



Cathodic film formation during chromium electrolysis on low-carbon steel using short duration current steps

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Abstract

Short duration galvanostatic electrolyses of chromium plating solutions (1.0 M CrO₃ and 0.01 M H₂SO₄) were performed on rotating disk electrode of low-carbon steel. The influence of sulphate concentration (0.01 and 0.02 M), cathodic current density (30, 60 and 90 A dm⁻²), temperature (25, 40 and 55 °C), electrode rotation rate (25 to 1000 rpm) and Na₂SiF₆ addition (0.01 M) on *E/t* curves and cathodic current efficiency was investigated. Electrical charge was always consumed to form a cathodic film and effective metallic chromium deposition only occurred when the potential reached a low and stable value. The determination of cathodic current efficiency after short duration electrolyses corroborated these results. The time required to form the cathodic film decreased with current density and addition of Na₂SiF₆ and increased with sulphate concentration, temperature and electrode rotation rate, suggesting that this film is not completely compact. A passive film is formed at the onset of the electrolysis process and a viscous layer is formed on the surface of the first film.

1. Introduction

The characteristics of the cathodic process during the electrolysis of CrO₃ containing sulphate anions have been frequently investigated since the invention of chromium plating baths in 1920 [1]. Exact mechanisms of chromium electrodeposition, however, are still open to conjecture [2, 3]. The main difficulty is the necessary formation and presence of a cathodic film on the surface of the metal being plated. The views regarding these films can be represented by three main schools of thought. Some theories proposed that the inhibiting, amorphous oxide film on the cathode is modified or broken down by the presence of SO₄²⁻ ions so that metallic chromium can be deposited [4–6]. Others suggested that the cathodic film is a viscous colloidal complex consisting of the products of the reduction of chromic acid to the bivalent state, together with Cr⁶⁺ and SO₄²⁻ ions [7–9]. The last school of thought, represented by Japanese researchers [10], suggested that the cathodic film is composed of two layers with different thicknesses and compositions. The outer layer, referred as the liquid film, and the inner layer, as the compact film, differ in that the first film contains sulphate ions, dissolves easily in the electrolyte and is about 10 times thicker than the compact film. The second film has a mass of about 5 mg m⁻², contains very few sulphate ions and does not dissolve easily in the electrolyte.

Recently, Mandich [2] has reported that the argument as to whether the reduction of Cr⁶⁺ ions to chromium is direct or indirect developed into a discussion of whether the cathodic film is useful or not, and how it should be modified to improve the process, in as much as the existence of this film is no longer in question. Therefore, in consideration of the importance of the chromate film in the production of tin-free steel (TFS), it is important to investigate the characteristic of the electrode process during the cathodic reduction of hexavalent chromium ions from a practical standpoint. The present investigation follows this line.

The chromium-coating procedure for the manufacture of TFS calls for a special process [11, 12]. The strip passes through a number of tanks during the plating process, and the chromium coating is deposited onto the strip surface cumulatively. The applicable current density ranges from 20 to 90 A dm⁻². The part of the anode near the solution level is insulated with a shielding plate to treat the strip passing through this section at a low current density. The effective anode length is about 500 mm. Considering a line speed of 300 m min⁻¹, for instance, this means that the effective electrolysis time is just 0.1 s for each pass. Accordingly, this study was planned to analyse electrode process of seconds' duration with one or two current steps.

2. Experimental details

E/t curves during cathodic polarization at current densities of 30, 60 and 90 A dm⁻² in solutions of 1.0 M CrO₃ containing 0.01 M H₂SO₄ and Na₂SiF₆ (0 and 0.01 M) were obtained by galvanostatic method using a potentiostat/galvanostat (PAR 273A) and the Headstart program. The experiments were carried out on a low-carbon steel rotating disc electrode using a Pine Instrument Electrodes motor and control unit. Electrolysis experiments were carried out at four different rotation rates ranging from 25 to 1000 rpm. The working electrode of approximately 0.34 cm² area was mounted in a PTFE holder. The surface was polished with abrasive papers up to 1000 grit. A platinum spiral wire was used as the auxiliary electrode, and a saturated calomel electrode (SCE) was utilized as the reference electrode. The experiments were conducted at 25, 40 and 55 °C. The chromium amount deposited on the electrodes was determined by coulometry in a 0.7 M Na₂HPO₄ solution, using a 0.06 A dm⁻² anodic current density. The anodic current efficiency was considered 100% for the oxidation reaction of Cr⁰ to Cr⁶⁺ [13]. In addition, some cathodic potentiodynamic polarization curves were obtained in solutions of 1.0 M CrO₃ containing H₂SO₄ (0.01–0.04 M) and Na₂SiF₆ (0 and 0.01 M) at a potential scan rate of 20 mV s⁻¹.

