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Chromium coating on partially tin precoated steel sheet

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Controlling the amount of chromium to be deposited on tin and iron substrates is important for the production of special steel sheet for welded can material, partially tin precoated and then fully coated with chromium. The deposition behaviour of chromium on tin and iron substrates was studied by means of the polarization behaviour of tin and iron in a chromium coating bath. For stable deposition, a higher current density is required on tin than on iron due to the higher hydrogen overvoltage on tin. Ageing in air after tin coating and preliminary electrolysis under the potential range of reduction of Cr^{6+} to Cr^0 in a chromium coating bath are effective in facilitating the formation of a cathode film and encouraging the deposition. A study on a continuous coating line showed that the amount of chromium to be deposited on tin and iron can be industrially controlled by a process involving a lower current density in the first step and a higher current density in the second.

1. Introduction

Tin-striped tin-free steel (TFS) [1] has been developed as a material for welded can stock. Steel sheet is first coated with tin stripes at a constant pitch across the width on both sides and then fully coated with chromium. This new type of material for welded can stock has high-speed seam weldability and the excellent lacquered corrosion resistance of tin free steel–chromium type (TFS–CT). The coating structure of the newly developed 'Tin-striped TFS' is shown in Fig. 1.

Conventional TFS–CT for can material has chromium of $50 \sim 100\,\mathrm{mg\,m^{-2}}$ as the lower layer and chromium oxide of $10 \sim 20\,\mathrm{mg\,m^{-2}}$ as the upper layer [2]. Different from the good corrosion-resistant, thick coating of chromium required for parts used with no post treatment, the coated layer of TFS–CT is required to have good formability and lacquer adhesiveness. This is the reason why a rather thin coating weight is preferred. To ensure quality equivalent to that of conventional TFS–CT, a chromium amount of about $100\,\mathrm{mg\,m^{-2}}$ on iron, and about $50\,\mathrm{mg\,m^{-2}}$ on tin is suitable to obtain high-speed weldability and lacquered corrosion resistance [3]. So the commercial production of tin-striped TFS calls for the technique of depositing different amounts of chromium on tin and iron at the same time.

Chromium ions in the coating bath are mainly hexavalent and are reduced to chromium in the steps $Cr^{6+} \rightarrow Cr^{3+} \rightarrow Cr^{2+} \rightarrow Cr^0$ through the cathode film formed in the electrolytic process [4].

The effect of the substrate on the reduction potential of $Cr^{6+} \rightarrow Cr^{3+}$ aq. (corresponding to peak II in Fig. 2) has been discussed [5]. However, the effects of the substrate, oxide film and preliminary electrolysis in the chromium plating solution on the electric current at the deposition potential of chromium (corresponding to peak IV in Fig. 2) are not well known. The effect of these variables was studied by observation of the cathodic polarization behaviour of tin and iron in the chromium coating bath.

The basic findings were then extended to the technique of commercial tin-striped TFS production on a continuous coating line.

2. Methods

2.1. *Samples for electrochemical study*

Blackplate, tinplate and pure tin sheet were used as materials. The blackplate was of continuously cast aluminium killed steel. It was cold rolled, continuously annealed, temper rolled to T-4CA hardness, alkaline electrolytically cleaned and immersion pickled before polarization measurements. Tinplate was prepared by coating $2.8\,\mathrm{g\,m^{-2}}$ tin on blackplate mentioned above in a Ferrostan bath [6]. Pure tin sheet was polished and immersion pickled just before the polarization measurements. The tinplate and pure tin sheet were left in air to form oxide films, if necessary.

2.2. *Polarization measurements*

The cathodic polarization characteristics of the materials were measured in a conventional chromium coating bath (CrO_3 $185\,\mathrm{g\,dm^{-3}}$, Na_2SiF_6 $4.8\,\mathrm{g\,dm^{-3}}$, H_2SO_4 $0.65\,\mathrm{g\,dm^{-3}}$, Cr^{3+} $5\,\mathrm{g\,dm^{-3}}$). The bath temperature was 45° C, and the solution was gently agitated. The materials ($1\,\mathrm{cm^2}$) were cathodically polarized under $50\,\mathrm{mV\,s^{-1}}$, unless otherwise specified.

