Kinetics and Mechanism of Chromium Electrodeposition from Methanesulfonate Solutions of Cr(III) Salts

V. S. Protsenko, A. A. Kityk, F. I. Danilov

Ukrainian State University of Chemical Technology,
Gagarin Av 8, Dnepropetrovsk, 49005, Ukraine, e-mail: Vprotsenko7@gmail.com

Kinetics and mechanism of the chromium electrodeposition process in methanesulfonate and sulfate solutions of Cr(III) ions have been investigated. The electroreduction of Cr(III) complex ions is shown to proceed stepwise with the formation of relatively stable intermediates – Cr(II) compounds. Chromium is established to be deposited via the discharge of Cr(II) hydroxocomplexes in these electrochemical systems. Some differences in electrodeposition behavior of methanesulfonate and sulfate trivalent chromium electrolytes are associated with the differences in their buffering capacity.

Keywords: trivalent chromium, electroplating, methanesulfonic acid, kinetics.

УДК 544.65:621.357

INTRODUCTION

Chromium electrodeposits are widely used in modern industry for improving performance characteristics of engineering tools and components. Chromium coatings are commonly obtained from electroplating baths based on chromic acid which is highly toxic and oxidative. With much closer attention to environmental problems, hexavalent chromium electroplating faces possible extinction, being detrimental to people's health and environment. In 2006 the European Union adopted the Restriction of Hazardous Substances (RoHS, 2006) thatch extremely restrains the use of hexavalent chromium in electrical and electronic equipment. Thus, the development of ecologically desirable alternative surface treatment technologies to replace the hexavalent chromium electroplating is an important problem in modern surface engineering.

In the past decades numerous attempts have been made to obtain viable trivalent chromium plating baths as a replacement for conventional hexavalent baths, for their less toxic properties [1–5]. However, chromium cannot be readily deposited from aqueous solutions of Cr(III) salts and still there are many problems that need to be solved in the trivalent chromium plating processes.

As shown recently [6, 7], environmentally-friendly Cr(III) baths containing methanesulfonic acid (MSA) may be used for chromium electrodeposition. The electroplating baths containing MSA are known to have many advantages [8]. Electrochemical systems on the base of MSA and its salts have been shown to be very promising for the electroplating of different metals and alloys [9–17].

It is evident that further development of trivalent chromium baths on the base of MSA is impossible without thorough ascertainment of the mechanism and kinetics of the electrode processes occurring during metal deposition. Earlier [18, 19] the main kinetic parameters of the Cr(III)→Cr(II) electroreduction process in methanesulfonate electrolyte have been determined. Meanwhile, the electrochemical process of chromium electrodeposition is well known to proceed step-wise with the formation of relatively stable intermediates – bivalent chromium compounds Cr(III)→Cr(II)→Cr(0), the electroreduction of the Cr(II) complex ions being the rate-determining step in the overall electrodeposition reaction [20]. Still, kinetics and mechanism of the second step in this succession of electrochemical changes in MSA containing solutions remain unexplored. The goal of the given work is to investigate the main features of the chromium electroplating reaction from a methanesulfonate electrolyte in comparison with a sulfate one.

EXPERIMENTAL

All solutions were prepared using distilled water and reagent grade chemicals. Chromium (III) methanesulfonate was synthesized by the chemical interaction between concentrated solutions of CrO_3 and H_2O_2 in methanesulfonic acid.

A methanesulfonate trivalent chromium bath with the following basic composition was applied (mol/L): 0.5 $Cr(MS)_3$, 0.75 HCOOH, 0.5 H_3BO_3, and 4 NH_4MS. For comparison, a sulfate trivalent chromium bath with the following composition was used (mol/L): 0.5 $KCr(SO_4)_2 \cdot 12H_2O$, 0.75 HCOOH, 0.5 H_3BO_3, 2 $(NH_4)_2SO_4$.

