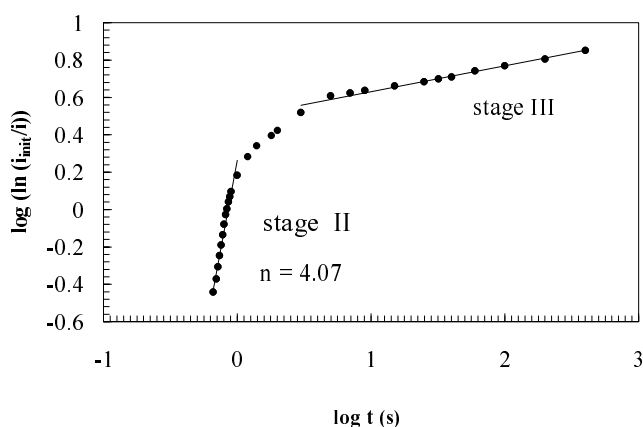
The results in Figures 2-4 suggest three different stages. In *stage I* the dissolution of metal continues up to the moment where salt precipitates; the concentration at the

electrode surface is saturated in accordance with our previous studies.[20] In *stage II* film growth occurs and the processes in this stage were our main targets of interest. In *stage III* the oxidation rate is relatively low, and much of the film is formed.

The numerical values of the exponent *n*, evaluated from the straight line in *stage II*, are shown in Table 1.

Table 1. Values of the exponent *n* for AISI 420 stainless steel at different values of cell voltage and pH of solution.

E (V)	pH = 2.42			pH = 2.85			pH = 3.31		
	n	σ	a	n	σ	a	n	σ	a
-0.10	6.07	3	3	6.33	3	3	4.07	1	3
0.00	6.28	3	3	6.01	3	3	4.08	1	3
0.10	6.16	3	3	6.27	3	3	4.29	1	3
0.20	6.29	3	3	5.92	3	3	4.18	1	3
0.30	6.04	3	3	5.99	3	3	4.18	1	3

As seen from Table 1, the value of *n* is close to the integer 6 in solutions of pH values 2.46 and 2.85, and about 4 at a pH value of 3.31 at all five passive potentials. According to Erofeev[19], in the case where the reaction nuclei grow from separate points on the surface in three directions, $n = \sigma + 3$, where as is already known, σ is the number of consecutive steps in the process of formation of the product nuclei. With regard to the fact that the passive film is a three-dimensional phase film (cf. ref. [16]), the number of directions was the same in all three cases (pH = 2.42, 2.85 and 3.31), namely *a = 3*. Thus, the value of *n = 6* in the case of pH = 2.46 and 2.85, indicates that the passivation process proceeds in three steps. Taking into account several previous studies in which both electrochemical methods as surface sensitive techniques were used[7-14,18,20-30] we propose the following conversion steps: the first step is formation of a prepassive film, the second step can be attributed to the formation of a passive layer, such as hydroxide or oxyhydroxide, and in the third step this film transforms in to the oxide form.

A certain change occurs at pH 3.31, namely *n* is close to 4 and $\sigma = 1$. The explanation for this could be a decrease of solubility.[20] An increase of pH lowers the solubility dramatically, i.e., for the reaction $2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$, a decrease of three orders of magnitude would occur per unit of pH. Therefore, one would expect that, in neutral solution, dissolution is immediately followed by precipitation, or oxidation would occur on the electrode surface directly.[10] In accordance with this, it would be possible that in a solution of pH = 3.31 oxidation could occur on the electrode surface directly, i.e. in a simple step.

Conclusions

- The theory of "topochemical reactions" was applied to explain possible transformation steps during the early stages of passivation of AISI 420 stainless steel in mixtures of 0.1M H_2SO_4 and 0.1M Na_2SO_4, with pH-values of 2.42, 2.85 and 3.33.

- The number of conversion steps σ and the number of directions *a* in which nuclei growth were obtained from the Erofeev equation.

- In solutions of pH 2.46 and 2.85 the exponent $n = \sigma + a$ at all five passive potentials was constant and close to 6, and at pH 3.31 about 4.

- Due to the fact that the passive film is a three-dimensional phase film, the number of directions was the same in all solutions, namely $a = 3$.

- On the basis of several previous studies we proposed that the passivation process proceeds in three conversion steps $(\sigma = 3)$ in solutions of pH = 2.46 and 2.85, where the first step i) is the formation of a prepassive film. The second step, ii) can be attributed to the formation of a passive layer, such as hydroxide or oxyhydroxide layer, and in the third step iii) this film changes in to an oxide form.

- For pH = 3.31 oxidation may occur on the electrode surface directly, i.e. in one conversion step only $(\sigma = 1)$.

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Povzetek

V prispevku smo obravnavali kinetiko pasivacije martenzitnega jekla AISI 420 v modelnem mediju. Kot korodirni medij smo izbrali mešanico raztopin 0,1M H_2SO_4 in 0,1M Na_2SO_4, različnih pH-vrednosti (2.42, 2.85 in 3.31). Študija je bila osredotočena na zgodnjo fazo nastanka pasivne plasti izbranega jekla. Uporabljena metoda za elektrokemijska merjenja je bila potenciostatska metoda, pri kateri smo merili tok kot funkcijo časa. Za analizo eksperimentalnih podatkov v področju najstrmejšega padca toka smo uporabili teorijo 'topokemijskih reakcij' , ki vključuje Erofeevo enačbo $\xi = 1 - e^{-kt^n}$ ($n = \sigma + a$), katere eksponent n daje število stopenj preosnove σ, ter smeri rasti a, nastalega filma. Dobljeni rezultati kažejo na dobro ujemanje z uporabljeno teorijo.