

Study on functions of chrome and fluoride ions in plating process of tin free steel by means of cyclic voltammetry

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Abstract: Plating solution of tin free steel (TFS) presents strong corrosion and special chemical action properties of chrome ions and fluoride ions. Electrochemistry behavior of their ions in the plating process of TFS was investigated by means of cyclic voltammetry (CV). The results show that hydrogen and oxygen evolution peaks can only be found in CV curves of the carbon anode in fluoride solution. CV curves of the carbon anode in chromium trioxide solution consist of five anodic peaks and two cathodic peaks. When fluoride ions are added into chrome ions solution, anodic peak disappears at peak potential of 1.18V. For CV curves of lead alloy anode, anodic peak can be found at peak potential of -0.2V in fluoride solution, and oxidation process is in asymmetry with reductive process in chromium trioxide solution or the mixed solution. As to CV curves of lead oxide anode, the current density of all peaks in chrome ions solution is lower compared with that of carbon anode and lead alloy anode. When fluoride ions are added into chrome ions solution, the current density of the oxidation process obviously decreases, while the absolute value of reductive process increase remarkably.

Keywords: tin free steel, plating process, electroplating, ions function, cyclic voltammetry

1 Introduction

Tin free steel (TFS) is conditionally referred to chrome coating or nickel coating without tin coating. Now TFS is a kind of steel plate coated with chrome and chromium hydrous oxide plating, which is obtained by chromate electrolysis treatment. The use of tin free steel (TFS) products in a variety of packaging applications, particularly in crown cap, twist off cap, bottom cover the top of three-piece cans and drawn can. Its use has increased steadily in recent years as TFS products exhibiting an attractive combination of low-cost, good adhesion, good high-temperature resistance, strong anti-sulfur compared with tinplate products^[1-2].

Now using Pb-Sn-Ag alloy as anodic materials of TFS is of the application in TFS production technology in China and abroad. However anodic materials are eroded in the process of TFS plating, because of plating solution containing Cr ions and F ions. So this would obviously lead to a change in technological parameters and in solution compositions as well as to worsening in TFS product quality. Anode materials selection for electrochemical engineering is a very important issue. The dynamics of anodic process, electrode, electrolytic tank and technological parameters critically depend upon the properties of anodic materials. Due to complexity of anodic materials and lack of information on electrochemical mechanism, it is difficult to select a proper anode to specified technology process starting from a solid fundamental consideration^[3-4]. It is an effectively route by using cyclic AC voltammetry to investigate the electrode dynamics process and interfacial electrochemistry between the relevant solution and anode. However, only relatively few reports regarding electrochemistry properties of anodic materials in fluoride solution for TFS plating are available

in literature [5-7]. The present study is aiming to investigate functions of chrome and fluoride ions in plating process of tin free steel via cyclic AC voltammetry. This would be significant for improving TFS product quality and corrosion resistance of anode materials.

2 Experimental

The curves of cyclic AC voltammetry were gained by means of a three-electrode cell set-up. The material being studied with area of 1cm^2 was used to form working electrode. A saturated calomel electrode (SCE) and platinum were used as reference and the counter electrode respectively. Lead alloy anode and graphite electrode were mechanically polished with emery papers up to 1000 grit to ensure similar surface roughness. The polished substrates were thoroughly washed with acetone and distilled water before passing through the plating procedure. Lead oxide anode was obtained from plating technology under condition of current density $10\text{A}/\text{dm}^2$ and plating time 2h.

Three electrolytic solutions were used in the experiments. These solutions were respectively containing Cr ions, F ions, as well as both of chrome and fluoride ions. Cr ion solution was made of chromium trioxide as solute with its concentrations of 130, 150 and 170g/L, respectively. F ion solution was made of ammonium fluoride as solute with its concentrations of 3, 5, and 7g/L, respectively. In Cr ion and F ion mixed solution, chromium trioxide concentration was fixed at 150g/L, while ammonium fluoride concentration was taken three levels of 3, 5 and 7g/L, respectively.

