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Preliminary communication

PRELIMINARY COMMUNICATION

Influence of chloride ions on the open circuit potentials of chromium in deaerated sulfuric acid solutions

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Abstract: Open circuit potential measurements and cyclic voltammetry of chromium in deaerated aqueous H₂SO₄ solution of pH 1 without and containing NaCl in the concentration range 0.5 – 4 M revealed that chromium exhibits two stable open circuit potentials having the character of a Wagner–Traud corrosion potential. One, $E_{\text{corr},1}$, was established on the passive surface formed by exposing Cr previously to air or passivated potentiostatically in a controlled manner, and the second one, $E_{\text{corr},2}$, at the bare Cr surface obtained by prolonged cathodic activation. There is a small difference in the $E_{\text{corr},1}$ values as a function of the passive layer properties. Addition of NaCl accelerates the hydrogen evolution reaction on the passive surface to some extent, while the same reaction on the bare surface was not affected by NaCl. On the other hand, presence of NaCl accelerates the anodic reaction on the bare surface, and it activates the dissolution of the passive layer so that the passive currents increase with addition of NaCl. This effect is so large that at concentration of NaCl larger than 3 M, the destruction of the passive layer was so fast that in a matter of seconds the Cr was activated, and the only one stable corrosion potential observed was $E_{\text{corr},2}$. No pitting of Cr in the presence of NaCl was observed up to the transpassive potentials.

Keywords: chromium, corrosion, open circuit potential, sulfuric acid, chloride ions.

INTRODUCTION

The corrosion properties of metallic chromium were studied by a number of authors and relevant data can be found in the corresponding publications. Heumann and Diekötter,¹ Wilde and Hodge,² Sukhotin and Khoreva,³ Safonov *et al.*⁴ and Popić and Dražić^{5–7} pointed out that chromium exhibits two fairly stable corrosion potentials in deaerated sulfuric acid solutions. The first corrosion potential of chromium in deaerated sulfuric acid solutions is formed by the hydrogen evolution reac-

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tion at the passive surface of chromium and anodic dissolution of chromium through the passive layer, and the second one by the hydrogen evolution reaction on the activated, bare surface of chromium and active anodic dissolution. The purpose of this communication is to report more experimental data on the influence of chloride ions on the electrochemical behavior of chromium in deaerated sulfuric acid, and especially to the further interpretation of factors determining the open circuit potentials in sulfuric acid containing higher concentrations of chloride ions.

EXPERIMENTAL

The experiments were performed with metallic Cr (Goodfellow, Berwin, Pa, USA). The electrodes were made in the form of a piece of metal rod (\varnothing 5 mm) sealed in methacrylate resin (exposed surface area 0.2 cm²). The electrochemical measurements were performed using a PINE potentiostat-galvanostat set-up and a PM 8134 Philips X-Y plotter. All the experiments were performed in aqueous mixtures of H₂SO₄, pH 1.0, without and with NaCl added in amounts to obtain solutions with the NaCl concentrations indicated in the Figures. Merck p.a. chemicals and doubly distilled water were used for the preparation of the solutions. An all-glass electrochemical cell with separated compartments and a thermostating jacket was used. The counter electrode was a Pt wire and the reference electrode a saturated calomel electrode (SCE). All the potentials are referred to the SCE. The solutions were continuously deaerated with purified nitrogen. The potential scan rate of the Cr electrode was 2 mV s⁻¹. This appeared to be sufficiently slow to consider that the polarization curves were obtained under quasi-steady state conditions. Of course, this was valid only for the part of the cyclic voltammogram relating to the bare Cr surface, while in the passive region, due to the permanent growth of the passive layer, a real steady state can never be achieved. Prior to the measurements, the electrodes were either activated by cathodic polarization at -0.900 V for 2 min, since the spontaneously formed open circuit potential of a chromium electrode which had previously been in contact with air was about -0.250 V, which corresponds to the passive state of the chromium surface, or just left in this condition. It appeared that the passive state was sensitive to the manner of preparation, hence that a reproducible passive layer was prepared by holding the potential at -0.200 V for 2 min. This potential corresponds to the positive potential limit used in the voltammetric scans.