3. Results and discussion

Figure 1 shows the cathodic polarization curves obtained in a 1.0 M CrO₃ and 0.01 M H₂SO₄ solution at 25 °C for 25, 500 and 1000 rpm rotation rates. The current density of the first peak increases with an increase of the rotation rate and a slight shift of the peak potential in the negative direction is observed. A second peak, not clearly defined, appears at nearly -0.85 V.

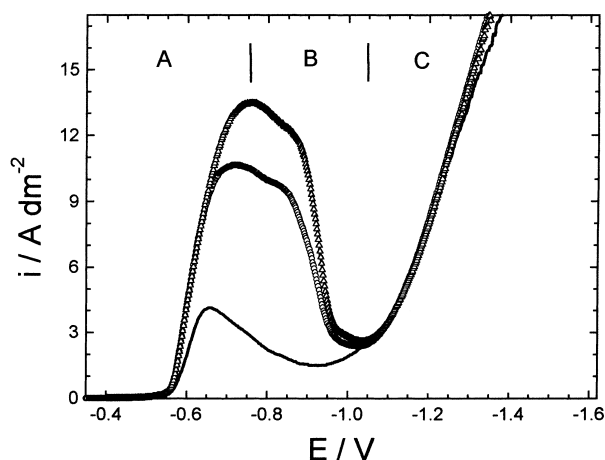


Fig. 1. Cathodic polarization curves obtained on low-carbon steel rotating disc electrode in a solution of 1.0 M CrO₃ and 0.01 M H₂SO₄ at 25 °C (20 mV s⁻¹). Rotation rates: (—) 25, (—○—) 500 and (···△···) 1000 rpm.

This polarization curve can be divided in three parts [14]. The first one (A) is associated to the reduction of Cr⁶⁺ to Cr³⁺ and the beginning of cathodic film formation. It is followed by the B region where H₂ evolution begins to occur and stops where the cathodic film is completely formed on the surface. The third region C is attributed to Cr⁶⁺ reduction, H₂ evolution and chromium deposition.

Figure 2 shows E/t curves of low-carbon steel electrode in a 1.0 M CrO₃ and 0.01 M H₂SO₄ solution at 25 °C obtained at 30 A dm⁻² cathodic current density with three electrode rotation rates: 25, 500 and 1000 rpm. In this current step, the electrolysis time was 1 s. The current density starts at zero and reaches 30 A dm⁻² with a current sweep rate of 3000 A dm⁻² s⁻¹ (i.e., in 0.01 s). No influence of the electrode rotation rate was observed. There was not an instantaneous potential drop to the chromium deposition region, but an arrest at a potential of about -1.3 V was observed before gradually reaching a stable potential at -1.55 V in 0.28 s. In order to define the beginning of chromium deposition, similar experiments were carried out using shorter electrolysis times, and the cathodic efficiency of the process was determined.

E/t curves for electrolysis times of 0.05, 0.10, 0.20 and 0.50 s using the same experimental conditions as above and 500 rpm rotation rate are presented in Figure 3(a). All E/t curves have the same form, but only the last one reached the stable potential of chromium deposition. E/t curves obtained in chromium anodic stripping after the electrolysis experiments are shown in Figure 3(b). The presence of deposited metallic chromium during the 0.5 s electrolysis is corroborated by the characteristic potential step of chromium anodic dissolution at nearly 0.64 V. The cathodic efficiency was about 12.4%. This value was lower than that obtained for the 1.0 s electrolysis (20.6%). However, the efficiencies of both experiments (0.5 and 1.0 s) give comparable values (about 28%) when the time spent (0.28 s) for the formation of the cathodic film is excluded from the