2.3. *Tin and chromium coating on continuous line*

The steel strip was 0.22 mm thick by 200 mm width with the same material characteristics as the blackplate used for electrochemical study. On a vertical

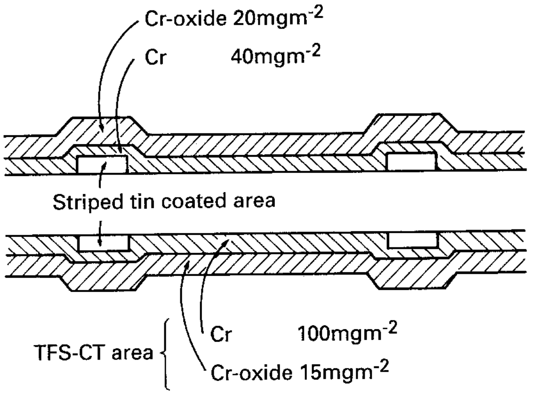


Fig. 1. Schematic model of 'tin-striped TFS'.

type continuous electroplating line, the steel strip was coated with tin stripes in the Ferrostan bath and with chromium in the conventional chromium bath mentioned above. The period between tin and chromium coating was about 3 h. For chromium coating, electrodes for three tanks (six passes) were prepared. The c.d. was set lower in the first four passes and higher in the last two. If necessary, current can be eliminated on the fifth pass.

2.4. *Determination of Cr amount*

Chromium amount was determined by coulometry in a 5% NaOH solution for the TFS part and in a 0.1 M Na_2HPO_4 solution for the tin part.

3. Results and discussion

A cathodic polarization plot of platinum sheet in a chromium coating bath is shown in Fig. 2 [7]. The polarization curve can be divided into four regions according to the nature of the reaction involved [8].

Peak 1; reduction of oxide film on substrate; peak II; $Cr^{6+} \rightarrow Cr^{3+}$; peak III; $Cr^{6+} \rightarrow Cr^{3+}$, $H^+ \rightarrow H_2$; peak IV; $Cr^{6+} \rightarrow Cr^{3+}$, $H^+ \rightarrow H_2$, $Cr^{6+} \rightarrow Cr^0$ (deposition of chromium).

Chromium is often deposited by controlling the applied current. The current density (c.d.) adopted in this case is equivalent to that of peak IV (larger than maximum value of region III).

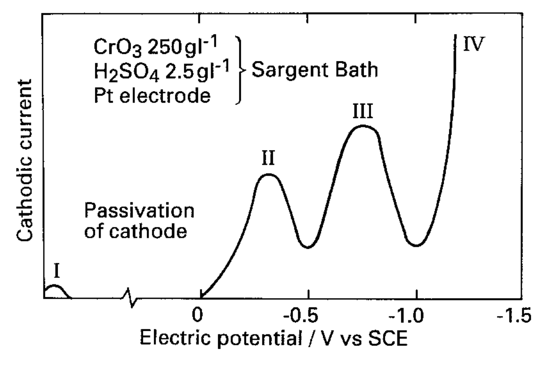


Fig. 2. Cathodic polarization curve of platinum sheet in chromium coating bath [5].