In order to obtain steady-state partial voltammograms, electrolysis was conducted in a potentiostatic mode (Reference 3000 – Gamry, potentiostat) in a thermostated three-electrode cell. The working electrode was a gold disc placed in a Plexiglas cartridge with a diameter of 7 mm. Before each experiment, the working electrode was subjected to the cathode

---

© Protsenko V.S., Kityk A.A., Danilov F.I., Электронная обработка материалов, 2014, **50**(5), 13–18.

degreasing in an alkaline solution, activated in a hydrochloric acid solution (1:1), then thoroughly washed with distillate and dried. The auxiliary electrode was a titanium-manganese dioxide anode separated from the catholyte by a porous glass diaphragm. The electrode potentials were measured relative to a saturated silver chloride reference electrode and then recalculated to a standard hydrogen electrode. The resistive component was compensated automatically by means of an IR-compensation system built in the potentiostat. The average current density was calculated on the ground of the overall charge that passed through the cell; the overall charge being determined automatically by means of the potentiostat software.

After completing the electrolysis, the working electrode was washed and dried; then the coating obtained was dissolved in a hydrochloric acid solution. After adding the solution of EDTA and the formation of the respective colored Cr(III) complex ions, the absorbance of the solution was measured by a standard photocolorimetric procedure at a wavelength of 540 nm. The chromium deposits weights were determined from these data. The weight gain of the working electrode allowed calculating the partial current density of the chromium electrodeposition reaction.

Hydrogen that escaped during electrodeposition was collected over the electrolyte and its volume was measured. The hydrogen volume was recalculated for the normal conditions and a correction was made for the presence of saturated water vapors at the temperature of experiment. Then the partial current density of hydrogen evolution was calculated. The algorithm for the calculations of the partial current densities of the reactions occurring during chromium deposition was described more detail in [20, 21].

Potentiometric titration was conducted by means of a combined glass pH electrode ESKCK-10603/7 and ionometer pH-150 MI.

All the experiments on electrodeposition and potentiometric titration were performed at 298 K.

RESULTS AND DISCUSSION

In our previous studies [18, 19], Cr(III) electroreduction process was investigated on the lead, cadmium and tin electrodes since the value of the overvoltage for the hydrogen evolution reaction (HER) on these metals is very high and the current waves of the Cr(III) electroreduction are well separated from those corresponding to the HER. However, it is impossible to study kinetics of the second electrochemical stage (Cr(II)→Cr(0)) even using these electrode materials because of the superposition of the current waves corresponding to the metal deposition and HER. Therefore, we applied the method of obtaining steady-state partial polarization dependences [20].

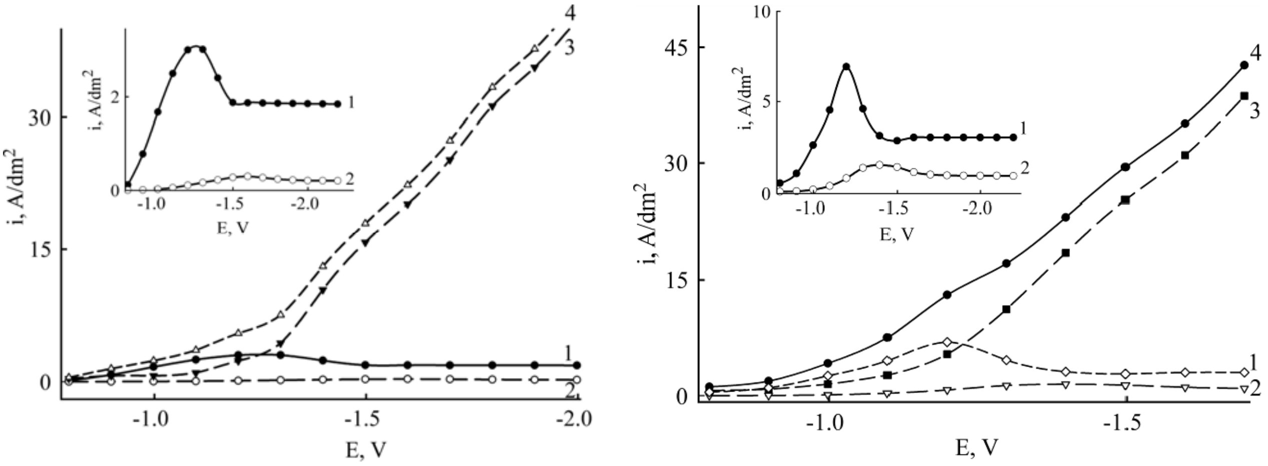
At the same time, the electrodeposition of metal chromium on the Cd, Sn, or Pb electrodes proved to be practically impossible. This may be presumably caused by a significant inhibition of the formation of Cr nuclei on these foreign substrates. That is why we applied a gold electrode as a substrate material for our investigation. The results of the study of chromium electrodeposition were found to be rather reproducible on the Au-substrate.

