JOURNAL OF APPLIED ELECTROCHEMISTRY **18** (1988) 739–744

Electrochemical characterization of electrodeposited chromium and nickel–chromium layers on a steel substrate

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Received 23 December 1987; revised 20 March 1988

Chromium was deposited on steel specimens and on electroplated steel specimens covered with a Watts nickel layer. The influence of the substrate and of the crack pattern of the electrodeposited chromium layer on the passivation and the reactivation behaviour has been studied by means of potentiodynamic polarization curve measurements and cyclic voltammetry. In the results of the above mentioned electrochemical measurements a strong influence of the substrate was found for a cracked chromium layer deposited on the steel specimen and for a cracked chromium layer deposited on a 30 μm Watts nickel layer. No influence of the substrate was found in the case of a crack-free chromium layer deposited on the steel substrate or on a Watts nickel layer. It is thus possible to determine whether the chromium layer is cracked or crack free by recording a polarization curve or a cyclic voltammogram for a chromium-plated system. A mechanism is proposed for the passivation and repassivation of cracked chromium layers electrodeposited on a steel substrate or on a Watts nickel layer.

1. Introduction

Owing to their favourable mechanical properties electrodeposited hard chromium layers on steel are very suitable for applications in hydraulic systems. In marine environments the chromium-plated steel surfaces show a susceptibility to a type of local corrosion, which is associated with the presence of cracks in the chromium layer. During electrodeposition of chromium layers cracks occur depending on the value of the process variables, e.g. the current density and the plating temperature [1].

Through a network of cracks there will be contact between the substrate and the environment. Consequently an influence of the substrate on the shape of the polarization curves and the cyclic voltammograms is expected.

Significant differences exist between the polarization curves and the cyclic voltammograms of bulk chromium, nickel and iron between -800 and -100 mV (SSE) regarding the position of the passivation potential and the current densities. The influence of the underlying metal could be an increase of the overall current density in this potential region and a decrease of the current density at the passivation potential of the underlying metal which is -100 mV for iron and -250 mV in the case of nickel.

2. Experimental details

2.1. *Specimen preparation and plating conditions*

In order to obtain a uniform thickness of the deposited chromium layers, spherical specimens were used. The steel specimens (0.95% C, 1.31% Cr, 0.31% Mn, 0.21% Si) were vacuum annealed for 1 h at 750° C and 10^{-5} Torr. The specimens were mounted in a chromium plating bath (250 g l^{-1} CrO_3, 2.5 g l^{-1} H_2SO_4 and 3.0 g l^{-1} Cr^{3+} (obtained through reduction of CrO_3 by addition of glucose)) and surrounded by a platinum gauze anode. The steel substrate was cleaned in an alkaline solution (30 g l^{-1} NaOH, 20 g l^{-1} Na_2CO_3, 25 g l^{-1} Na_3PO_4 and 5 g l^{-1} Na_2SiO_3) for 2 min at a current density of 2 kA m^{-2} and a temperature of 50° C. The specimen was then pickled for 30 s in 10 vol.% HCl and etched anodically in the chromium plating bath for 2 min at a current density of 2 kA m^{-2} before depositing a chromium layer. Between these treatments the substrate was rinsed in double distilled water.

The chromium layers were deposited using various plating temperatures and deposition current densities. The combinations investigated are shown in Tables 1 and 2.

Specimens with a nickel and a chromium layer were prepared as follows. The steel specimen was cleaned anodically using a current density of 2 kA m^{-2} for 2 min at a temperature of 50° C in the alkaline solution. Subsequently it was pickled for 30 s in a 10 vol.% H_2SO_4 solution. A 30 μm nickel layer was deposited from a Watts nickel plating bath (240 g l^{-1} $NiSO_4$, 75 g l^{-1} $NiCl_2$, 40 g l^{-1} H_3BO_3) at a plating temperature of 55° C and a plating current density of 0.3 kA m^{-2}. Generally Watts nickel layers are crack free from 8 μm. After pickling for 30 s in the H_2SO_4 solution a cracked chromium layer was deposited at a current density of 5 kA m^{-2} and a temperature of 60° C, while crack-free chromium layers were deposited

0021-891X/88 $03.00 + .12

Table 1. Plating conditions for samples used for polarization measurements

Specimen	*Chromium plating temperature* T *(° C)*	*Current density* I *(kA m^{-2})*	*Layer thickness (μm)*	*Cracked Cr?* *Ref [1]*	*This paper*
Chromium	–	–	–	–	–
Nickel	–	–	–	–	–
Steel	–	–	–	–	–
Cr-plated steel	40	5	40	yes	yes
	60	5	40	yes	yes
	75	5	40	yes/no	no
	90	9	40	no	no
Ni–Cr-plated	60	5	30/30	yes	yes
	90	9	30/30	no	no

at a current density of 9 kA m^{-2} and a temperature of 90° C.