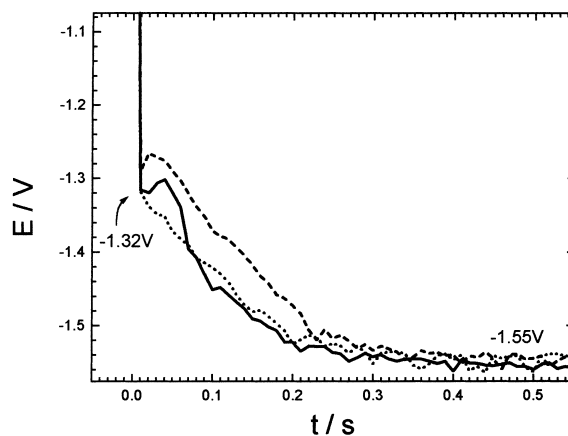


Fig. 2. E/t curves at low-carbon steel rotating disc electrode in a solution of 1.0 M CrO₃ and 0.01 M H₂SO₄ (30 A dm⁻², 1 s, 25 °C). Rotation rates: (—) 25, (- - -) 500 and (·····) 1000 rpm.

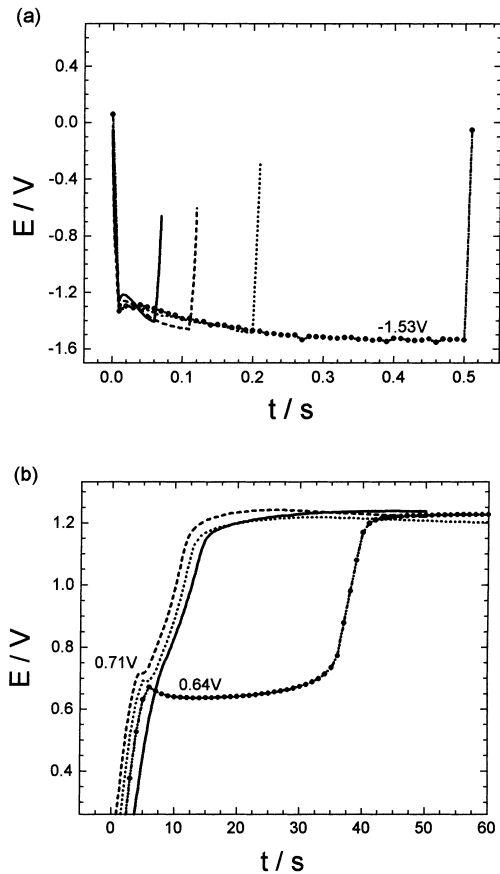


Fig. 3. (a) E/t curves at low-carbon steel rotating disc electrode in a solution of 1.0 M CrO_3 and 0.01 M H_2SO_4 (30 A dm^{-2} ; 0.05, 0.10, 0.20, 0.50 s; 25°C). Rotation rate: 500 rpm. (b) E/t curves obtained in the chromium anodic dissolution. Key: (—) 0.05, (- - -) 0.10, (· · · · ·) 0.20 and (●—●) 0.5 s.

calculation. On the other hand, E/t curves obtained for 0.1 and 0.2 s experiments showed only a short potential arrest at potential value above the chromium dissolution potential (0.64 V), indicating that no or very little metallic chromium had been deposited. No arrest was observed for the 0.05 s experiment. From these results it was deduced that effective chromium deposition only occurs when the potential reaches a low and stable value of nearly -1.55 V .