It should be stressed that the difficulties arising with the chromium electrodeposits from Cr(III) baths are connected, first of all, with the hydrolysis of Cr(III) complex ions. To prevent the intensive hydrolysis, some sufficiently stable complexes of Cr(III) have to be formed. However, the stability of the Cr(III) complexes should not be raised too high as the rate of chromium deposition will diminish. Taking into account all these considerations, we have chosen for our study a trivalent chromium electrolyte containing formic acid or formate.

The partial polarization curves of electrochemical reactions of Cr(III)→Cr(II), Cr(II)→Cr(0), and $2H^+ \rightarrow H_2$ occurring on the cathode in methanesulfonate and sulfate electrolytes are shown in Fig. 1. As one can see, the partial polarization curves of Cr(III) discharge look like waves with a current peak. After reaching a current peak, a limiting current of Cr(III) electroreduction appears. The partial polarization curves of chromium deposition look the same, whereas the current peak is exhibited weaker.

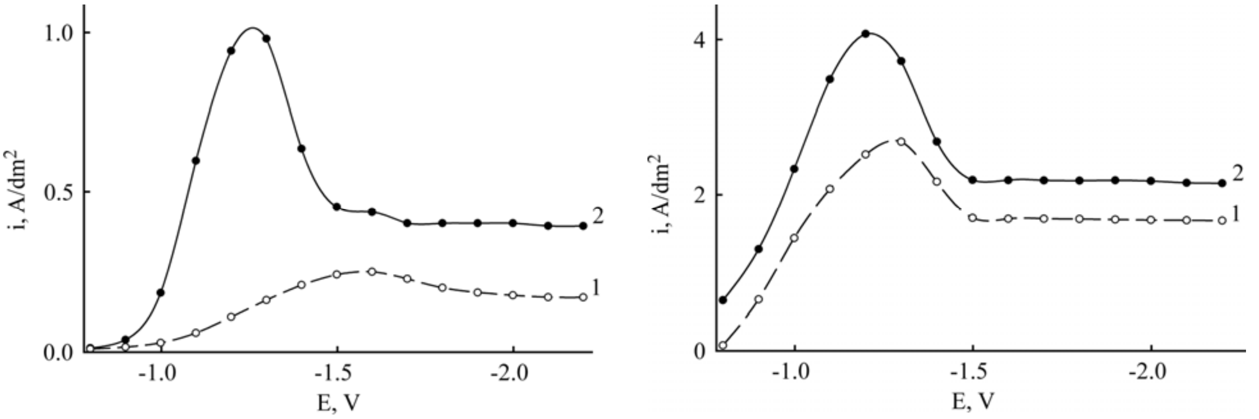
It was stated that bright metal coatings may be obtained in methanesulfonate electrolyte in a sufficiently wide range of electrode potentials (up to –1.6 V); this corresponds to the ascending segment of the partial polarization curve i(Cr(II)→Cr(0)), E. In the sulfate electrolyte, this range is somewhat narrower and high-quality bright deposits may be obtained only at the electrode potentials up to –1.4 V (Figs. 1 and 2). The formation of a cathode film containing Cr(III) hydroxide is observed both in the methanesulfonate electrolyte and in the sulfate one, at potentials that are more negative than those indicated above. The Cr(III) hydroxide film on the cathode may be easily recognized visually by a dark green thin coat on the electrode surface. Note that both the current of Cr(III) electroreduction and the current of metal deposition are higher in a sulfate bath than those in case of methanesulfonate electrolyte.