RESULTS AND DISCUSSION

As depicted in Fig. 1, the open circuit potential of chromium in sulfuric acid, as shown elsewhere,⁷ achieves several stable open circuit potentials, which have the characteristics of Wagner–Traud type corrosion potentials. $E_{\text{corr},1,(\text{air})}$, refers to a chromium electrode introduced into the solution directly from air (having a spontaneously formed oxide layer), $E_{\text{corr},1,(-200 \text{ mV})}$ to an electrode passivated in a controlled way by holding it at -0.200 V for 2 min, and $E_{\text{corr},2,(-900 \text{ mV})}$, to an electrode activated (*i.e.*, oxide layer was reduced) by a 2 min cathodic polarization at -0.900 V. To facilitate the reading, in the further text these potentials will be used in a shorter manner, $E_{\text{corr},1,(\text{air})}$, $E_{\text{corr},1}$ and $E_{\text{corr},2}$, respectively.

It is important to note that at concentrations up to 3 M, the presence of NaCl did not have any significant influence on the corrosion potential, either on a passivated or an activated surface. However, at concentrations higher than 4 M, the corrosion potential $E_{\text{corr},2}$ was established almost spontaneously, as indicated in Fig. 1 by the filled diamonds. This indicates that chloride ions attack the passive layer at a

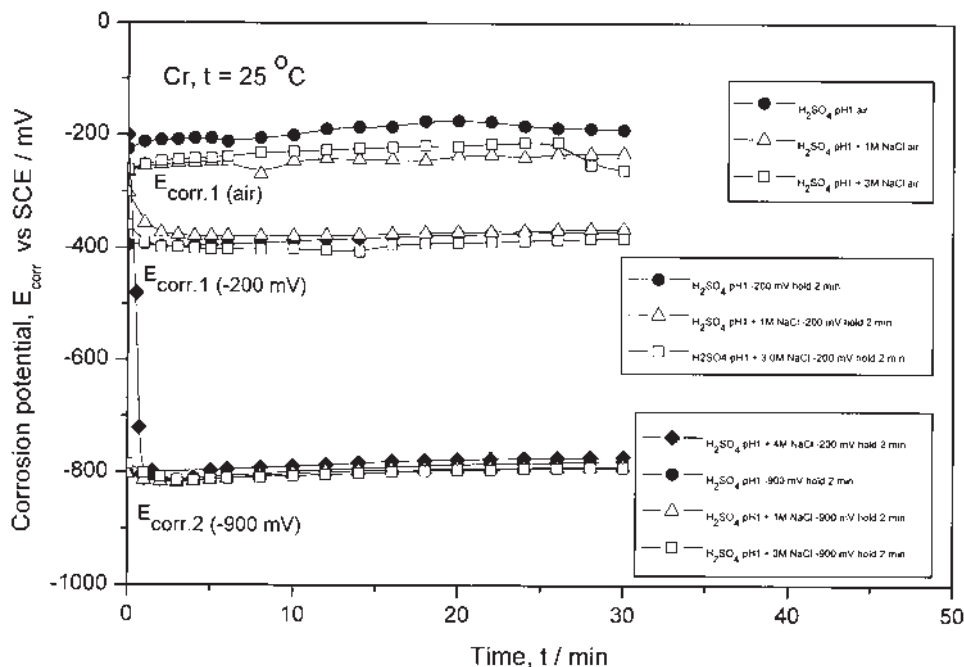


Fig. 1. Open circuit potentials *versus* time for chromium in deaerated aqueous sulfuric acid of pH 1 without and with the addition of NaCl.

rate proportional to their concentration, which at high concentrations is fast enough to activate the surface without any cathodic polarization. As there are no signs of simultaneous pitting, this should be interpreted as a more or less uniform chemical dissolution of the passive layer. Pitting was not observed in Cl^- ions containing solutions even at potentials up to the transpassive dissolution of chromium.