2.2. *The polarization curves and cyclic voltammograms*

The experiments were performed in a standard Green cell using a 0.5 M H_2SO_4 solution. Purified nitrogen gas was bubbled through the solution for at least 2 h prior to the experiments, and also during the experiments, to prevent interference with the electrode reactions from dissolved oxygen. Platinum counter electrodes and a saturated sulphate reference electrode (SSE) were used. All potentials are given relative to this reference electrode (0 mV NHE = −660 mV SSE). The temperature of the electrolyte varied between 21 and 23° C. The scan rate was 20 mV min^{-1} and the potential varied between −1200 and +600 mV. The cyclic voltammograms were recorded with the same experimental set-up in which the *X–t* recorder was replaced by an *X–Y* recorder. The scan rate was 20 mV s^{-1} and the potential was varied cyclically between −1200 and +600 mV.

The pretreatment of the working electrode consisted of a cathodic polarization for 5 min at a potential which yields a current density of 0.1 kA m^{-2}. Afterwards the electrode was exposed for 5 min at the corrosion potential. Then the polarization curve or the cyclic voltammogram was recorded.

2.3. *The optical microscopy*

The crack distribution of the chromium layers was investigated in polished cross-sections of the spherical plated specimens. In order to provide a support during cutting and polishing a nickel layer was electrodeposited on the chromium layer after pickling in a concentrated HCl solution. Acoustic emission measurements had indicated [1] that the latter did not introduce cracking. Cross-sections of the spherical steel specimens were obtained by means of spark-cutting. The cut specimens were mounted in bakelite and polished using diamond paste down to 1 μm. Anodic etching of the cross-sections was performed at 80° C using an anodic current density of 0.45 kA m^{-2} for 10–30 s in a solution containing 83 g l^{-1} $K_3Fe(CN)_6$ and 83 g l^{-1} NaOH. This resulted in excellent visibility of cracks.

2.4. *SEM and EPMA investigations*

In order to obtain information about the structure and the contents of the cracks in the chromium layer, SEM (scanning electron microscopy) and EPMA (electron probe microanalysis) were used. For these observations slices were spark-cut out of the spherical steel specimens. These slices had a diameter of 10 mm and a thickness of 2 mm. They were polished using diamond paste down to 3 μm. A chromium layer was then

Table 2. Plating conditions for samples used for cyclic voltammetry

Specimen	*Chromium plating temperature* T *(° C)*	*Current density* I *(kA m^{-2})*	*Layer thickness (μm)*	*Cracked Cr?* *Ref [1]*	*This paper*
Chromium	–	–	–	–	–
Nickel	–	–	–	–	–
Steel	–	–	–	–	–
Cr-plated steel	60	5	6	yes	yes
	60	5	9	no	no
	60	5	11	no	no
	60	5	17	yes	yes
	60	5	30	yes	yes
	90	9	30	no	no
Ni–Cr-plated steel	60	5	30/30	yes	yes
	90	9	30/30	no	no