The formation of a trivalent chromium hydroxide on the electrode surface is caused by the acceleration of hydrogen evolution reaction with the cathode polarization [20, 21]. The HER occurs simultaneously with the electroreduction of chromium-containing ions and leads to the growth of pH. Thus the value of pH corresponding to the Cr(III)-hydroxide formation is reached in the near-electrode layer [22]. Hydroxide compounds of Cr(III) are adsorbed on the



(a) (b)

Fig. 1. Partial polarization dependences for cathode processes occurring in methanesulfonate (a) and sulfate (b) electrolytes; pH 3. (1) Cr(III) + e$^-$ → Cr(II), (2) Cr(II) + 2e$^-$ → Cr(0), (3) $2H^+ + 2e^- \rightarrow H_2$, (4) total current density.



(a) (b)

Fig. 2. Partial polarization dependences for processes of Cr(II) + 2e$^-$ → Cr(0) (a) and Cr(III) + e$^-$ → Cr(II) (b) occurring in (1) methanesulfonate and (2) sulfate electrolytes; pH 3.

electrode surface and block it. As a result, the currents of Cr(III) as well as the Cr(II) discharge diminish and a minimum appears in polarization curves.

The processes of the Cr(III)-hydroxide formation in the near-electrode layer should be influenced by the pH changes in the solution. An increase in the pH value results in a decrease in the maximum current density of the Cr(III) ions discharge both in a methanesulfonate electrolyte and in a sulfate one (these partial polarization curves are not presented in the given paper). Such behavior could be explained by the effect of the Cr(III)-hydroxide film on the rate of electrochemical reactions. The higher the pH value in bulk solution, the more intensive is the hydroxide formation in the near-electrode layer and the smaller is the current density of the chromium (III) ions discharge.

In the initial segment of a polarization curve, the rate of the electrochemical reaction of metal deposition increases with an increase in pH (Fig. 3). This may be explained by the concept on the catalytic action of OH$^-$ ions in the chromium electrodeposition reaction [20].

As follows from the data given above (see Fig. 1), the current density of the incomplete electroreduction of Cr(III) ions is greater than that at chromium electrodeposition. It means that only a part of the total amount of Cr(II) ions formed at the first stage of the Cr(III) discharge is reduced further to the metal. The excess of bivalent chromium ions is accumulated in the bulk electrolyte. Hence, the electroreduction of Cr(II) compounds is a limiting stage of the electrochemical consecutive transformation under consideration.

Taking into account all the aforementioned facts, we may assert that the mechanism of chromium deposition both in a methanesulfonate electrolyte and in a sulfate one is described by the following reaction scheme [20, 23]:

$$[\mathrm{Cr(II)(HCOO)}_m(\mathrm{H_2O})_n]_{ads}^{(2-m)} \Leftrightarrow$$

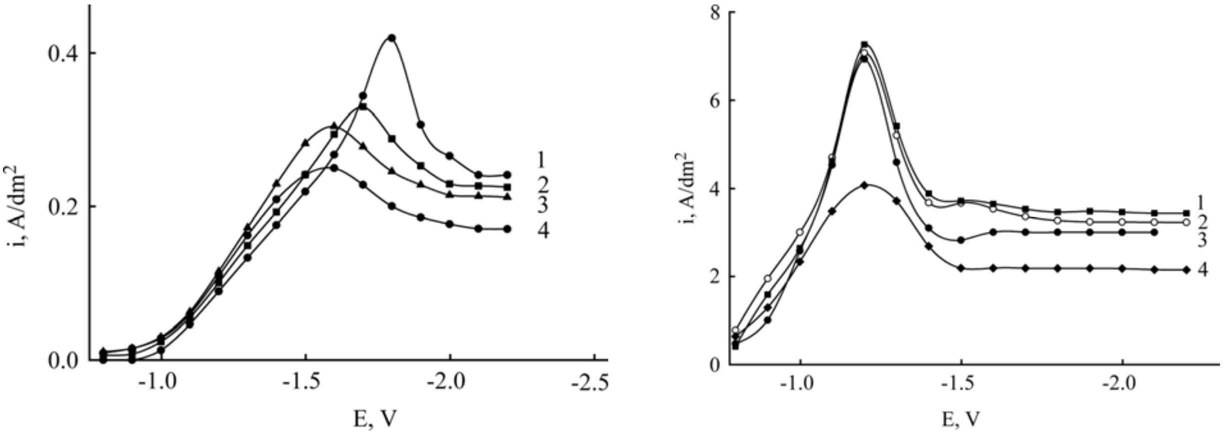
$$\Leftrightarrow [\mathrm{Cr(II)(HCOO)}_{m-k}(\mathrm{H_2O})_{n-1}(\mathrm{OH})]_{ads}^{(1-m+k)} + k\mathrm{HCOO}^- + \mathrm{H}^+,$$

$$[\mathrm{Cr(II)(HCOO)}_{m-k}(\mathrm{H_2O})_{n-1}(\mathrm{OH})]_{ads}^{(1-m+k)} + 2e^- \rightarrow$$

$$\rightarrow \mathrm{Cr}^0 + (m-k)\mathrm{HCOO}^- + (n-1)\mathrm{H_2O} + \mathrm{OH}^-,$$

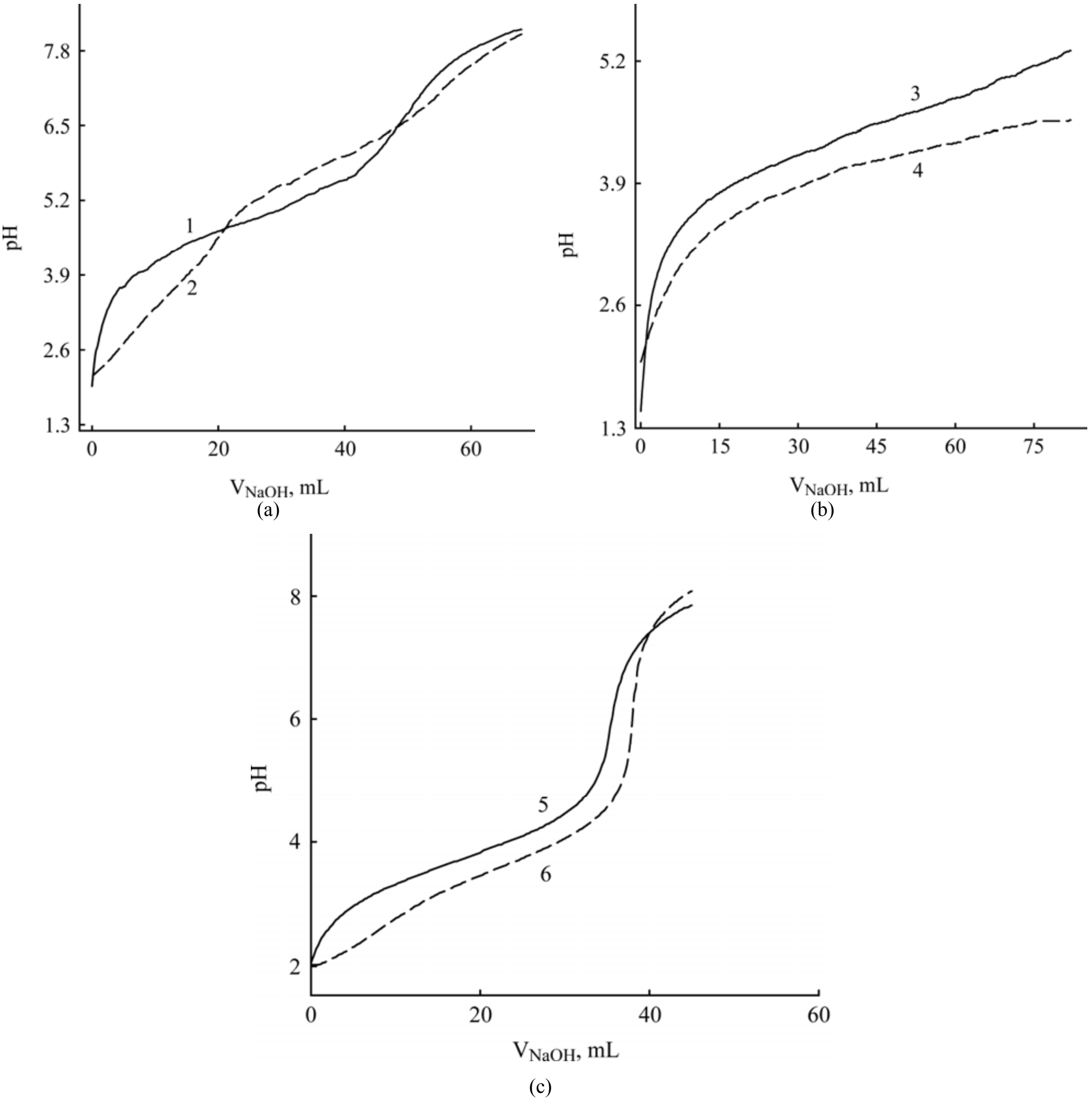
where *L* is the ligand with electrical charge *n*; *m* = 1, 2; *k* = 0, 1, 2; and *n* = 1, 2.