Figure 4 shows E/t curves for low-carbon steel electrode in 1 M CrO_3 and 0.02 M H_2SO_4 at 25°C for 500, 750 and 1000 rpm rotation rates during cathodic polarization at 30 A dm^{-2} current density. The potential moves initially in the negative direction until -1.35 V and returns to the positive direction at nearly -1.0 V . This behaviour is typical of a nucleation process, and suggests the formation of a compact film. Then, the potential stabilizes at -1.0 V where the cathodic film forms. The time that the potential remains at -1.0 V increases with an increase of electrode rotation rate. This observation seems to confirm the existence of the liquid film whose behaviour depends on the hydrodynamic condition of the electrode and solution. Metallic chromium only deposits at the lowest potential (about -1.6 V). The current

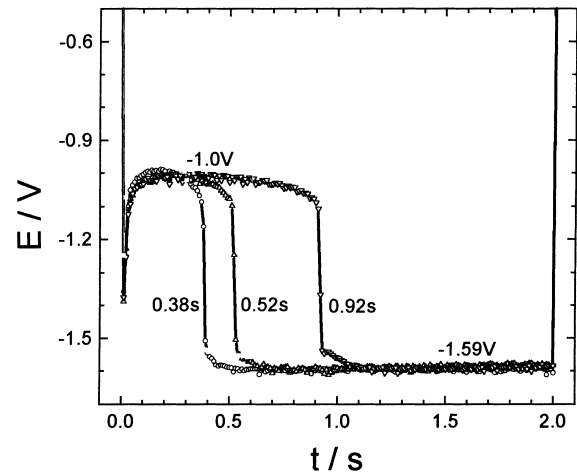


Fig. 4. E/t curves at low-carbon steel rotating disc electrode in a solution of 1.0 M CrO_3 and 0.02 M H_2SO_4 (30 A dm^{-2} ; 25°C). Rotation rate: (—○—) 500, (—△—) 750 and (—▽—) 1000 rpm.

efficiency decreases with the increase of rotation rate, 19.1, 17.6 and 12.0% for 500, 750 and 1000 rpm, respectively. When the time required for the formation of cathodic film (at about -1.0 V) is not considered for the calculation, the efficiencies are nearly the same (22.2 to 23.6%). The comparison of these results with those obtained in solutions with 0.01 M H_2SO_4 (Figure 2) shows that an increase of sulphate content increases the time required to form the cathodic film. An increase of sulphate concentration would turn difficult its formation.

E/t curves obtained with two current steps of 30 A dm^{-2} and 0.1 s duration separated by a 0.4 s null-current step are shown in Figure 5(a). This current cycle simulates the process of the first and second passes of a continuous line with 300 m min^{-1} speed. The solution was 1 M CrO_3 and 0.01 M H_2SO_4 and the electrode rotation rates were 25 and 500 rpm. The gradual potential drop observed in the first pass is likely due to the reduction of oxide film formed spontaneously on the metal when exposed in air before immersion and when the metal is immersed in the bath. In this pass, no or very little metallic chromium is deposited as observed from the experiments above (Figure 3). During the null-current step a new passivating chromium oxide is formed but its lower electrical resistivity allows, in the second pass, the formation of the cathodic film at a stable potential of about -1.2 V and a rapid potential drop to the chromium deposition region. From Figure 5 the influence of the electrode rotation rate is evident. For the highest rate, the time required to deposit chromium is higher (Figure 5(a)) and consequently, for the same electrolysis conditions, the amount of deposited chromium is lower (Figure 5(b)). This suggests that the cathodic film may not be completely compact and may partially disperse in the bath with high rotation rate. The existence of a cathodic film consisting of a duplex (compact and liquid) film has previously been considered [10].