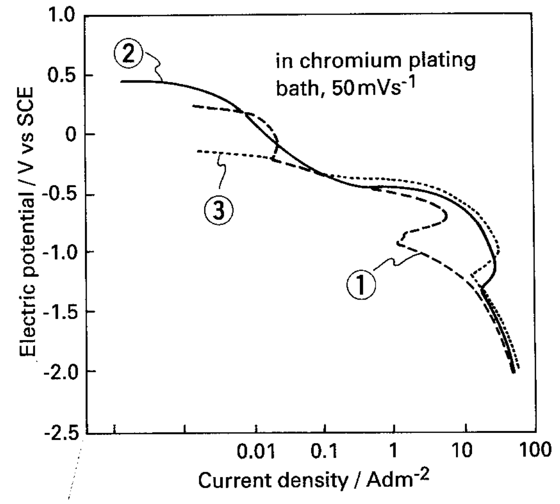


Fig. 3. Cathodic polarization curves in chromium coating bath. (1) Cold rolled steel sheet. (2) Tin-coated steel sheet (2.8 g dm^{-2} after 3 h from coating). (3) Pure tin (immediately after pickling).

3.1. *Effect of substrate*

Figure 3 shows the cathodic polarization curves of blackplate, tinplate and pure tin sheet in a chromium coating solution. Although peaks corresponding to peaks I and II in Fig. 2 are not clear, peak III is observed between −0.5 and −1.0 V. Peak III on iron is small, and the maximum c.d. is a little under 10 A dm^{-2}. Peak III on tin is large, and the maximum c.d. is about 40 A dm^{-2}. The transition potential from peak III to IV on tin is lower than on iron. These characteristics of tin are observed for both the tinplate and pure tin sheet.

3.2. *Deposition of chromium at peaks III and IV*

Figures 4 and 5 show deposition efficiency of chromium determined when the blackplate and tinplate were potentiostatically electrolyzed at peaks III and IV. Chromium is not substantially deposited on iron and tin at peak III, but is deposited at peak IV with efficiency comparable to that of conventional

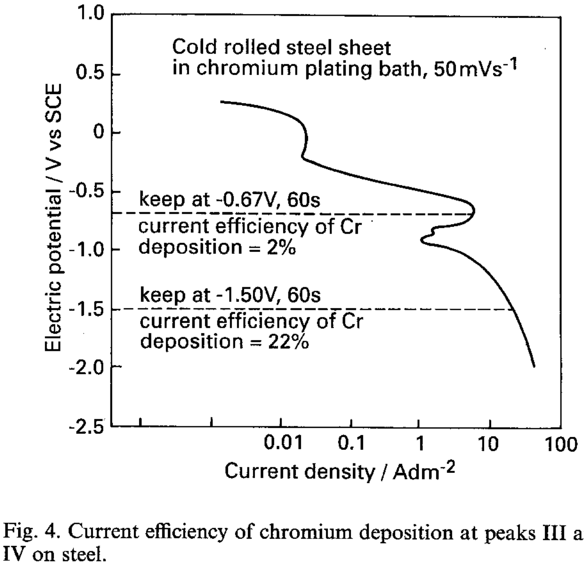


Fig. 4. Current efficiency of chromium deposition at peaks III and IV on steel.

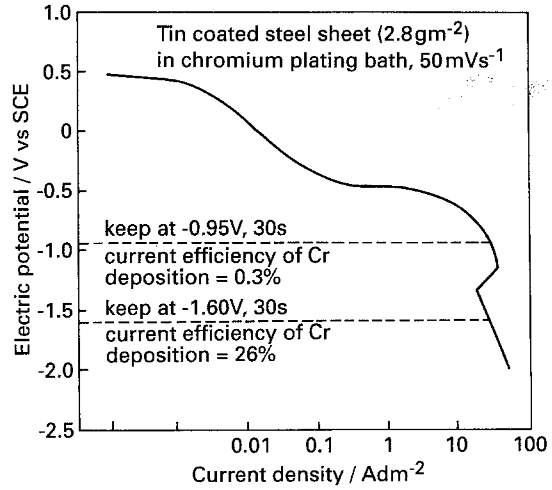


Fig. 5. Current efficiency of chromium deposition at peaks III and IV on tin coated steel.