Chemical and electrochemical transformations concerned occur near the electrode surface where the



(a) (b)

Fig. 3. Partial polarization dependences for cathode process Cr(II) + 2e$^-$ → Cr(0) occurring in methanesulfonate (a) and sulfate (b) electrolytes at different values of pH: (1) pH 2.0, (2) pH 2.5, (3) pH 3.0, (4) pH 3.5.



(a) (b)

(c)

Fig. 4. Potentiometric titration curves for: (1) methanesulfonate and (2) sulfate trivalent chromium electrolytes (a), 1 N solutions of (3) Cr(MS)$_3$ and (4) $Cr_2(SO_4)_3$ (b), (5) methanesulfonate and (6) sulfate supporting electrolytes (c), respectively. Compositions of the supporting electrolytes, mol/L: 0.75 HCOOH, 0.5 H_3BO_3, 2 $(NH_4)_2SO_4$ and 0.75 HCOOH, 0.5 H_3BO_3, 4 NH_4MS, respectively.

concentrations of interacting particles may differ from those in the bulk solution. Note that the composition of chromium complexes is shown in the scheme conventionally. It is possible that certain other adsorbed complexes different from those shown above or several Cr(II) hydroxocomplexes of diverse compositions concurrently can also be electroactive.

Although chromium electrodeposition process proceeds in methanesulfonate and sulfate electrolytes via the same mechanism, nevertheless there are several differences in electrochemical behavior in these electrochemical systems. For instance, it should be specified that lowering the current with cathode polarization in a methanesulfonate electrolyte is more dramatical than in a sulfate one (see above). This feature is presumably due to the differences in the buffering capacity of sulfate and methanesulfonate solutions. In order to examine this assumption, potentiometric titration experiments were performed.

When alkali are introduced into the electrolyte, the change in pH values is less sharp in the sulfate chromium electrolyte than in the methanesulfonate one (Fig. 4a); this is especially noticeable in the initial segment of the titration curves.

The initial segment of the potentiometric titration curves refers to the formation of Cr(III) hydroxide; this can be proved if inspecting the curves for the "pure" solutions of $Cr(MS)_3$ and $Cr_2(SO_4)_3$ (see Fig. 4b). The second inflection, that appears in the region pH 5–8, is due to the presence of $(NH_4)_2SO_4$ and NH_4MS, respectively, in the electrolyte under study. Note that inflection is exactly the same in case of the potentiometric titration of supporting electrolytes (see Fig. 4c).