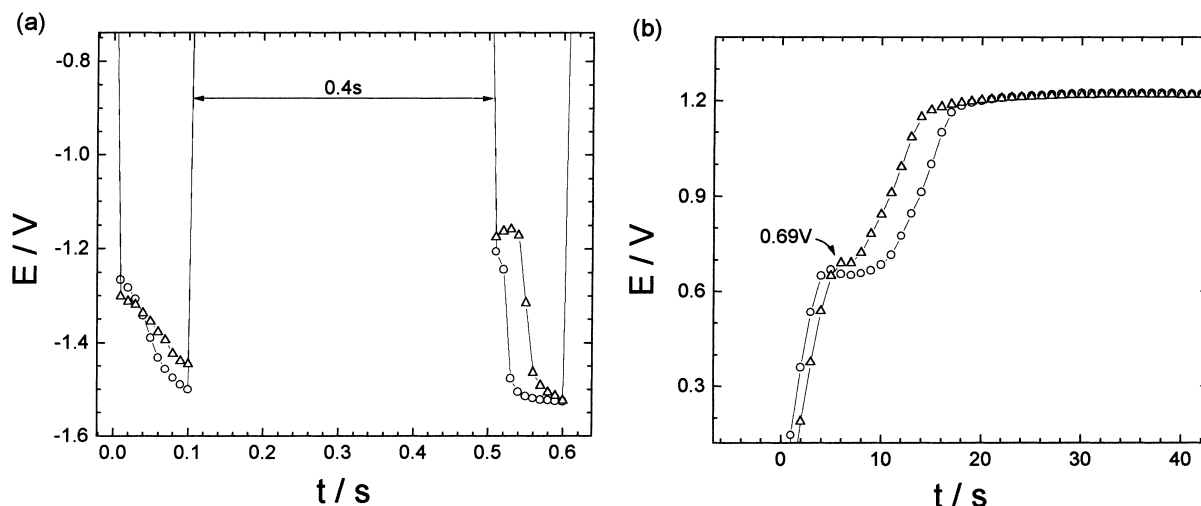


Fig. 5. (a) E/t curves at low-carbon steel rotating disc electrode in a solution of 1.0 M CrO_3 and 0.01 M H_2SO_4 (30 A dm^{-2} , two steps of 0.1 s, 25°C). Rotation rates: (—○—) 25 and (—△—) 500 rpm. (b) E/t curves obtained in the chromium anodic dissolution.

The results of the experiments with higher current densities are shown in Figure 6 for 60 and 90 A dm^{-2} , and an electrode rotation rate of 500 rpm. E/t curves have the same form, but the cathodic film formation time decreases with an increase of current density and is shorter than for 30 A dm^{-2} experiment in both steps. For these higher current densities, the chromium deposition potential was reached in the first pass whereas this did not occur with 30 A dm^{-2} (Figure 5(a)). In spite of high current densities used in these experiments, the time necessary for the formation of the cathodic film in the first pass (about 0.05 s) was very close to one electrolysis pass time of a continuous coating line operating at 500 m min^{-1} (0.06 s). When the chromium deposition was not reached in the first pass, the chromium deposit obtained during the following passes tended to present oxidation stains. The appearance of

such stains is one of the main problems in the manufacture of tin-free steel. The current efficiencies were 21.5 and 25.9% for 60 and 90 A dm^{-2} , respectively, higher than the value obtained for 30 A dm^{-2} in the same condition.

The results of the experiments at higher temperatures (40 and 55°C) are shown in Figure 7(a) for the same chromium plating solution as above, and for a current density of 60 A dm^{-2} . An electrolysis time is required to reach the chromium deposition potential, and the potential drop is gradual for all temperatures in the first pass. The current efficiency values were 21.5, 13.5 and 11.5% for 25, 40 and 55°C , respectively (see Figure 7(b) for chromium anodic dissolution). The main reason for this great difference is the electrical charge consumed to reach the potential of chromium deposition in the first pass. This difference diminishes when

