Surface Modification of Stainless Steel-304 Electrode. 2. An Experimental Comparative Study of Electrochemically, Hydrothermally and Chemically Modified Oxide Films

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Stainless steel-304 was modified electrochemically by potentiostatic and potentiodynamic methods (triangular and square-wave potential-time programs) in 1 mol dm^{-3} NaOH solution, hydrothermally in 1 mol dm^{-3} NaOH at 200 °C, and chemically in 0.5 mol dm^{-3} K$_2$Cr$_2$O$_7$ solution. Oxide films were characterized voltammetrically by the charge of Fe(OH)$_2$/FeOOH surface electrochemical reaction. The stability of the oxide films was measured in 0.5 mol dm^{-3} H$_2$SO$_4$ by anodic potentiodynamic polarization and by open-circuit potential-time measurements. The hydrothermally grown oxide film was most stable. The most efficient oxide growth was achieved by the use of square-wave type of modification. The oxide modified by this procedure exhibited lower stability than the oxide grown by triangular potential-time program, which was much more stable due to the uncompleted reduction of chromium oxide. The importance of careful control of experimental conditions, where a small change in surface treatment could lead to a significant change in corrosion behaviour, is pointed out.

Key words: stainless steel-304, surface modification, oxide growth, passive oxide films

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INTRODUCTION

The surfaces of technologically important alloys such as stainless steels are often additionally protected by different types of surface treatments. Organic coatings, ceramic oxides and chemical vapor deposition have been used for improving the alloys' resistance against corrosion in different, sometimes aggressive environments.[1] These environments modify the original surface in various ways, sometimes by the formation of protective passive films, but in many cases by the appearance of corrosion. It is known, for example, that localized corrosion is a major cause of steam generator failures and shut-downs of nuclear power plants, accompanied by great economic, and potentially dangerous, environmental impacts.[2] In the petroleum, pharmaceutical and chemical industry the equipment is exposed to various aggressive media.[3,4]

Surface modifications of stainless steel-304 in the present work were both electrochemically and chemically similar to modifications which we have previously described for Inconel–600.[5] Electrochemical modifications were achieved by the application of an external potential field in either potentiostatic or potentiodynamic mode. Chemical modifications were done either hydrothermally by the effect of pressurized water at an elevated temperature, or by an effect of strongly oxidizing environment. This paper focuses on comparative analysis of several different types of surface modifications of stainless steel-304, followed by the behaviour of modified surfaces in typical electrochemical experiments, which reflect their corrosion properties in acid solution.

EXPERIMENTAL

Stainless steel-304 (Goodfellow), composition FeCr18Ni10, was used either in the form of wire (0.25 cm^2 of geometrical area), fixed by epoxy resin into a glass tube, for electrochemical and chemical modifications, or in the form of foils (1.25 cm^2 area) for hydrothermal modifications. The cleaning procedure, described previously,[6] was the same for all types of specimens and modification procedures.

Cyclic voltammetric characterization, anodic potentiodynamic polarization and open-circuit potential-time measurements of all modified specimens, have been carried out by the use of EG&G 273/97 potentiostat/galvanostat. Three – compartment electrochemical cell with platinum foil as a counter electrode and saturated calomel electrode (SCE) as a reference electrode was used.

Electrochemical modifications have been carried out potentiostatically at 0.5 V for 30 min, and potentiodynamically by either cycling voltammetry at a sweep rate of 50 mV s^{-1} between –1.2 V and 0.5 V, or by square-wave (SQW) potential pulses between –1.2 V and 0.5 V at 0.017 Hz, for 1 hour in 1 mol dm^{-3} NaOH (Fluka, Switzerland, *puriss. p.a.*) solution.

Hydrothermal modification was carried out in an autoclave (hastelloy C 276 alloy, Sotelem, France), 200 cm^3 volume, filled with 100 cm^3 NaOH solution at 200 °C for 4 hours. The pressure of pure nitrogen was 110×10^5 Pa.

The stainless steel-304 surface was modified chemically by treatment with 0.1 mol dm^{-3} K$_2$Cr$_2$O$_7$ (Kemika, *p.a.*, Croatia) solution for 24 hours.