The cyclic voltammogram for a Cr electrode in sulfuric acid containing 1 M NaCl is shown in Fig. 2 which resembles the voltammograms obtained for Cr in sulfuric acid of pH 1 not containing Cl^- ions.⁵ The obvious difference is the much higher passivation peak, which was to be expected. The inset presents the small cathodic peak appearing in the range of -0.300 V to -0.600 V in the reverse sweep, which cannot be seen on the main diagram since its current scale is far less sensitive. As shown elsewhere,⁵ this cathodic current is due to the electrochemical hydrogen evolution reaction on an oxide-covered surface, and its rate determines the open circuit, in fact, the corrosion potential, $E_{\text{corr},1}$, while the hydrogen evolution reaction on a cathodically activated surface, assumed to be bare, determines the corrosion potential, $E_{\text{corr},2}$.

The effects of NaCl on the electrochemical behavior of chromium in sulfuric acid of pH 1 can be seen in Figs. 3 and 4. Figure 3 presents the potentiodynamic curves in the positive direction for chromium electrodes in sulfuric acid (pH 1) containing 0 – 4 M NaCl, enlarged so that only the active dissolution peak can be seen. Five important features can be seen on this diagram.

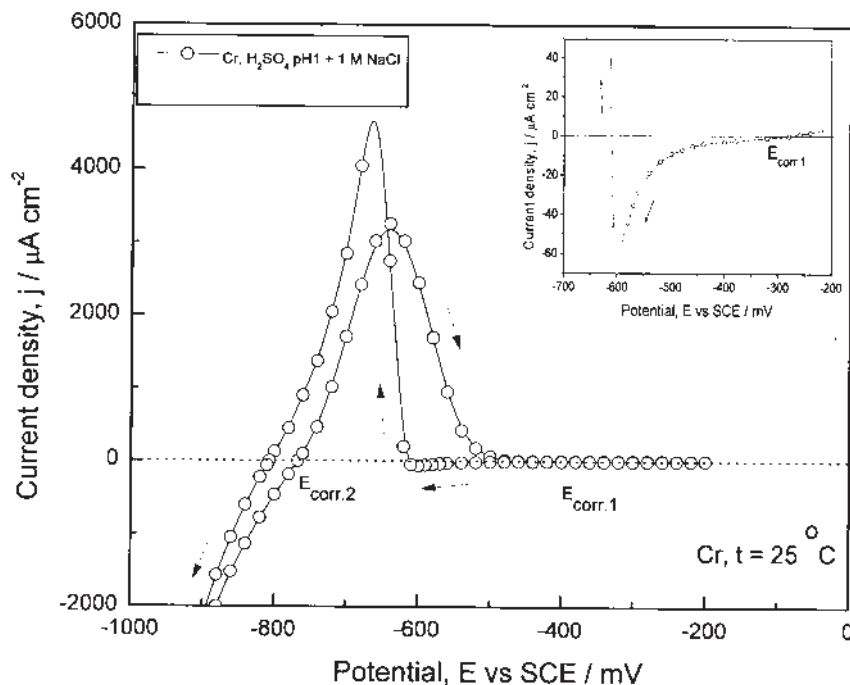


Fig. 2. Cyclic voltammogram for a chromium electrode in deaerated sulfuric acid solution containing 1M NaCl. Inset: Enlarged reversed scan in the potential range of the cathodic peak.

(i) Similar to the case with other transition metals, the passivation current increases considerably with increasing NaCl concentration (almost 10 times in the presence of 4 M NaCl).