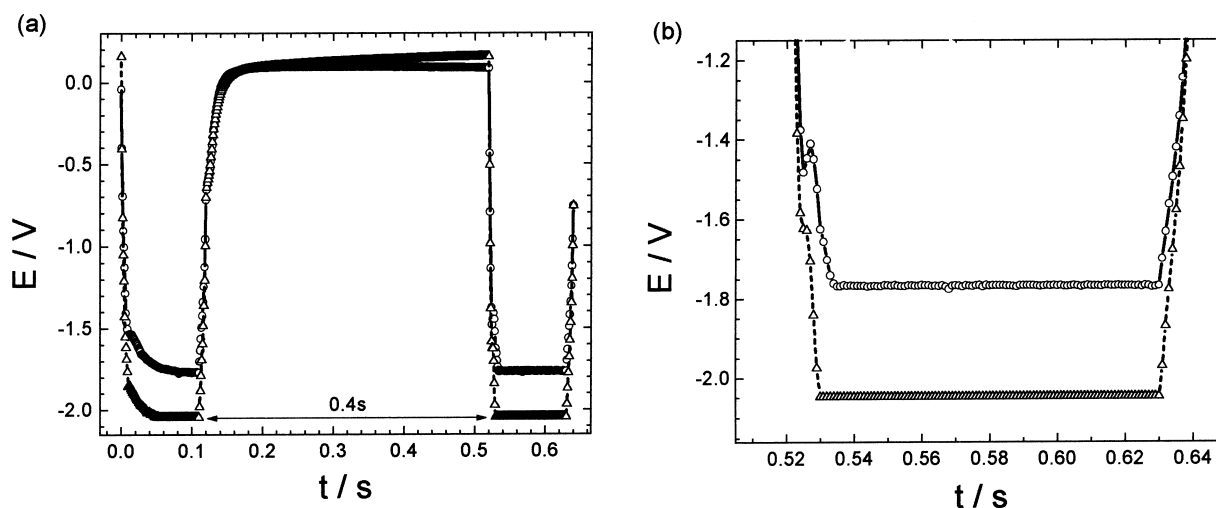


Fig. 6. (a) E/t curves at low-carbon steel rotating disc electrode in a solution of 1.0 M CrO_3 and 0.01 M H_2SO_4 (60 and 90 A dm^{-2} , two steps of 0.1 s, 25°C). Rotation rate: 500 rpm. (b) is an enlargement of the second pass of (a). Key: (—○—) 60 and (- - -△- -) 90 A dm^{-2} .

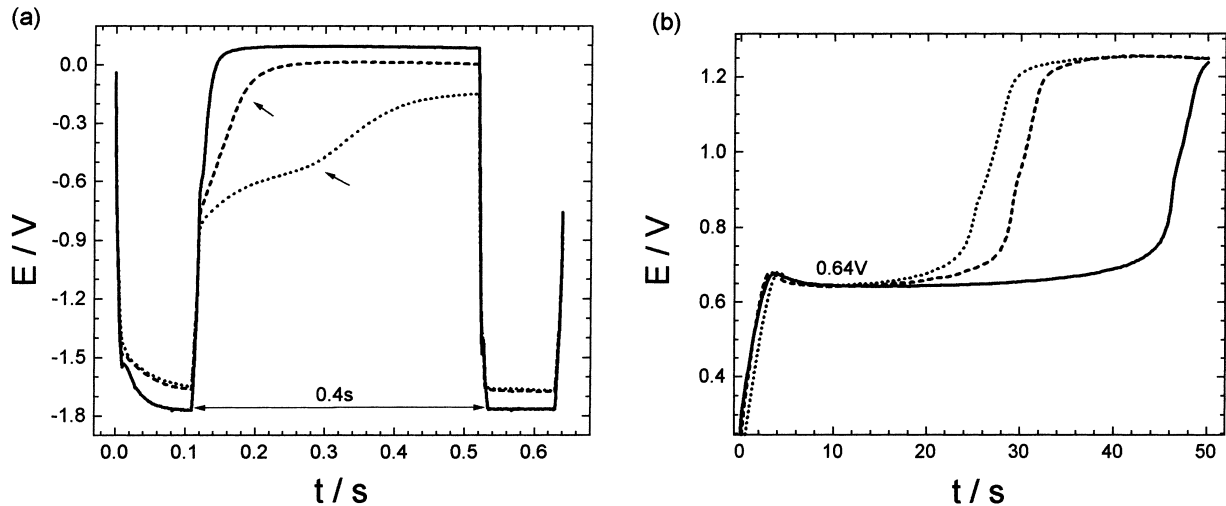


Fig. 7. (a) E/t curves at low-carbon steel rotating disc electrode in a solution of 1.0 M CrO_3 and 0.01 M H_2SO_4 (60 A dm^{-2} , two steps of 0.1 s, 25, 40 and 55 °C). Rotation rate: 500 rpm. (b) E/t curves obtained in the chromium anodic dissolution. Key: (—) 25, (---) 40 and (·····) 55 °C.