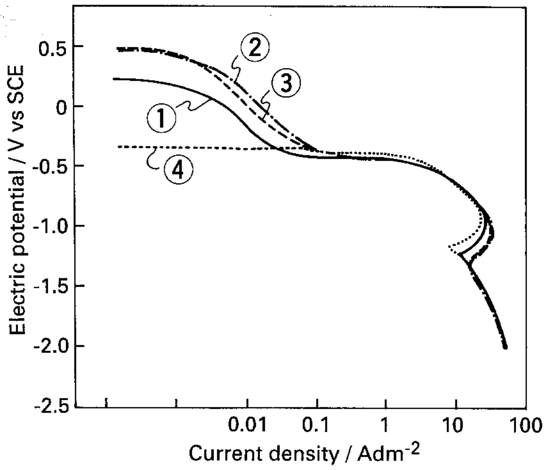


Fig. 7. Effect of ageing time on cathodic polarization curve of tin coated steel in chromium coating bath. Tin coated steel sheet (2.8 g m^{-2}) in chromium plating bath (50 mV s^{-1}). (1) — 20 min after tin coating; (2) -·-·- 3 h after tin coating; (3) ---- 72 h after tin coating; (4) ----- immediately after pickling.

chromium coating. The deposition of chromium on tin was confirmed first at a potential in the peak IV region. This fact agrees with the analysis result of the film formed by cathodic polarization of tin sheet in CrO_3–H_2SO_4 bath by ESCA [9].

Chromium may be deposited or not on tin substrate depending on the potential at c.d. of 30 A dm^{-2}, but a stable deposition of chromium takes place on iron. This is a noteworthy finding from the practical viewpoint and suggests that a higher c.d. than the maximum in region III is required to avoid the non-deposition phenomenon.

The difference of the hydrogen overvoltage is considered mainly responsible for the less noble potential of peak IV on tin than on iron. The hydrogen overvoltage is 0.08 V for iron and is 0.45 V lower or 0.53 V for tin [10]. The higher the hydrogen overvoltage, the less hydrogen gas evolution is likely to occur during cathodic polarization and the less the pH of the solution near the substrate surface is likely to rise. The cathodic film formed in the chromium coating process is that of a hydrated polymeric oxide mainly composed of trivalent chromium [11]. The rise in solution pH near the surface is considered essential for forming and maintaining the cathode film. It is postulated that the formation of the cathode film on tin is retarded by the delay in pH rise of the solution near the surface. In Fig. 3, the potential at which c.d. drop starts at peak III differs by about 0.5 V between iron and tin. This difference supports the above discussion.

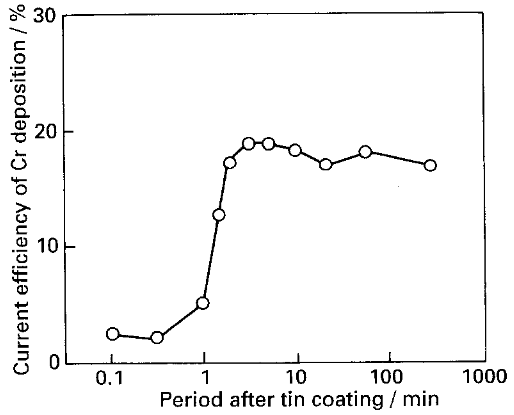


Fig. 6. Effect of ageing time on current efficiency of chromium deposition on tin. Tin coating 2.8 g m^{-2}; chromium coating 50 A dm^{-2} × 1 s, 45 °C static bath. In air at room temperature.

3.3. *Effect of ageing after tin coating*

Tin-striped TFS is made by first coating steel with tin stripes, then coating with chromium. The effect of ageing time from tin coating to chromium coating on the deposition of chromium is shown in Fig. 6. Chromium is hardly deposited within 1 min after tin coating and deposits stably a few minutes later. The deposition of chromium on tin just after pickling is difficult, even if the sample is left to stand for a few minutes after tin coating. It was confirmed, however, that chromium can be deposited on tin just after pickling, if the c.d. is raised to about 80 A dm^{-2}.