A higher buffering capacity of the sulfate chromium (III) bath (in comparison with the methanesulfonate bath) seems to be associated with the presence of HSO_4^- ions. In practical chromium electroplating, low buffering capacity of the methanesulfonate electrolytes may be eliminated by the introduction of special buffer agents into the plating bath.

CONCLUSIONS

The electroreduction of Cr(III) complex ions in methanesulfonate solutions proceeds stepwise via the formation of relatively stable intermediates – Cr(II) compounds. Only a part of the total amount of Cr(II) complexes formed at the first stage of Cr(III) discharge is further reduced to the metal. Hence, the rate of the chromium deposition is determined by the current density of Cr(II) ions electroreduction. Chromium deposits via the discharge of the electroactive Cr(II) hydroxocomplexes formed in the near-electrode layer due to the dissociation of inner-sphere-coordinated water molecules. Thus, kinetics and mechanism of chromium deposition from sulfate and methanesulfonate trivalent chromium baths proved to be analogous.

Some differences in the electrodeposition behavior of methanesulfonate and sulfate chromium plating baths are connected with a lower buffering capacity of methanesulfonate solutions (in comparison with sulfate electrolytes).

REFERENCES

1. Kwon S.C., Kim M., Park S.U., Kim D.Y., Kim D., Nam K.S., Choi Y. Characterization of Intermediate Cr–C Layer Fabricated by Electrodeposition in Hexavalent and Trivalent Chromium Baths. *Surf Coat Technol.* 2004, **183**, 151–156.
2. Baral A., Engelken R. Modeling, Optimization, and Comparative Analysis of Trivalent Chromium Electrodeposition from Aqueous Glycine and Formic Acid Baths. *J Electrochem Soc.* 2005, **152**, C504–C512.
3. Surviliene S., Nivinskiene O., Cesuniene A., Selskis A. Effect of Cr(III) Solution Chemistry on Electrodeposition of Chromium. *J Appl Electrochem.* 2006, **36**, 649–654.
4. Zeng Z., Zhang Y., Zhao W., Zhang J. Role of Complexing Ligands in Trivalent Chromium Electrodeposition. *Surf Coat Technol.* 2011, **205**, 4771–4775.
5. Danilov F.I., Protsenko V.S., Gordiienko V.O., Kwon S.C., Lee J.Y., Kim M. Nanocrystalline Hard Chromium Electrodeposition from Trivalent Chromium Bath Containing Carbamide and Formic Acid: Structure, Composition, Electrochemical Corrosion Behavior, Hardness and Wear Characteristics of Deposits. *Appl Surf Sci.* 2011, **257**, 8048–8053.
6. Saravanan G., Mohan S., Gnanamuthu R.M., Vijayakumar J. Effect of $AlCl_3$, CH_3SO_3H on Thickness, Current Efficiency and Corrosion Properties of Brusn Plated Cr(III) Formate Urea Baths. *Surf Eng.* 2008, **24**, 458–463.
7. Mohan S., Vijayakumar J., Saravanan G. Influence of CH_3SO_3H and $AlCl_3$ in Direct and Pulse Current Electrodeposition of Trivalent Chromium. *Surf Eng.* 2009, **25**, 570–576.
8. Gernon M.D., Wu M., Buszta T., Janney P. Environmental Benefits of Methanesulfonic Acid: Comparative Properties and Advantages. *Green Chem.* 1999, **1**(6), 127–140.
9. Danilov F.I., Sknar I.V., Sknar Yu.E. Kinetics of Nickel Electroplating from Methanesulfonate Electrolyte. *Russ J Electrochem.* 2011, **47**(9), 1035–1042.
10. Martyak N.M., Seefeldt R. Additive-effects During Plating in Acid Tin Ethanesulfonate Electrolytes. *Electrochim Acta.* 2004, **49**, 4303–4311.
11. Low C.T.J., Walsh F.C. The Stability of an Acidic Tin Methanesulfonate Electrolyte in the Presence of a Hydroquinone Antioxidant. *Electrochim Acta.* 2008, **53**, 5280–5286.
12. Wang H., Pritzker M. Effect of Low Concentrations

of Pb^{2+} on Sn Electrodeposition in Methyl Sulphonic Acid Solutions. *Electrochim Acta*. 2008, **53**, 2430–2440.