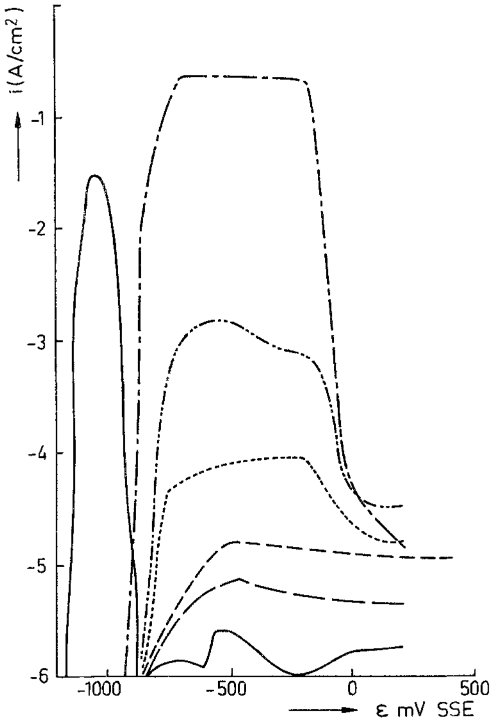

Fig. 1. Polarization curves of chromium (——), steel (–·–·), steel with a chromium layer deposited at: 40° C and 5 kA cm^{-2} (–··–··), 60° C and 5 kA m^{-2} (····), 75° C and 5 kA cm^{-2} (-- -- --) and 90° C and 9 kA m^{-2} (– – – – – –).

electrodeposited at a temperature of 60° C and a current density of 5 kA m^{-2} or at a temperature of 90° C and a current density of 9 kA m^{-2}.

3. Results

The combinations of current densities and plating temperatures employed are shown in Table 1. Figure 1 shows polarization curves of the chromium plated steel while the corresponding observed crack patterns on the specimens are shown in Fig. 2. The polarization curves of the nickel–chromium-plated steel specimens are presented in Fig. 3. Chromium layers deposited at a temperature of 60° C and a current density of 5 kA m^{-2}, and at a temperature of 90° C and a current density of 9 kA m^{-2} were used for the cyclic voltammograms. The recorded cyclic voltammograms are shown in Figs 4–6.

It was not possible to obtain any information about the contents of cracks in a chromium layer deposited directly on the steel. The structures of a cracked and of a crack-free chromium layer are shown in Fig. 7.