Cyclic voltammetry tests were performed in a conventional 250mL three-compartment Pyrex cell using electrochemical workstation, model PARSTAT 2273(American Princeton Company). A defined sample area of 2cm^2 was exposed to the electrolyte, and all the current value was normalized to the geometrical surface area. A luggin capillary was placed near the working electrode to minimize the solution resistance. A platinum foil was used as counter electrode, and a saturated calomel electrode (SCE) was used as reference electrode. All electrode potentials were referred to SCE if no otherwise stated. Cyclic voltammetry tests were carried out under conditions of potential range from -1.5V to 2V with the frequency of 1000Hz and sweep rate of $2\text{mV}\cdot\text{s}^{-1}$.

3 Results and discussions

3.1 Cyclic voltammetry curves of carbon anode

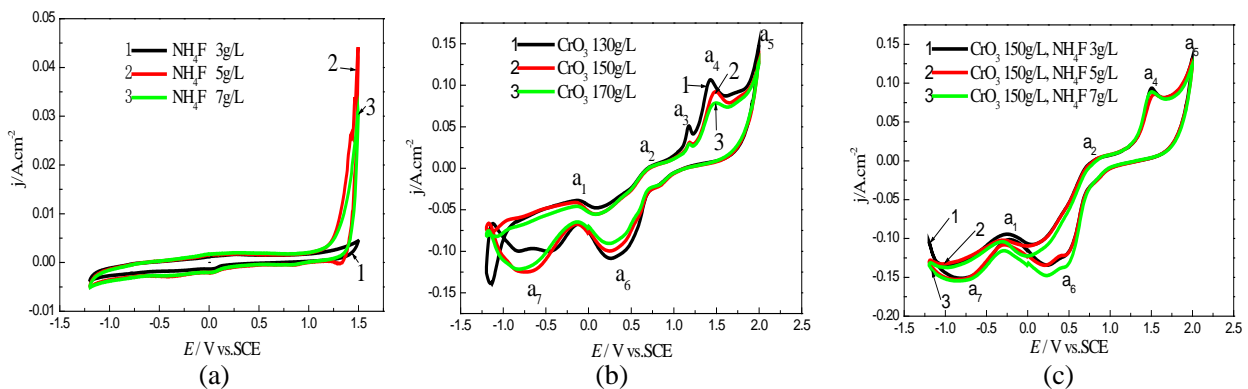


Fig.1 CV curves of the carbon anode in different ions solution

Fig.1 shows CV curves of the carbon anode in different ions solution. As can be seen from Fig.1 (a), only hydrogen and oxygen evolution peaks are presented in CV curves of the carbon anode in fluoride solution, no other oxidation-reduction reactions there. It can be seen from Fig.1 (b) that oxidation-reduction process presents a characteristic of reversibility. CV curves consist of five anodic peaks a_1, a_2, a_3, a_4, a_5 , and two cathodic peaks a_6, a_7 , peak potential of which are $-0.1V, 0.7V, 1.18V, 1.50V, 2.0V, 0.28V$ and $-0.7V$, respectively. The current density of anodic peak decreases and that of cathodic peak decreases with increasing Cr ion concentration. Because electrolytic solution was only made up of Cr ion solution, it could be concluded that oxidation- reduction reaction might occur among the ions of Cr^{6+}, Cr^{3+} and Cr^{2+} . Meanwhile, to balance with increasing of Cr ions concentration, the polymerization to form chromium-oxide ion clusters with a manner: $H_2CrO_4 \rightarrow H_2Cr_2O_7 \rightarrow H_2Cr_3O_{10} \rightarrow H_2Cr_4O_{13}$ might happen as well [8]. When the concentration of chromium trioxide was below 200 g/L, polymerized cluster of chromium-oxide ions could be H_2CrO_4 . While when electrical field was carried out in Cr ion solution, a reaction of transformation of $H_2CrO_4 \rightarrow H_2Cr_2O_7$ might be presented, which is corresponding to a_1 peak. With the increasing electric field strength, polymerized cluster of chromium-oxide ions might be changed from $H_2Cr_2O_7$ to $H_2Cr_3O_{10}$, which is corresponding to peak a_2 . In addition, peaks a_3 and a_4 could be related to the transformations of $Cr^{2+} \rightarrow Cr^{3+}$ and $Cr^{3+} \rightarrow Cr^{6+}$. While peak a_5 might be the oxygen evolution ones. Peaks a_6 and a_7 peaks may indicate the transfer from Cr^{6+} to Cr^{3+} and from Cr^{3+} to Cr^{2+} , respectively. However, polymerize cluster of chromium-oxide ions might make dispersable power and coverage ability of electrolyte depress. This is leading to a decrease in electrolyte conductivity and current density of anodic peak. The increasing of current density of cathodic peak indicates that the ions transformation is improved. When F^- ions were added into Cr ions electrolytic solution, anodic peak a_3 of CV curves disappeared from Fig.1(c), and absolute values of cathodic peak current density increase. It is suggested that F^- ions might inhibit Cr ions transformation from Cr^{2+} ions to Cr^{3+} ions, leading to improving the diffusion of ions in electrolytic solution.