larger electrolysis time is used, but a decrease of current efficiency is always observed with an increase of temperature. For example, for 1 s electrolysis in the same condition, efficiencies of 26.2, 22.9 and 20.1% were measured for 25, 40 and 55 °C, respectively. This behaviour can be due to the competitive reaction of H_2 evolution. The rate of H_2 formation increases faster than that of chromium deposition with the increase of temperature. Consequently, the cathodic efficiency decreases [15]. Another explanation could be the increase of the dissolution rate of the cathodic film with the increase of the temperature [16]. The relative chromium amount deposited on the electrodes in the first pass could also be appreciated by the forms of E/t curves in Figure 7(a) during the null-current step. A large potential arrest before reaching a more positive stable potential was observed during the null-current step for the higher temperatures (see arrows on Figure 7(a)). This curve behaviour is probably a consequence of the attack, by the solution, of the electrode surface where no chromium was deposited. The shift of potential in the more positive direction is more rapid when the surface is completely covered with chromium [17].

E/t curves obtained in solution of 1.0 M CrO_3 , 0.01 M H_2SO_4 and 0.01 M Na_2SiF_6 for 30, 60 and 90 A dm^{-2} and a 500 rpm electrode rotation rate are shown in Figure 8. The electrolysis times required to reach the chromium deposition potential were shorter in this solution than that observed in the solution without addition of Na_2SiF_6 (see Figures 2 and 6(a)). A reason is probably the pickling effect of Na_2SiF_6 containing solution on controlling the dissolution of the oxide film when the electrode is immersed in this solution. An other reason might be the nature of the cathodic film formed in this solution. Hoare et al. [18] observed that, in conventional plating from a fluoride-catalysed bath, a viscous cathodic film could not be detected at the cathode surface, in contrast to that observed in sulphate-catalysed baths. It is believed that the

HF-polychromate complex films are much less viscous than the HSO_4^- -polychromate complex films. The addition of Na_2SiF_6 in industrial chromium coating lines is considered essential in order to avoid the appearance of oxidation stains. It is probable that in baths containing Na_2SiF_6 , the formation of metallic chromium is so rapid that chromium is deposited in the first pass even with high speed continuous lines.

4. Conclusions

In the galvanostatic chromium electrodeposition process, the potential drops gradually in the negative direction and effective chromium deposition only occurs after a certain electrolysis time in a low and stable potential region. This time is reduced when high

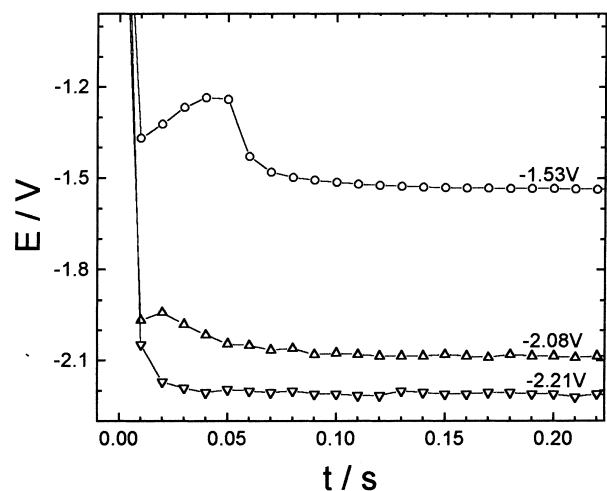


Fig. 8. E/t curves at low-carbon steel rotating disc electrode in a solution of 1 M CrO_3 , 0.01 M H_2SO_4 and 0.01 M Na_2SiF_6 (30, 60 and 90 A dm^{-2} , 0.5 s, 25 °C). Rotation rate: 500 rpm. Key: (—○—) 30, (—△—) 60 and (—▽—) 90 A dm^{-2} .

cathodic current densities are applied, but increases when higher temperatures or high sulphate concentrations are used. Using two-step current experiments, a correlation was found between this time and the electrode rotation rate in the second step. The cathodic film formation was characterized by a potential arrest and rapid potential decay to the chromium deposition potential. The time required to form metallic chromium increases with an increase of electrode rotation velocity suggesting that this film is not completely compact. The Na_2SiF_6 addition in chromium plating solutions reduced the electrolysis time for the cathodic film formation.

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