4. Discussion

The potentiodynamic polarization curve of a steel

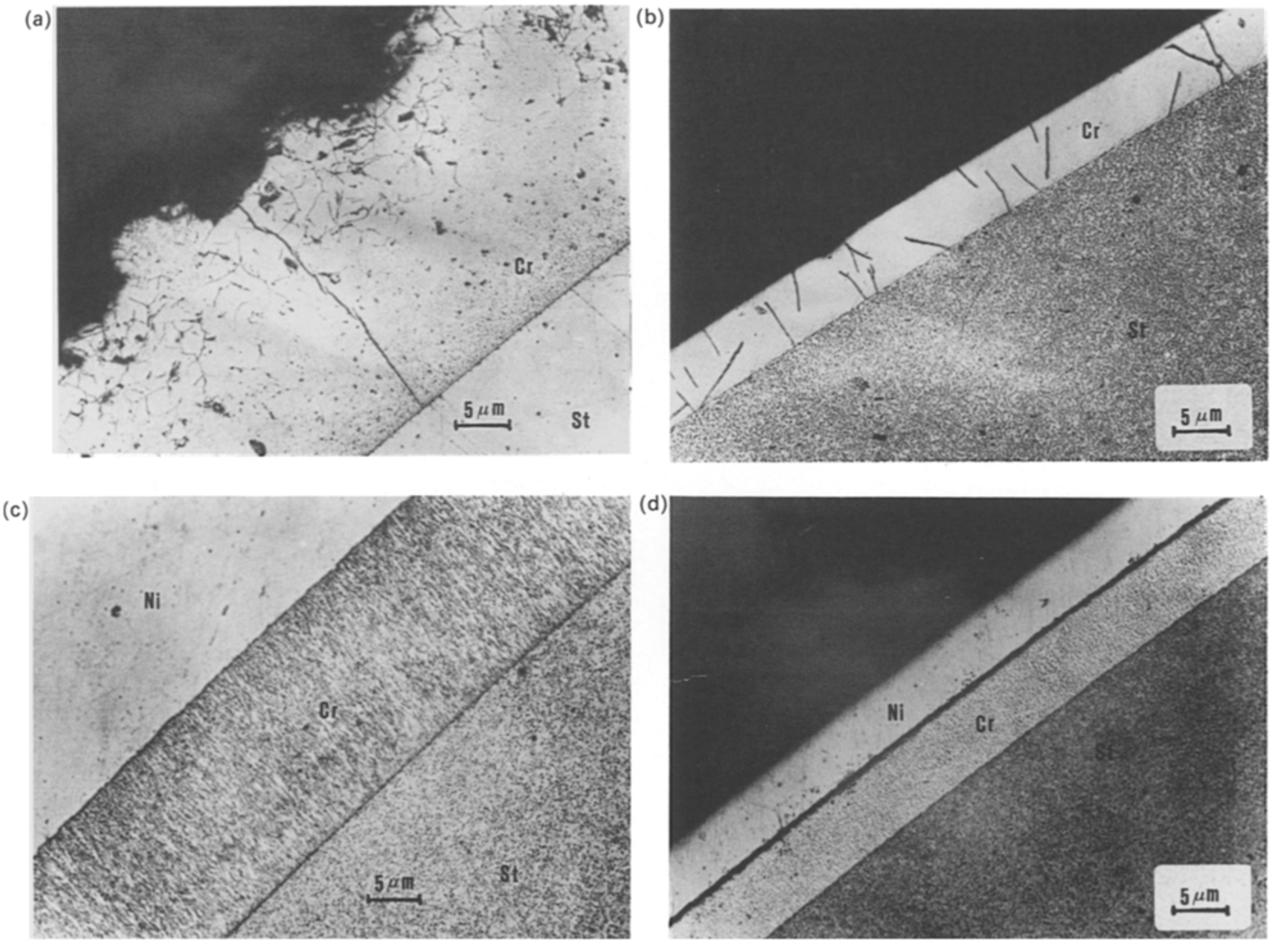

Fig. 2. Cross-section of a chromium layer deposited on a steel substrate at (a) 40° C and 5 kA m^{-2}; (b) 60° C and 5 kA m^{-2}; (c) 75° C and 5 kA m^{-2}; (d) 90° C and 9 kA m^{-2}.

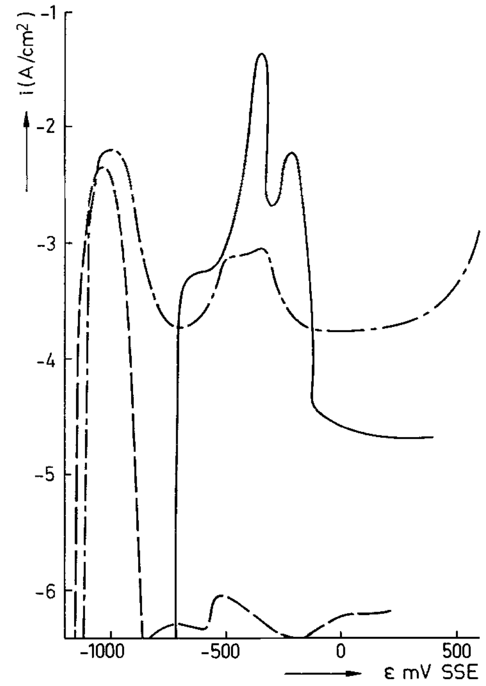

Fig. 3. Polarization curves of chromium (– – – –), nickel (——) and a 30 μm chromium layer deposited at 60° C at 5 kA m^{-2} on a 30 μm Watts nickel layer (–·–·).

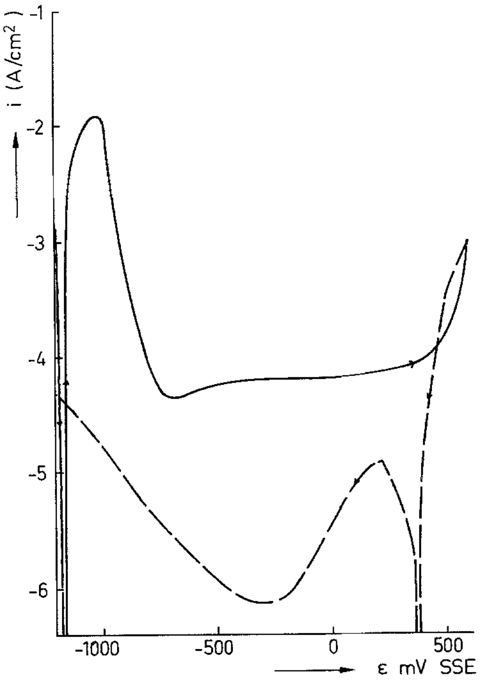

Fig. 5. Cyclic voltammogram of a chromium layer deposited at 90° C and 9 kA m^{-2} on steel: (– –) anodic scan; (——) cathodic scan.

specimen with a cracked chromium layer shows the influence of chromium and iron (see Fig. 1). However, if the chromium is crack free, the influence of the substrate will not be visible in the resulting polarization curve or cyclic voltammogram. The influence of the underlying metal on the polarization curve becomes more pronounced as the amount of cracking in the chromium layer increases.