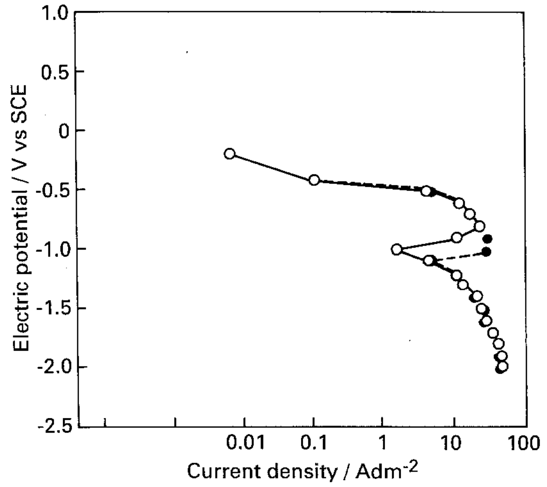


Fig. 8. Effect of ageing time on cathodic polarization curve of tin coated steel in chromium coating bath (potentiostatic method). Tin coated steel sheet (2.8 g m^{-2}) in chromium plating bath (potentiostatic). (1) ○—○ 24 h after tin coating; (2) ●—● immediately after pickling.

The effect of ageing time after tin coating on cathodic polarization characteristics was investigated. The results are shown in Figs 7 and 8. For the convenience of experiment, pickling just before chromium coating substituted for no-ageing after tin coating. In Fig. 7, the immersion potential becomes more noble with ageing, probably under the influence of surface oxidation of tin. With potential sweep, the polarization curves of samples left to stand in air after tin coating approach the polarization curve of the sample pickled just before this measurement and show almost identical behaviour when the c.d. exceeds 0.1 A dm^{-2}. As the polarization curves approach and meet starting from the immersion potential, the surface oxide layer changes. When the polarization curves reach the peak III and IV regions, the effect of ageing after tin coating is considered to have disappeared.

The potential reaches the desired electrolytic potential in about 0.1 s in the commercial chromium coating process, so that it is inappropriate to study the effect of the surface oxide layer by the slow potential sweep method. For this reason, as shown in Fig. 8, an attempt was made to change the potential stepwise by the potentiostatic polarization method, measure the current of each step with a fresh sample, and connect the measured points to draw a polarization curve. In the potential region of 0 to −0.5 V, where the surface oxide layer is reduced, there are no large differences between the samples. The transition potential from peak III to IV is higher for the sample left to stand in air for one day after tin coating. Since the cathode film readily forms, chromium deposition readily proceeds. This supports the results shown in Fig. 6.

Ageing after tin coating is mainly significant in the formation of tin oxide on the surface. The reason why the formation of the cathode film is facilitated more on tin oxide than on tin will be discussed later.

At a potential less noble than the maximum current potential of peak III in CrO_3 solution containing sulphuric acid, oxides containing Sn^{2+} and Sn^{4+} in equal proportions are considered to be formed on tin [9]. The cathode film formed on tin is considered to have the structure $Sn{-}O{-}Cr^{3+}$ in peak III region and is assumed to lead to the deposition of chromium in the peak IV region. If the structure of tin oxide formed during ageing after tin coating contributes to the formation of the above structure, the presence of the tin oxide film explained in Figs 6 to 8 may possibly promote the formation of the cathode film.

3.4. *Effect of preliminary electrolysis in Cr coating bath*

When chromium is coated on a tin surface in a continuous line, multiple passes are used in many cases. To understand the phenomena that occur in the second and subsequent passes, it is important to investigate the cathodic polarization characteristics after preliminary electrolysis.