(ii) The "passive" current for 4 M NaCl is *ca.* 1 mA cm^{-2} , *i.e.*, the surface is not really passive any more, and if the Cl^- ion concentration would be further increased, this current would probably increase and the passivation peak would disappear, as is the case with iron. In other words, passivation would not be possible. For this reason, the open circuit potential in a solution containing 4 M NaCl spontaneously drops to the potential $E_{\text{corr},2}$, *i.e.*, the surface of the chromium activates by itself, no cathodic activation is necessary (see Fig. 1, filled diamonds).

(iii) The cathodic current density in the presence of Cl^- ions *decreased* to some extent as compared to the same current density in the Cl^- ion free solution. This result is not surprising since the adsorption of Cl^- ions is known to inhibit both the cathodic and anodic reaction of, *e.g.*, iron in sulfuric acid.^{8,9} However, there is a literature report¹⁰ that Cl^- ions have an accelerating effect on the cathodic evolution of hydrogen on chromium in sulfuric acid, with an explanation that the acceleration was due to a change of the diffuse, *i.e.*, ψ_1 potential. It is not clear why the effect of Cl^- ions on ψ_1 would be different for chromium and iron (*i.e.*, accelerating and inhibiting effect, respectively) when the potentials of zero charge for both met-

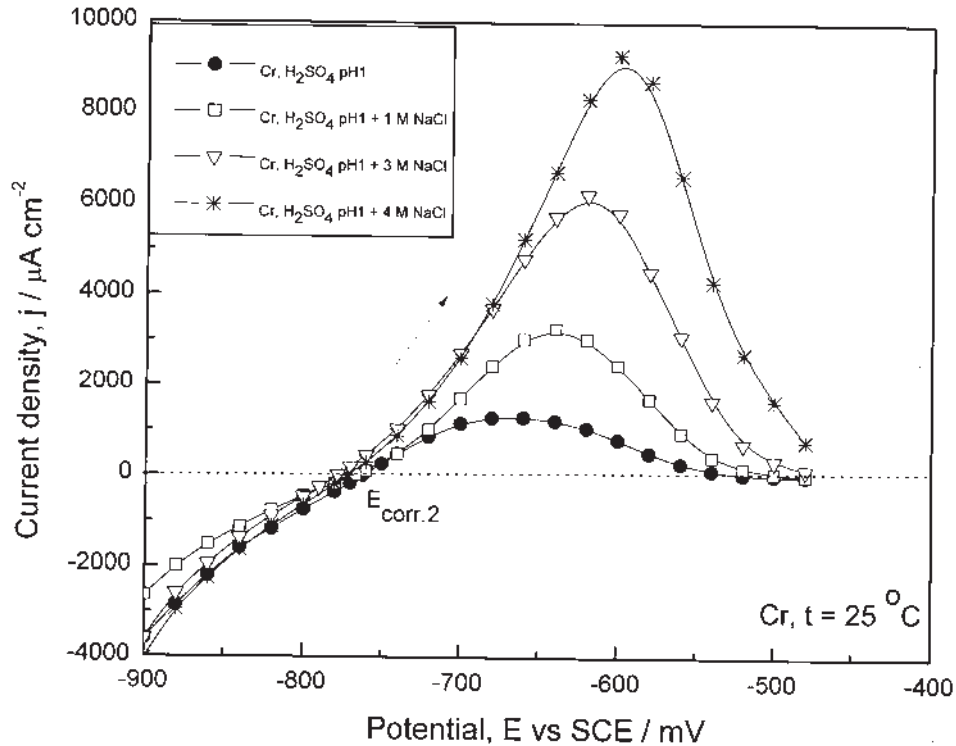


Fig. 3. Potentiodynamic curves in the positive direction for the range of active electrochemical dissolution of Cr in sulfuric acid (pH 1) containing different concentrations of NaCl.

als are similar, *ca.* -0.650 V (SCE).¹¹ The results presented here are not in accordance with this observation..