The scanning electron micrography (SEM) was carried out by the use of a Philips Model 515 microscope.

RESULTS AND DISCUSSION

The Cyclic Voltammetric Characterization of Modified Surfaces

In a previous paper[6] we have presented experimental conditions for the hydrous oxide growth on stainless steel-304 under the conditions of cycling voltammetry in 1 mol dm^{-3} NaOH solution and described surface electrochemical reactions in oxidation/reduction processes. The voltammetric charge of iron oxidation between –1.2 V and –0.5 V was used in the determination of the oxide growth efficiency. The same procedure was used in the present paper in measuring the efficiency of the oxide growth after various types of surface modifications.

The oxide growth when a metal in an electrochemical cell is subjected either to a potentiostatic or potentiodynamic mode (triangular potential-time program and SQW) will be discussed first. In a potentiostatic mode, the growth of a metal oxide follows either a direct or indirect logarithmic law controlled by place exchange.[7] It was reported that a direct logarithmic law explains experimental results more precisely, not only in the initial stages of oxide formation, but also in a multilayer oxide growth.[8] Indeed, a direct logarithmic dependence of the voltammetric charge of oxide formation on stainless steel-304 as a function of time was obtained.[9] In the place exchange mechanism of an oxide growth, chemisorbed oxygen from OH groups changes its place with a metal atom. This process cannot proceed infinitely because the film reaches a finite thickness and the place exchange becomes rate determining. A different situation appears when an oxide grows under the conditions of potential cycling, either in cyclic voltammetric or SQW mode. On a positive potential, the oxide grows in the usual way, *i.e.* by place exchange. On the negative side, depending upon the nature of the metal, experimental conditions, *etc.*, the oxide is either completely or incompletely reduced. Metal atoms are in a hydrous environment, surrounded by water and solvent molecules. These metal atoms are more easily oxidized in a subsequent potentiodynamic scan, and consequently, more »fresh« metal atoms can be oxidized.[10] In other words, a deeper penetration into metal lattice can be achieved as compared to the potentiostatic polarization.

Table I and Figures 1 and 2a show: firstly, that the electrode modified potentiostatically is similar in shape and in the quantity of anodic charge of iron oxidation to the potentiodynamically untreated (subjected to only one cycle) electrode. In other words, the oxide under potentiostatic conditions does not grow deep into the alloy's bulk. Secondly, it is also evident that potentiodynamically modified electrodes, namely the electrode modified by triangular potential-time program, and SQW modified stainless steel-304 electrode, also differ to some extent. Uncycled electrode, during its first cycle in positive direction (Figure 1) exhibits a chromium oxidation peak between 0 and 0.5 V, which overlaps the current due to $Ni(OH)_2/NiOOH$ transition.

TABLE I

Voltammetric charge of $Fe(OH)_2$ oxidation peak for differently modified stainless steel-304 electrodes

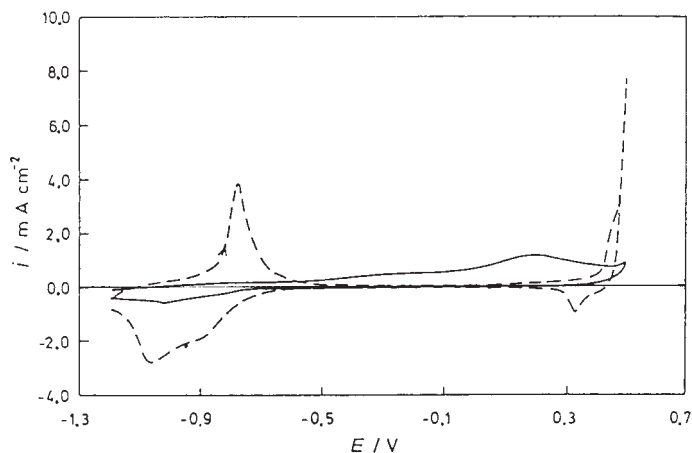| Type of modification	Q $(mC\ cm^{-2})$
Potentiodynamic (square-wave)	39.8
Hydrothermal	22.3
Potentiodynamic (triangular 1 cycle)	1.4
Potentiodynamic (triangular 30 cycles)	10.7
Chemical	2.1
Potentiostatic	1.2

Figure 1. Cyclic voltammograms at a sweep rate of 50 mV s^{-1} of the stainless steel-304 electrode in 1 mol dm^{-3} NaOH. First cycle (full line), 30th cycle (dashed line) at 50 mV s^{-1} from –1.2 V to 0.5 V.