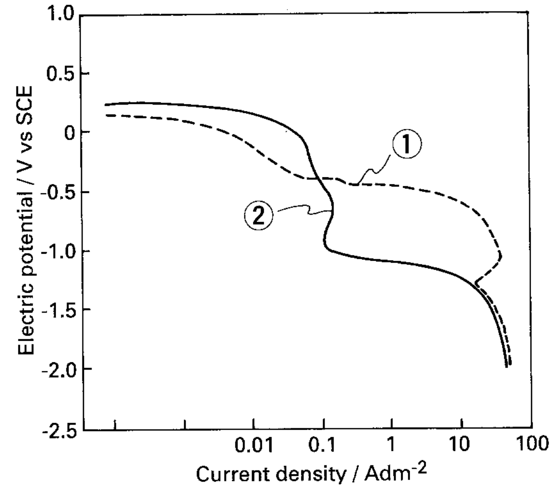


Fig. 9. Effect of chromium predeposition on cathodic polarization curve of tin coated steel in chromium coating bath. Tin coated steel sheet (2.8 g m^{-2}) in chromium plating bath (50 mV s^{-1}). (1) As-tin coated; (2) after cathodic polarization to −2.0 V (deposited chromium ~ 1 g m^{-2}).

As an extreme case, tin-coated steel was cathodically polarized to −2.00 V to deposit about 1.0 g m^{-2} of chromium and was again cathodically polarized. The results are shown in Fig. 9. The huge peak III peculiar to tin is lost, indicating that chromium is coated with extreme stability. This agrees with the phenomenon in which peak III does not appear for chromium with high hydrogen overvoltage, because peak III overlaps the next peak IV [12].

Figure 10 shows the results obtained when preliminary electrolysis was performed for a short time in the peak III and peak IV regions. When the samples are electrolysed before chromium coating in the peak III region ((2) and (3) in Fig. 10), the cathode film is more difficult to form than with the as-tin coated sample. There is a possibility that the cathode film may be broken due to dissolution or hydrogen generation in the process, during which the sample is again swept from the immersion potential to a less noble potential after the formation of the cathode film containing Sn^{4+} and Sn^{2+}. When the samples are electrolyzed before chromium coating in the peak IV region ((4) and (5) in Fig. 10), the cathode film forms more readily with increasing time of the preliminary electrolysis at which chromium is considered to deposit.

3.5. *Technique for controlling the amount of Cr on iron and tin*

The difference in electrochemical characteristics of iron and tin in the chromium coating bath are due to the difference in the maximum value of peak III as shown in Fig. 3. At a c.d. of a few tens of A dm^{-2}, the reaction on tin proceeds only in the peak III region and chromium does not readily deposit. Utilizing this characteristic, an attempt was made to deposit chromium only on iron in the first step of the chromium coating process and to freely control the chromium amount by adjusting the

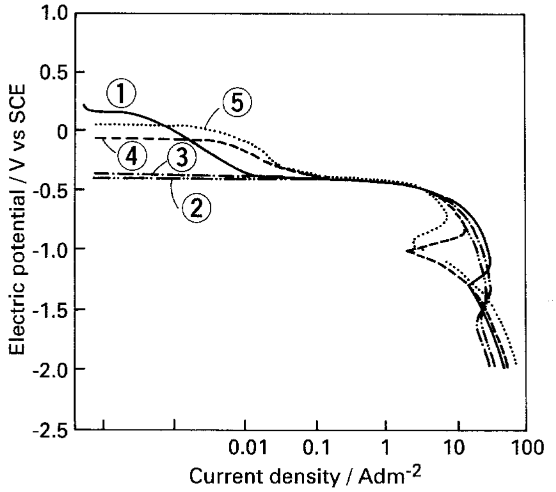


Fig. 10. Effect of preliminary electrolysis on cathodic polarization curve of tin-coated steel in chromium coating bath. Tin coated steel sheet (2.8 g m^{-2}) in chromium plating bath (50 mV s^{-1}). (1) — As-tin coated; (2) –··– after preelectrolysis at −0.9 V × 1 s; (3) –·– after preelectrolysis at −0.9 V × 3 s; (4) ---- after preelectrolysis at −1.4 V × 2 s; (5) ----- after preelectrolysis at −1.4 V × 3 s.

distribution of current between the first and last steps.