(iv) The adsorption of Cl^- ions obviously have an accelerating effect on the anodic reaction, but above 2 M NaCl the rate does not change, obviously due to the saturation of the surface with adsorbed Cl^- ions. This accelerating effect at larger concentration of Cl^- ions (contrary to the inhibiting effects at concentrations smaller than *ca.* 0.1 M NaCl) was observed long time ago for iron by Kolotyrkin *et al.*¹² and was the basis for his iron dissolution mechanism with the participation of anions in the rate determining step. This model can be applied also here.

(v) The increase of the passivation current with the increasing NaCl concentration indicates an inhibition of the formation of the passivating chromium oxide in the presence of Cl^- ions, proportional with their concentration. The observed effect of spontaneous activation of chromium in 4 M NaCl (see Fig. 1, filled diamonds) is obviously related to the dissolution reaction of Cl^- ions.

The potentiodynamic curves, as the reverse parts of the voltammograms for different concentrations of NaCl corresponding to the inset to Fig. 2, are depicted in Fig. 4. They show the development of cathodic peaks for solutions containing 0 – 3 M NaCl. Two main features can be noticed:

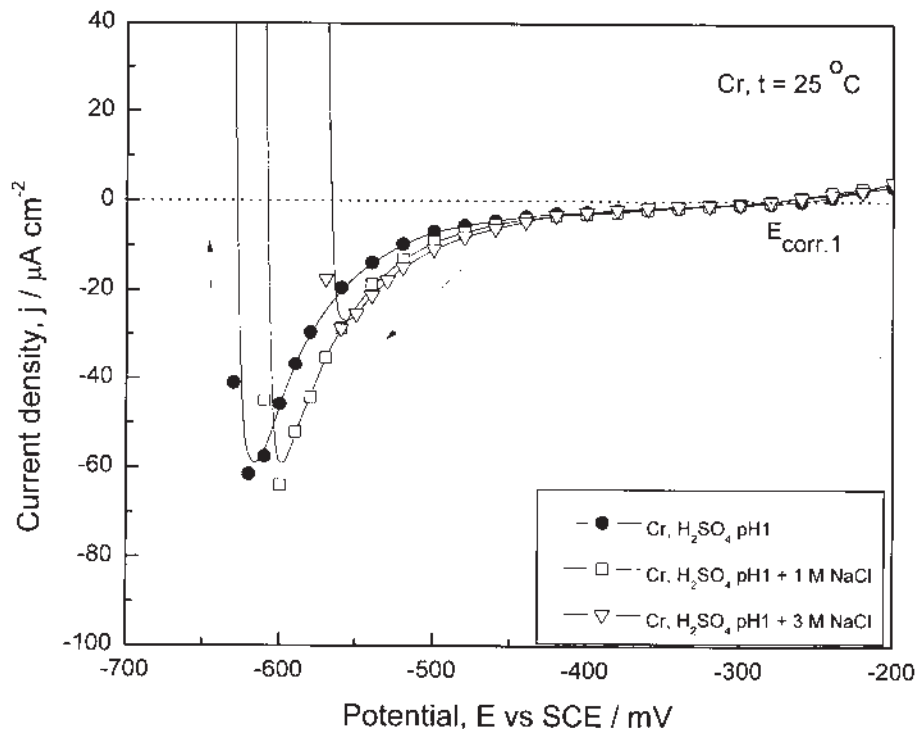


Fig. 4. Potentiodynamic curves in the negative direction for the range of potentials where the cathodic peaks on a passive Cr surface appear in sulfuric acid solution (pH 1) containing different concentrations of NaCl.

(i) Cathodic peaks representing the depassivation potentials become more positive with increasing NaCl concentration, while the peak currents simultaneously decrease. For the solution containing 4 M NaCl, there was no cathodic peak and no stable corrosion potential, $E_{\text{corr},1}$, but the surface was spontaneously chemically activated, as shown in Fig. 1 (filled diamonds).