The cycled electrode (Figure 1) exhibits a well-resolved peak of Ni(OH)$_2$/ NiOOH transition at 0.5 V, accompanied by the absence of chromium oxidation peak. The SQW modified electrode (Figure 2a), on the other hand, exhibits chromium oxide formation peak with the absence of visible nickel oxidation. As a matter of fact, this cyclic voltammogram in the positive region about 0.3 V is similar to that of noncycled electrode. The explanation is as follows. During triangular potential-time program at 50 mV s^{-1}, the potential is not held for a sufficiently long time at negative values (about -1.2 V) where chromium oxide species are reduced. In the SQW type of modification, the potential is held for 30 s at -1.2 V, which seems to be enough time
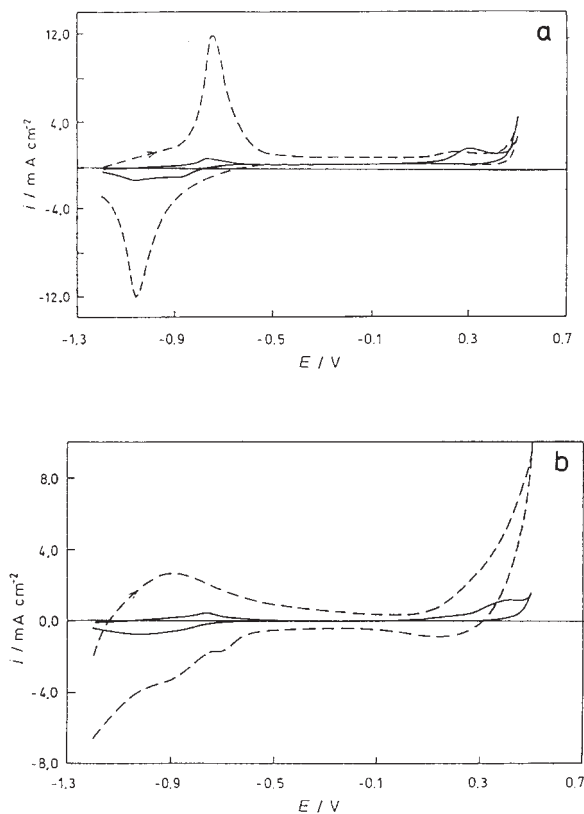

Figure 2. Cyclic voltammograms at a sweep rate of 50 mV s^{-1} in 1 mol dm^{-3} NaOH of the stainless steel-304 electrode modified (a) potentiostatically at 0.5 V for 30 min (full line), and stainless steel-304 electrode modified by SQW pulses between -1.2 V and 0.5 V at 0.017 Hz for 1 hour (dashed line); and (b) of the stainless steel-304 electrode modified chemically (full line) and of the electrode modified hydrothermally (dashed line).

to reduce chromium oxide, or at least the major part of it. Consequently, the cyclic voltammogram after SQW modification exhibits chromium oxidation peak which overlaps the peak of nickel oxidation. These phenomena will be essential for a difference in their stabilities in acid solution, as it will be shown later on in the text.

The shape of the cyclic voltammogram of chemically modified electrode (Figure 2b) is similar to the cyclic voltammogram of the electrode modified potentiostatically (Figure 2a). The growth of the oxide, as far as the electrochemical oxidation of iron is concerned, is not significant (Table I). In both cases, much less hydrated oxides were prepared. This was not the case of the hydrothermally modified electrode (Figure 2b). The cyclic voltammogram differs from all other cyclic voltammograms, particularly in the positive potentials about 0.3 V. As a matter of fact, a part of oxide film is reversibly reduced at around 0.1 V, at the potentials which correspond to $Ni(OH)_2$/NiOOH oxidation/reduction process. It seems that hydrothermal conditions led to either preferential dissolution of iron or to a significant oxidation of nickel.