3.5.1. Study of maximum c.d. during lower c.d. electrolysis. Although electrolysis at lower c.d. is designed to deposit chromium on iron alone in the first step, application of as high a c.d. as possible is preferred from the viewpoint of productivity.

Figure 11 shows the maximum c.d. at which no chromium is deposited on tin. The upper limit is about 30 to 40 A dm^{-2}, with the value being dependent on the line speed (or current application time per pass).

The reason for the dependence on time per pass was investigated. With the application of current, the cathode film is formed, and deposition of chromium is initiated. As soon as the deposition is started, it should proceed at an increasing rate (because peak III is very small on chromium), if the electrolysis is suspended before the deposition of chromium, the cathode film deposited up to then is dissolved again. The upper limit of c.d. is thus considered to be affected by the electrolysis time [13].

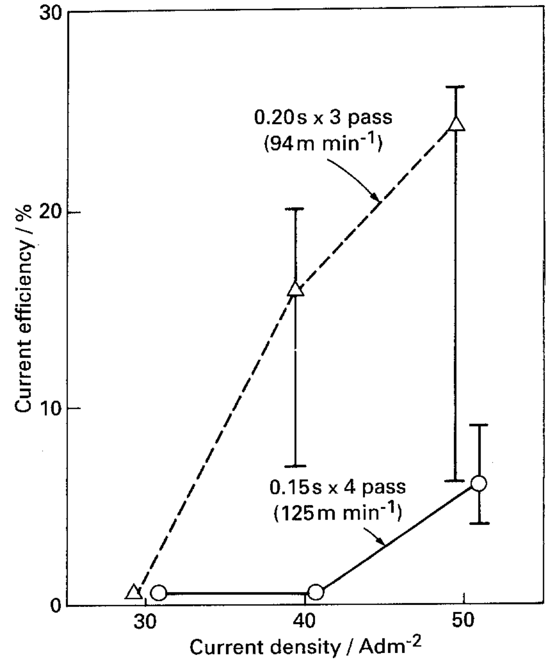


Fig. 11. Effect of current density of chromium coating on chromium deposition efficiency on tin.

3.5.2. Study of minimum c.d. during higher c.d. electrolysis. Higher c.d. electrolysis in the last step is designed to deposit chromium stably on the entire surface. Minimum c.d. in the step was studied. The results are given in Table 1. The horizontal bars in the right-hand column indicate the current efficiency variations among three points across the width of the steel sheet.

According to tests 8 to 12, it is reasonable to think that the lower limit of c.d. in the higher c.d. region is 100 A dm^{-2}. A c.d. of 80 A dm^{-2} or lower destabilizes the deposition of chromium or causes chromium non-coating.

The difference in the chromium amount of about 30 mg dm^{-2} on iron and on tin in test 1 (involving lower c.d. electrolysis only) is maintained after the last step (electrolysis in the third tank in Table 1) on other test samples. This result attests to the validity of this proposed technique.

Comparison of tests 2 to 4 with tests 5 to 7 shows that a 'no-current pass' (immersion pass; down pass at third tank in Table 1) between the first and last steps can reduce the variations in the amount of chromium deposited on tin. As described in Section 3.4, when preliminary electrolysis is performed in the peak III region, the peak III region expands in the subsequent electrolysis step to retard the deposition of chromium. On the other hand, when a no-current pass is provided, the cathode film formed by preliminary electrolysis in the peak III region is dissolved to facilitate the stable deposition of chromium in the subsequent step.

When higher c.d. electrolysis is performed in a single pass, as in test 13, on the other hand, the chromium amount is practically the same for the entire surface, and fails to meet the purpose of the present study.