3.2 Cyclic voltammetry curves of lead alloy anode

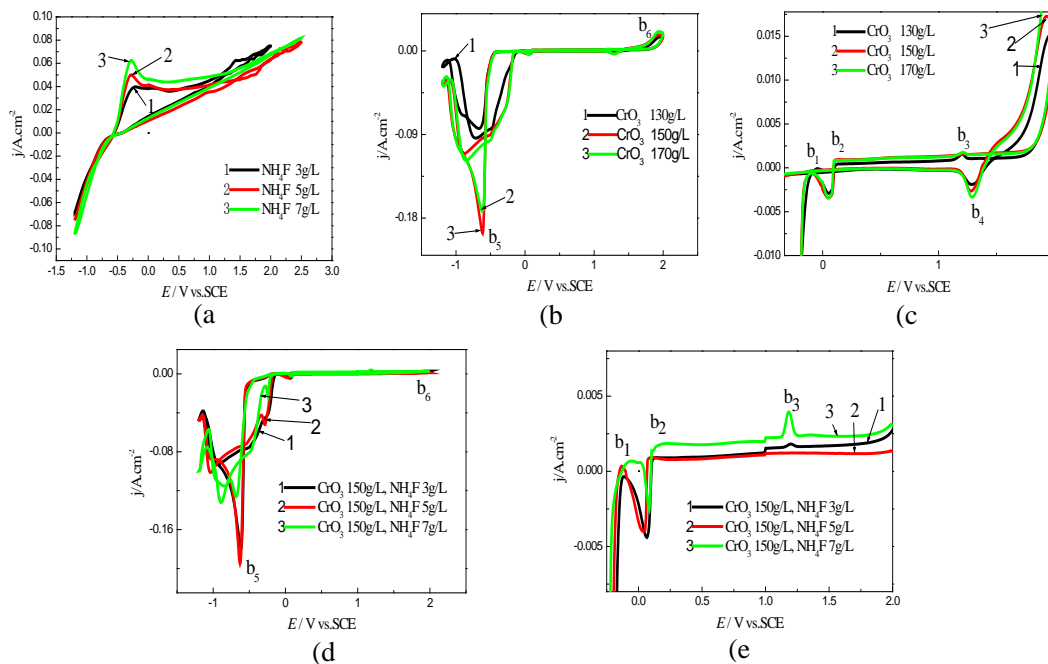


Fig.2 CV curves of lead alloy anode in different ions solution

Fig.2 shows CV curves of lead alloy anode in different ions solution. It is showed from Fig.2 (a) that anodic peak is found at peak potential of -0.2V, no cathodic peak there. This might be correlated with the chemical transformation from Pb to PbO in oxidation process. While lead oxide, as an instable oxide, might be easily eroded by F⁻ ions in reductive process. Fig.2(b) shows that CV curves of lead alloy anode in Cr ion solution, partly enlarged image of which is showed in Fig.2(c). From Figs. 2(b) and 2(c), the asymmetry between the oxidation and reduction process can be seen. Anodic peaks b₁, b₂, b₃ are observed at peak potential of -0.2V, 0.2V and 1.3V, respectively. The peak b₁ might be corresponding to the oxidation of Pb to PbO, b₂ - the chemical reaction of Pb, PbCrO₄ or PbO to PbO_{1+x} (0<x<1). While peak b₃ could be corresponding to the reaction to form β-PbO₂ from PbCrO₄, PbO_{1+x} or a little Pb. For cathodic scanning of Cr ion solution, cathodic peaks b₄ and b₅ are obviously found at peak potential of 1.35V and -0.6V, respectively, which might be corresponding to β-PbO₂ be reduced to PbCrO₄ and PbCrO₄ to Pb, respectively. With increasing of Cr ion concentration, anodic and cathodic peaks potential remained, but current density corresponding to peaks b₃ and b₄ increased. This may indicate that higher Cr ion concentration might promote β-PbO₂ formation, and enhance deeply the reduction to PbCrO₄. When F ions were added into Cr ion solution, the cathodic peak b₄ could not found in CV curve showed in Fig. 2(d) and Fig. 2(e). It might be reason that β-PbO₂ formed on the anode surface due to the erosion by F ion solution, β-PbO₂ reduction to PbCrO₄ did not appear^[9-10].