The Morphology of Modified Surfaces

Morphologies of potentiodynamically (triangular potential-time program), hydrothermally and chemically modified surfaces are shown in Figure 3. Surface roughness is evident in all of these samples. However, there are some differences. The electrochemically modified surface exhibits a spongy structure which is highly hydrated, as evidenced in a previous paper.[6] Chemically modified surface has a smaller roughness factor. Obviously, repetitive oxidation/reduction cycles in electrochemically modified surface enabled deeper penetration into the alloy's structure, when compared to the chemical attack of $K_2Cr_2O_7$. Hydrothermal modification produced also a rough surface with thicker grains.

The Stability of Modified Surfaces in 0.5 mol dm^{-3} H$_2$SO$_4$

Anodic potentiodynamic polarization curves of modified stainless steel-304 surfaces are shown in Figures 4 and 5. All metal surfaces except for the potentiodynamically modified one exhibit typical features, which include active/passive transitions (potential of the maximum current in the active range), passive range between –0.2 V and 0.8 V, and transpassive region. These curves also show the stability of the material and resistance against corrosion through their position on a current axis. It is seen that the potentiodynamically (triangular potential-time program) modified surface exhibits enhanced stability when compared to the uncycled electrode (Figure 4a).
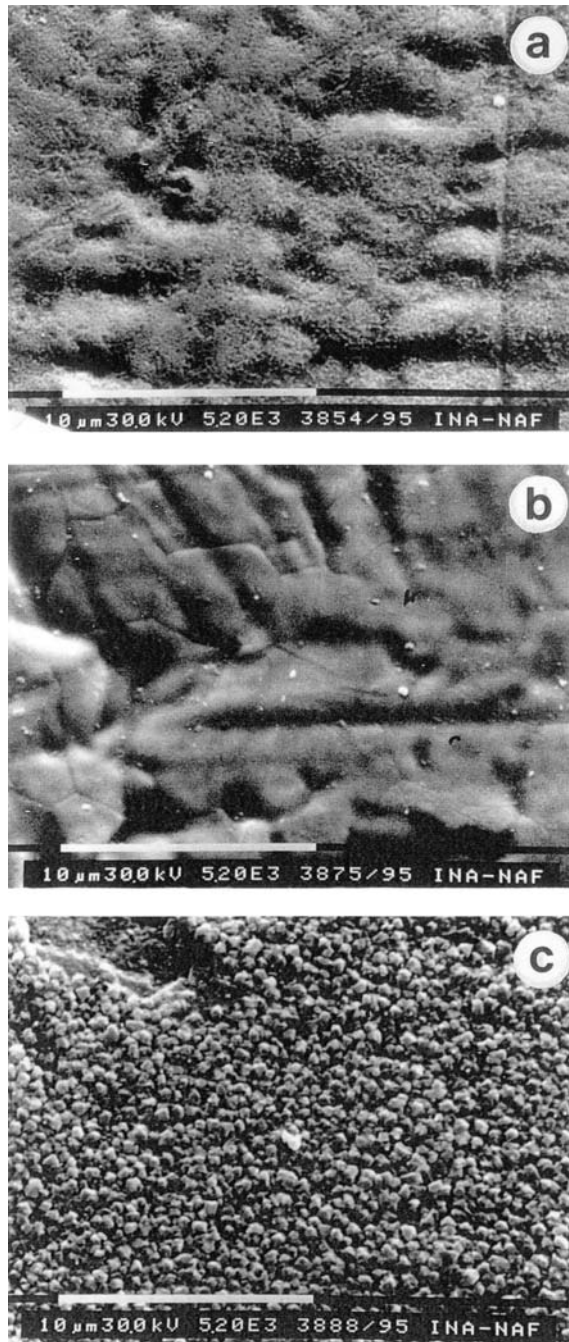
Figure 3. SEM micrographs of stainless steel-304 electrodes modified (a) electrochemically by 30 triangular cycles; (b) modified chemically; (c) modified hydrothermally.
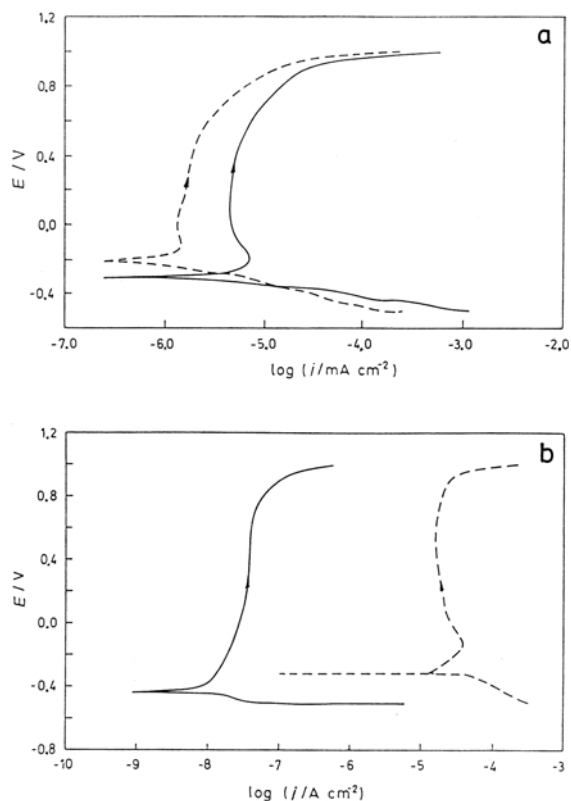
Figure 4. Anodic potentiodynamic curves 1 mV s^{-1} in 0.5 mol dm^{-3} H$_2$SO$_4$ for the stainless steel-304 electrodes modified (a) by one triangular potentiodynamic potential sweep (full line) and by 30 cycles (dashed line); and (b) same as (a) but for electrodes modified potentiostatically (full line) and for the electrode modified by SQW polarization (dashed line).