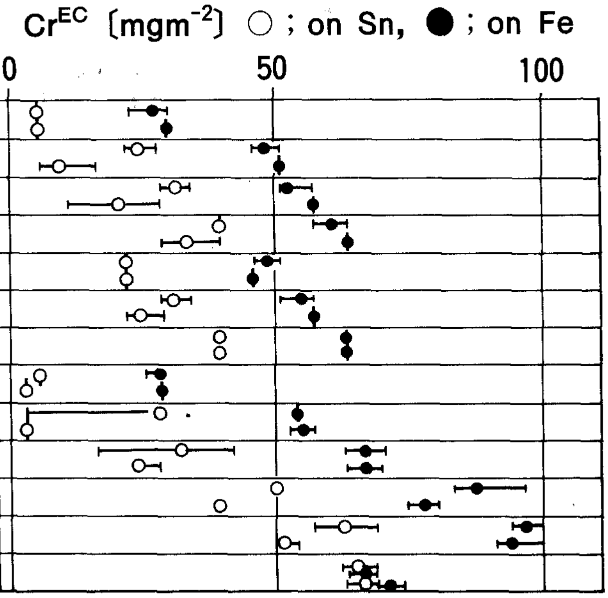
4. Conclusions

Controlling the amount of chromium to be deposited on tin and iron substrate is very important in the manufacture of 'tin-striped TFS' or steel coated first with tin stripes and then entirely with chromium.

The deposition behaviour of chromium on tin and iron substrates was investigated by means of cathodic polarization. A study performed on a continuous electroplating line on the basis of the findings showed that the amount of chromium deposited on tin and iron substrates can be industrially controlled by a chromium coating process involving a lower c.d. in the first step and a higher c.d. in the last step.

Table 1. Test results of chromium coating on tin-striped steel sheet on continuous plating line

No	1 st Tank C_D/Adm^{-2}		2 nd Tank C_D/Adm^{-2}		3 rd Tank C_D/Adm^{-2}		Qdm^{-2} low high C_D C_D
	DOWN	UP	DOWN	UP	DOWN	UP	
1	40	40	40	40	—	—	24 —
2	40	40	40	40	100	—	24+15
3	40	40	40	40	120	—	24+18
4	40	40	40	40	140	—	24+21
5	40	40	40	40	—	100	24+15
6	40	40	40	40	—	120	24+18
7	40	40	40	40	—	140	24+21
8	40	40	40	40	—	—	24 —
9	40	40	40	40	—	60*	24+16
10	40	40	40	40	—	80*	24+21
11	40	40	40	40	—	100*	24+26
12	40	40	40	40	—	120*	24+32
13	——		——		120		— 48



Line Speed ; 125m min^{-1} on No. 1 ~12, 94m min^{-1} on No.13

*Anode Length ; Up Pass of 3 rd Tank on No. 9 ~12 is 550mm, Others are all 310mm

The following conclusions may be drawn:

(i) The peak III reaction, in which no chromium is deposited, is higher in current and less noble in potential on tin than on iron. A higher c.d. is required for the stable deposition of chromium on tin in peak IV reaction. The high hydrogen overvoltage of tin hampers the formation of a cathode film indispensable for the deposition of chromium.

(ii) As soon as chromium is deposited on tin, the peak III reaction is inhibited, facilitating the deposition of chromium.

(iii) The deposition of chromium on tin is facilitated by the presence of an oxide film formed during ageing after the tin coating step.

(iv) Preliminary electrolysis in the peak III region in the chromium coating bath is effective in inhibiting the formation of the cathode film, whereas it is effective in encouraging the formation of the film in the peak IV region.

(v) The amount of chromium deposited on tin and iron substrates can be controlled by a chromium coating process with a lower c.d. in the first step and a higher c.d. in the last step.

(vi) The upper limit of c.d. in the first step is 30 to 40 A dm^{-2}, and the lower limit in the last step is about 100 A dm^{-2}.

(vii) A 'no-current pass' between the first and second steps is effective for stable deposition of chromium.

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