Starting the potential scan at − 1200 mV immediately after the standard pretreatment of the specimen, a peak associated with the anodic dissolution of chromium and the formation of a Cr_2O_3 layer appears at − 1000 mV (see Fig. 1). At − 800 mV the iron in the

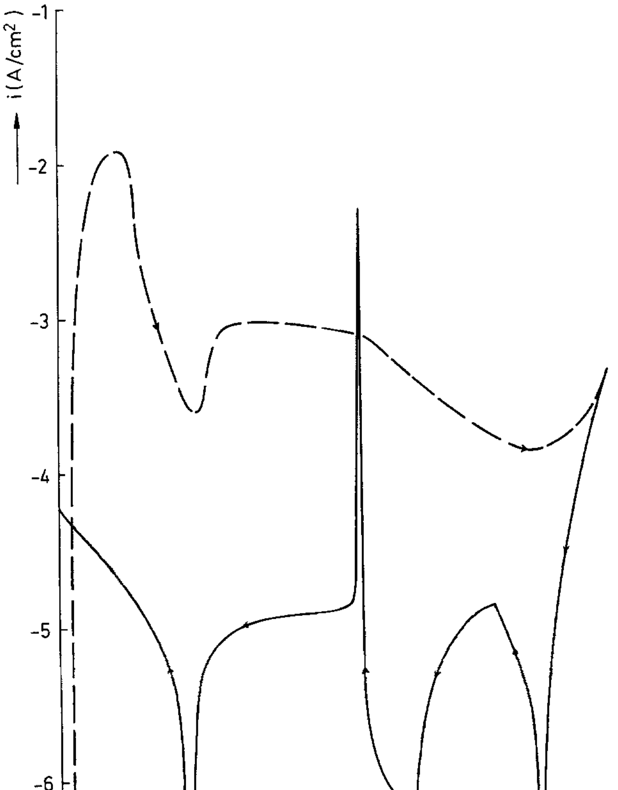

Fig. 4. Cyclic voltammogram of a chromium layer deposited at 60° C and 5 kA m^{-2} on steel: (——) anodic scan; (– –) cathodic scan.

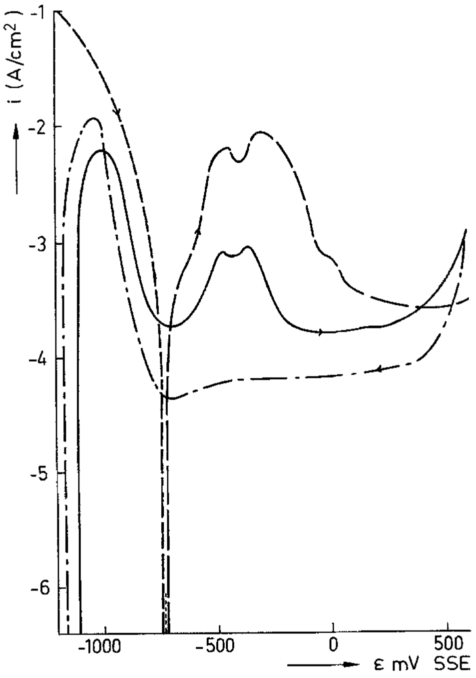

Fig. 6. Cyclic voltammograms of nickel (– – – –) (anodic scan only) and a 30 μm chromium layer deposited at 60° C and 5 kA m^{-2} on a 30 μm Watts nickel layer: (——) (anodic scan) and (–·–·) (cathodic scan).