3.3 Cyclic voltammetry curves of lead oxide anode

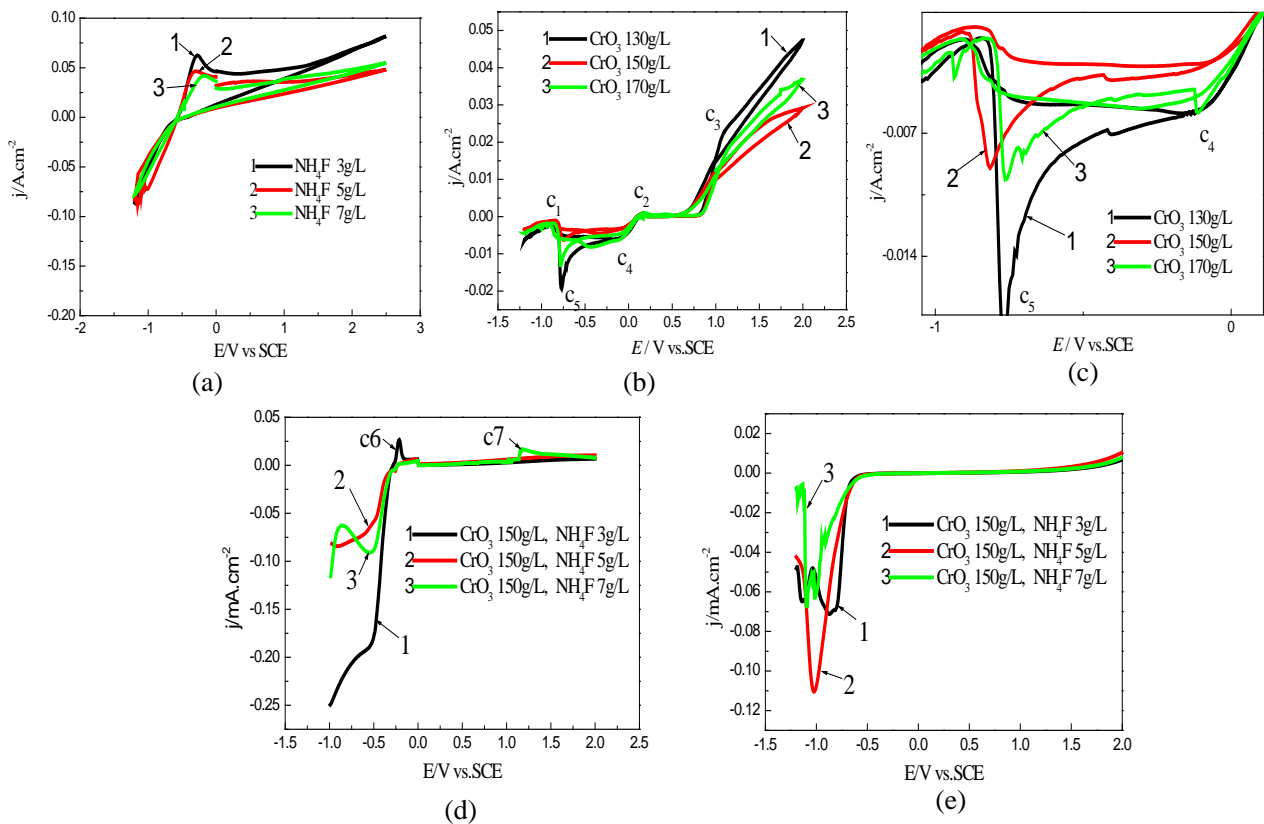


Fig.3 CV curves of lead oxide anode in different ions solution

Fig.3 shows that CV curves of lead oxide alloy anode in different ions solution. Compared Fig. 3(a) with Fig.2(a), CV curves of lead oxide anode in fluoride solution are nearly the same to those of lead alloy. Fig. 3(b) shows that CV curves of lead oxide alloy anode in chromium trioxide solution, which is partly enlarged in Fig.3(c). From Fig. 3(b) and Fig.3(c), anodic peaks c_1 , c_2 and c_3 are found in oxidation process, and cathodic peak c_4 , c_5 for reductive process. The current density for each of the corresponding peaks was lower, and decreased with the increasing Cr ion concentration. According to above analysis and other references, peak c_1 might be corresponding to the formation of $PbCrO_4$, and peak c_2 the transformation from the substrate Pb, $PbCrO_4$, and PbO to PbO_{1+x} ($0 < x < 1$). If peak potential is above 0.75V, peak current density would be remarkably increased. This indicates that PbO might be transferred to α/β - PbO_2 , which is corresponding to peak c_3 . Peak c_5 might be correlated to the change from PbO to Pb. When F ions are added into chromium trioxide solution, CV curves of lead oxide anode would be obviously changed either for oxidation process or reductive process. The changes are shown in Fig. 3(d) and Fig.3(e), respectively. Compared with CV curves in Cr ion solution, the current density of oxidation process obviously decreased, and that absolute value of reductive process increased remarkably. For the oxidation process, the location for peak c_6 and c_7 is similar to that for peak b_1 and b_3 in Fig.2. This suggests peak c_6 correlated to the change of Pb to PbO, and peak c_7 – the change to form β - PbO_2 from $PbCrO_4$, PbO_{1+x} or a little Pb. In addition, current density of peak c_6 decreased and that of peak c_7 increased in comparison with that of peak b_1 and b_3 , respectively. This indicated that PbO_2 of anode surface might be eroded by F ions, corrosion properties