(ii) The rate of the hydrogen evolution reaction on the oxide covered surface occurring between the corrosion potential and the potential of the cathodic peaks,⁵ is only slightly affected by the presence of Cl^- ions, even up to a concentration of 3 M. This is rather surprising since the chemical attack affecting the passive layer obviously has to include the adsorption of Cl^- ions on the passive layer. On the other hand, if the coverage with Cl^- ions is very high, there would be no free space for a large adsorption of H_{ads} , needed for the Heyrovski step as the rate determining step in the hydrogen evolution reaction, as proposed in Ref. 5. This could mean, therefore, that the first, Volmer, step is rate determining, with a fast Heyrovski step.

CONCLUSIONS

From the results presented in this work, it can be concluded that the open circuit potentials which spontaneously establish on a chromium electrode in deae-

rated sulfuric acid solutions without and with the addition of Cl^- ions up to a concentration of 3 M are the real corrosion potentials of a Wagner–Traud type due to the simultaneous occurrence of the hydrogen evolution reaction, either on an oxide-covered Cr surface with the anodic dissolution of Cr through the passive layer, establishing one stable potential, $E_{\text{corr},1}$, or by cathodic hydrogen evolution and anodic dissolution of the bare surface when the Cr surface is depassivated by some mean (cathodic activation, mechanical action, *etc.*). In the second case a stable corrosion potential $E_{\text{corr},2}$ establishes. Addition of Cl^- ions up to a concentration of 3 M does not affect considerably this behavior, probably because there is no inhibiting effect on the cathodic evolution reaction on the passivated surface (see Fig. 4). Cathodic hydrogen evolution on the bare surface is somewhat inhibited in the presence of Cl^- ions, but the anodic dissolution of chromium in the active state is somewhat accelerated (see Fig. 3), hence the effect on the corrosion potential $E_{\text{corr},2}$ is rather small. For concentrations of NaCl higher than 3.5 M, the passive Cr surface activates spontaneously, and only one, $E_{\text{corr},2}$ is observed.

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ИЗВОД

УТИЦАЈ ХЛОРИДНИХ ЈОНА НА ПОТЕНЦИЈАЛ ОТВОРЕНОГ КОЛА ХРОМА У ДЕАЕРИСАНИМ РАСТВОРИМА СУМПОРНЕ КИСЕЛИНЕ

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Мерења потенцијала отвореног кола, као и мерења применом цикличне волтаметрије у деаерисаним воденим растворима H_2SO_4 , рН 1, без и са додатком NaCl у концентрационом опсегу 0,5–4 М, открила су да хром показује два стабилна потенцијала отвореног кола који имају особине Wagner–Traud-овог корозионог потенцијала. Један корозиони потенцијал, $E_{\text{corr},1}$, се успостављао на пасивираној површини, која се формира претходним излагањем Cr ваздуху, или потенциостатским пасивирањем на контролисан начин, а други, $E_{\text{corr},2}$, се образовао на голој површини Cr која је формирана катодном активацијом у довољно дугом периоду времена. Постоји извесна мала разлика у вредностима $E_{\text{corr},1}$ као функција особина пасивног слоја. Додатак NaCl у одређеној мери убрзава реакцију издвајања водоника на пасивираној површини, док NaCl нема утицаја на исту реакцију на голој површини Cr. Са друге стране присуство NaCl убрзава анодну реакцију на голој површини хрома и активира растварање пасивног слоја, тако да се струја пасивације повећава са додатком NaCl. Утицај NaCl је толико велики, да при концентрацијама већим од 3 М, разарање пасивног слоја постаје брзо, да се Cr за време од неколико секунди активира и тада се уочава само један стабилни корозиони потенцијал $E_{\text{corr},2}$. Није уочена појава питинга у присуству NaCl, све до потенцијала у транспасивној области.

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