The potentiostatically modified electrode is most stable (Figure 4b), the passive current is below 1×10^{-7} A cm^{-2}, about three orders of magnitude lower current compared to SQW modified electrode, (Figure 4b). Hydrothermally and chemically modified electrodes exhibit similar anodic potentiodynamic behaviour (Figure 5), with passive currents between 1×10^{-5} A cm^{-2} and 1×10^{-6} A cm^{-2}.

An additional light is shed on the stability of modified electrodes in acid solution by open-circuit potential-time measurements (Figure 6). All electrodes, except for that modified by SQW pulses, remained in the passive state above –0.2 V during the measured period of 1 hour. The potential of the SQW modified electrode was from the very beginning of the measurement close to the active potential and dropped within 100 s to the active po-
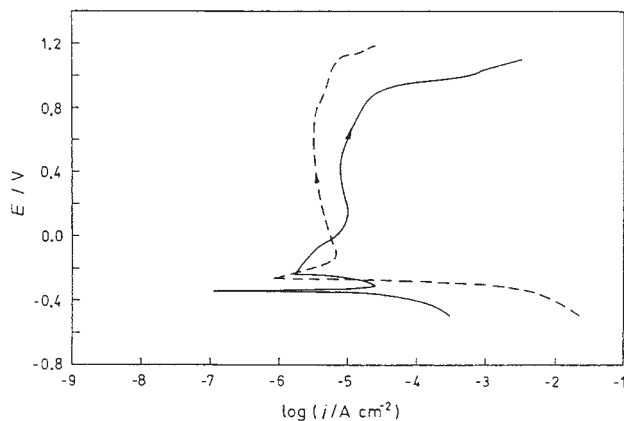
Figure 5. Same as Figure 4, but for the electrode modified chemically (full line) and for the electrode modified hydrothermally (dashed line).
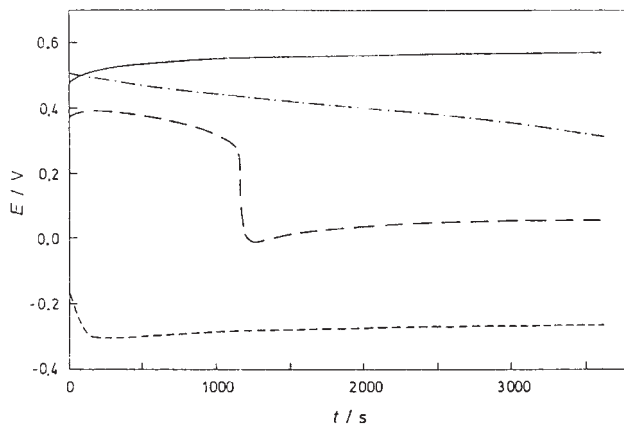