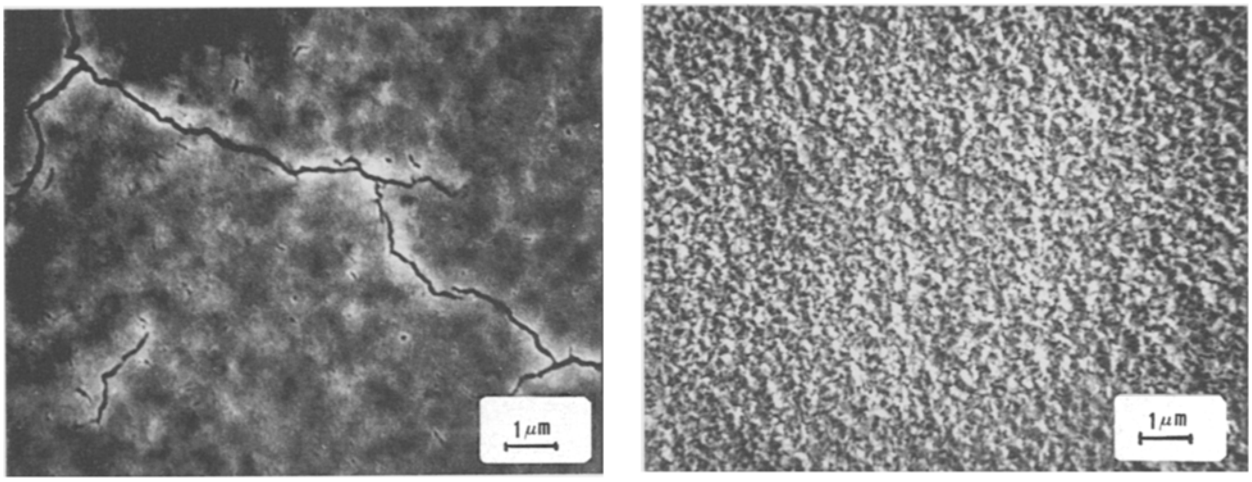

Fig. 7. Surface of a chromium layer deposited at 60° C and 5 kA m^{-2} and the surface of a chromium layer deposited at 90° C and 9 kA m^{-2}.

cracks will be oxidized to Fe^{2+}. When the solubility product of $FeSO_4$ has been reached, $FeSO_4$ will precipitate in the cracks and will form a porous protective layer, as is suggested for the primary passivation of iron [2]. At -100 mV iron oxide is formed. This potential is the passivation potential of iron. The current density drops due to the passivation of iron. The $FeSO_4$ dissolves as there is no new supply of Fe^{2+} ions.

The polarization curve of a crack-free chromium layer deposited on a steel substrate strongly resembles the polarization curve of bulk chromium [2, 3].

The anodic scans of the cyclic voltammograms of the cracked and crack-free chromium layers deposited on a steel substrate are quite similar to the potentiodynamic polarization curves as far as the shape of the curves is concerned (see Fig. 4). Due to the employed scan rate of 20 mV s^{-1} the decrease of the current density at the passivation potential is less clear. At $+400$ mV Cr_2O_3 is oxidized to chromate which dissolves. The scan was reversed at $+600$ mV.

The first peak to appear during the cathodic scanning is that associated with the reduction of the chromate to Cr_2O_3 at $+225$ mV. In the case of a cracked chromium layer an anodic current maximum is observed at -100 mV. The iron oxide in the cracks is reduced and the iron in the cracks becomes active. Fe^{2+} dissolution takes place very rapidly at a potential of -100 mV. Therefore a high concentration of Fe^{2+} is present. The solubility product of $FeSO_4$ is reached and a porous protective layer reappears. This causes the observed repassivation. The current density remains anodic while in the case of a crack-free chromium layer the current density remains cathodic between $+400$ and -1200 mV. A diagrammatic representation of the phenomena occurring during the anodic and cathodic scan of a cyclic voltammogram is given in Fig. 8.

Chromium layers of different thicknesses were deposited on the steel substrates. The cyclic voltammograms indicated that chromium layers are cracked above 11 μm and below 6 μm. The observed influence of the steel substrate below 6 μm is probably due to incomplete coverage of the steel specimen or to porosity of the chromium layer. Above 11 μm the chromium layers are cracked because of the large internal stresses in the chromium layers [4]. Chromium layers between 6 and 11 μm are crack free. Overkamp found that crack-free chromium layers could be deposited at 60° C and 5 kA m^{-2} if the plating time did not exceed 20 min [1]. The thickness of 11 μm corresponds to a plating time of 20 min as the growth rate of the chromium layer is 33 μm h^{-1} at 60° C and 5 kA m^{-2}.