of which were stronger with the increasing F ion concentration. As can be seen from Fig. 3(e), reductive peak can be obviously found at peak potential of -0.9V, and two reductive peaks for fluoride concentration 3 and 7g/L, one peak of fluoride concentration of 5g/L. These reasons could be due to PbO_2 firstly be reduced to PbO_{1+x} ($0 < x < 1$), and secondly PbO_{1+x} ($0 < x < 1$) be reduced to Pb.

4 Conclusions

Cyclic voltammetry curves were measured to investigate the electrochemistry properties of anode materials (carbon, Pb and PbO) in three series of solutions: a-containing chromium ions; b-containing F ions and the mixture of these two solutions.

The results from the investigation indicate that polymer formation of Cr ions, F⁻ ions and their mixed solution has a remarkable effect on electrochemical properties of anodic materials. For CV curves of the carbon anode in different ions solution, hydrogen and oxygen evolution peaks can only be found in fluoride solution. The corresponding CV curves consist of five anodic peaks and two cathodic peaks in chromium trioxide solution. However, anodic peak disappears at peak potential of 1.18V in the mixed solution. This suggests that F⁻ ions inhibit Cr ions transformation. For CV curves of lead alloy anode, anodic peak can be found at peak potential of -0.2V in fluoride solution, and the oxidation process is in asymmetry with the reductive process in chromium trioxide solution or the mixed solution. In comparison with that of Cr ions solution, the cathodic peak has not been found at peak potential of 1.35V in CV curves of the mixed solution. This indicates that β - PbO_2 of anode surface might be eroded in F ions solution. As to CV curves of lead oxide anode, the current density of all peaks in Cr ion solution is lower, which is decreased with the increasing Cr ion concentration.

When F ions are added into the Cr ion solution, the current density of the oxidation process obviously decreases, while the absolute value of reductive process increases remarkably.

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