Figure 6. Open-circuit potential in 0.5 mol dm^{-3} H$_2$SO$_4$ of the stainless steel-304 electrodes modified hydrothermally (———); potentiostatically (—·—·—); chemically (———); and modified by SQW polarization (------).

tential at about −0.3 V. As already said, the SQW modified electrode, due to the reduction of chromium oxide, is less stable when compared to potentio-dynamically (with triangular potential-time program) modified electrode, where a greater amount of chromium oxide remained unreduced. Obviously, the hydrous oxide layer in the case of the SQW modified electrode is porous and not protective. It is the thickest one, as far as the voltammetric charge of iron oxidation is concerned (Table I), dissolved at the fastest rate. The hydrothermally modified oxide layer was the most stable without any deterio-

ration of the passive layer towards more negative values of the potential. As seen in Table I, a relatively thick oxide film was formed, which was more compact. Potentiostatically and potentiodynamically (by triangular polarization) modified electrodes exhibited similar stability. The chemically modified electrode was stable for the first 1000 s, followed by a sudden decrease in potential. However, the potential remained at about 0 V, still in the passive state.

CONCLUSIONS

The efficiency of oxide growth on stainless steel-304 and its stability in aggressive acid solution depend on the experimental conditions of the surface treatment. Sometimes, at first sight, similar experimental conditions, led to significant differences in corrosion behaviour. The structure of the oxide film, the oxidation state of chromium in the first place, and not the thickness of the oxide film, is the prerequisite for oxide stability. The deepest penetration into the alloy's structure can be achieved by the use of the square-wave potential-time program. Somewhat less, but also thick and hydrated oxide layers were obtained electrochemically by the use of the triangular potential-time program and by hydrothermal modification. The most compact oxide layers were those prepared potentiostatically and chemically. As far as the stability of the oxide film in an acid solution is concerned, the most stable film was the film modified hydrothermally.

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SAŽETAK

Površinska modifikacija elektrode od nehrđajućeg čelika 304.
2. Usporedbena eksperimentalna studija elektrokemijski, hidrotermalno i kemijski modificiranih oksidnih filmova

Dražen Marijan, Marijan Vuković i Renata Slavković

Nehrđajući čelik 304 bio je elektrokemijski modificiran potenciostatskom i potenciodinamičkom metodom (s trokutastim i kvadratnim pobudnim potencijalom) u otopini NaOH (1 mol dm^{-3}), te hidrotermalno u istoj otopini NaOH na 200 °C i kemijski u otopini $K_2Cr_2O_7$ (0.5 mol dm^{-3}). Oksidni filmovi karakterizirani su voltammetrijskim nabojem površinske elektrokemijske reakcije Fe(OH)$_2$/FeOOH. Stabilnost oksidnih filmova mjerena je anodnom potenciodinamičkom polarizacijom, te na potencijalu otvorenog kruga u H_2SO_4 (0.5 mol dm^{-3}). Najstabilniji je bio film nastao hidrotermalno. Najdjelotvorniji rast oksidnog sloja postignut je oksidacijom kvadratnim pobudnim potencijalom, ali je taj oksid pokazao manju stabilnost u usporedbi s filmom nastalim trokutastim pobudnim potencijalom, koji je bio stabilniji zbog nepotpune redukcije kromova oksida. Naglašena je važnost pažljive kontrole eksperimentalnih uvjeta, gdje male promjene u obradbi površine mogu uzrokovati velike promjene u ponašanju u procesima korozije.