The polarization curves of nickel–chromium-plated steel (see Fig. 3) exhibit a mixed influence of nickel and chromium. The nickel layer is crack free but the chromium layer is not. There is no influence of the iron substrate. The influence of nickel however is

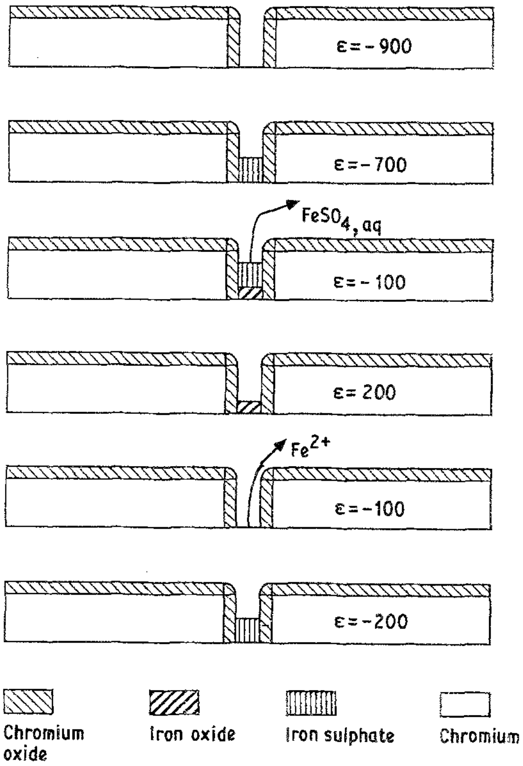

Fig. 8. Schematic representation of the events during the anodic and cathodic scan of a cyclic voltammogram.

clearly visible. At least two anodic current density maxima appear. No anodic current density maximum is observed in the reverse scan of the cyclic voltammograms. This indicates that the nickel oxide formed during the anodic scan remains stable. No porous sulphate layer is formed. The influence of chromium is clearly visible by the appearance of a current density maximum at −1000 mV as a result of chromium oxidation and the formation of a Cr_2O_3 layer and a reduction peak at +225 mV during the cathodic scan as a result of the reduction of chromate.

The appearance of at least two current density maxima between −800 and −100 mV during an anodic potential scan can be explained by the assumption that nickel is oxidized to NiO at −550 mV and to Ni_3O_4 at −300 mV [5, 6]. This last oxidation is to be associated with the passivation of the nickel electrode. Briggs and Jones [7] share this point of view. More current maxima may appear depending on the type and the concentration of anions in the solution [8], the cathodic pretreatment of the nickel electrode [9], the pH of the solution [10] and the sweep rate [11]. According to Vilche and Arvia [12] most of the research done on the study of anodic dissolution and passivation of nickel is not consistent because the potentiodynamic behaviour of the nickel electrode depends on a number of variables which usually are not changed systematically. As a result no clear explanation for the mechanism of anodic dissolution and passivation of nickel electrodes in acid solutions is available.

5. Conclusions

Potentiodynamic polarization curves and cyclic voltammograms measured on steel specimens provided with a crack-free electrodeposited chromium layer are similar to those measured on bulk chromium.

The influence of the underlying metal on the polarization curve of a cracked chromium layer deposited on a steel specimen consists of an increase of the current density between −800 and −100 mV and a decrease of the current density at the passivation potential of the underlying metal. The current density between −800 and −100 mV increases as the crack density increases. Chromium layers deposited at 60° C and 5 kA m^{-2} are crack free between 6 and 11 μm.

The influence of the underlying metal on the cyclic voltammograms obtained on a cracked chromium layer deposited on a steel substrate consists of an increase of the current density between −800 and −100 mV in the anodic scan of the voltammogram and the appearance of an anodic current density maximum at −100 mV in the cathodic scan of the voltammogram.

The electrochemical results obtained for a cracked chromium layer on steel can be explained by a combination of a passivation–repassivation model for iron and chromium.

The influence of a Watts nickel layer between the steel substrate and a cracked chromium layer on the polarization curve as well as on the cyclic voltammograms consists of the appearance of at least two anodic current density maxima between −700 and −300 mV. During the reverse scan no significant influence of the nickel layer is observed.

It was thus shown that, due to the high sensitivity and the good reproducibility of the electrochemical measurements, it is possible to determine whether or not a chromium layer deposited on a steel substrate or on a nickel plated steel substrate is cracked, by recording a polarization curve or a cyclic voltammogram.

Acknowledgements

The authors would like to thank Mr J. H. Gerretsen for useful discussions and suggestions and Dr C. J. van der Wekken for the critical reading of the manuscript.

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