13. Balaji R., Pushpavanam M. Methanesulphonic Acid in Electroplating Related Metal Finishing Industries. *Trans Inst Met Finish*. 2003, **81**(5), 154–158.
14. Danilov F.I., Vasil'eva E.A., Butyrina T.E., Protsenko V.S. Electrodeposition of Lead-tin Alloy from Methanesulphonate Bath Containing Organic Surfactants. *Prot Met Phys Chem Surf.* 2010, **46**(6), 697–703.
15. Danilov F.I., Protsenko V.S., Vasil'eva E.A., Kabat O.S. Antifriction Coatings of Pb-Sn-Cu Alloy Electrodeposited from Methanesulphonate Bath. *Trans Inst Met Finish*. 2011, **89**(3), 151–154.
16. Pleshka E.D. Adhesion of Iron Coatings with Steel and Cast Iron. *Surf Eng Appl Electrochem*. 2008, **44**(2), 92–97.
17. Pleshka E.D. Iron Coatings from Multicomponent Methyl Sulfate Chloride Electrolyte. *Surf Eng Appl Electrochem*. 2008, **44**(4), 264–270.
18. Protsenko V.S., Kityk A.A., Danilov F.I. Voltammetry Study of Cr(III)/Cr(II) System in Aqueous Methanesulfonate Solutions. *J Electroanal Chem*. 2011, **661**, 213–218.
19. Kityk A.A., Protsenko V.S., Danilov F.I. Voltammetry Study of Cr(III)/Cr(II) System in Methanesulfonate and Sulfate Solutions: Temperature Dependences. *J Electroanal Chem*. 2013, **689**, 269–275.
20. Protsenko V., Danilov F. Kinetics and Mechanism of Chromium Electrodeposition from Formate and Oxalate Solutions of Cr(III) Compounds. *Electrochim Acta*. 2009, **54**, 5666–5672.
21. Danilov F.I., Protsenko V.S., Gordiienko V.O. Electrode Processes Occurring During the Electrodeposition of Chromium-carbon Coatings from Solutions of Cr(III) Salts with Carbamide and Formic Acid Additions. *Russ J Electrochem*. 2013, **49**(5), 475–482.
22. Kuznetsov V.V., Vinokurov E.G., Kudryavtsev V.N. Effect of Hydrodynamic Electrolysis Conditions on the Kinetics of Cathodic Processes in Chromium (III) Sulfate Electrolytes. *Russ J Electrochem*. 2000, **36**(7) 756–760.
23. Protsenko V.S., Butyrina T.E., Danilov F.I. Applying a Theory of Generalized Variables to Electrochemical Kinetics: Interpreting the Results of Studying Chromium Deposition from Cr(III) Baths. *Prot Met.* 2007, **43**(4), 398–406.

Received 30.09.13

Summary

Исследована кинетика и механизм процесса электроосаждения хрома из метансульфонатных и сульфатных растворов, содержащих ионы Cr(III). Показано, что электровосстановление комплексных ионов Cr(III) протекает ступенчато с образованием относительно стабильных интермедиатов – соединений Cr(II). Установлено, что в исследованных электролитах хром осаждается в результате разряда гидроксокомплексов Cr(II). Некоторые отличия в закономерностях электроосаждения в метансульфонатных и сульфатных электролитах на основе трёхвалентного хрома связаны с различиями в их буферной емкости.

Ключевые слова: трехвалентный хром, электроосаждение, метансульфоновая кислота, кинетика.