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Effect of Cr(III) solution chemistry on electrodeposition of chromium

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Abstract

This work provides a new insight into the interaction of urea with formate during the chromium electrodeposition from a sulphate-based Cr(III) solution. The influence of solution chemistry on chromium electrodeposition in a Cr(III) bath containing sodium formate and urea as complexing agents was studied by FT-IR, XPS and AFM. The results show that good quality Cr coatings may be obtained only in those cases when the secondary ligand with the carbamidic group predominates over urea in the electrolyte. This suggests that electrodeposition of good quality chromium deposit is possible due to the formation of active chromium–carbamid complexes $[Cr(carbamid)_n(H_2O)_{6-n}]^{3+}$. These complexes delay the formation of the stable oligomeric species, and thus provide a prolonged working lifetime in the Cr(III) formate-urea electrolyte.

1. Introduction

The main advantage of a Cr(III) plating bath in comparison with a Cr(VI) bath is that Cr^{3+} ions are non-toxic. However, it is almost impossible to deposit the Cr coating from a simple aqueous Cr(III) solution due to a very stable $[Cr(H_2O)_6]^{3+}$ complex. According to the published data [1] the slow deposition rate in Cr(III) sulphate electrolyte is related to the appearance of very stable μ-sulphato-bridged oligomeric species of Cr(III). To destabilize the strong hexa-aqua chromium(III) complex some of the complexing agents (formic acid, urea, acetate, glycine, etc.) may be used [1–7]. The most important fact is that Cr(III) does not oxidize organic compounds. Although the pH in the bulk of the electrolyte may be about 1–2, the diffusion layer pH can reach 4. At this pH co-coordinated water molecules may be converted to OH^- groups, which leads to the formation of μ-hydroxo bridged species. This reaction may continue with the formation of larger and larger molecules where the chromium atoms are linked with OH^- groups (olated compounds). This is the cause of losses in both the deposition rate and the quality of Cr deposit [2, 8]. The coordinated water molecules, OH^- groups, or other ligands may be replaced by anions in the solution. Anions that easily enter into the co-coordinated sphere and displace OH^- groups can effectively prevent olation [8]. Some of organic ligands influence the plating rate and the quality of the coatings due to the formation of Cr(III) active complexes [1–5]. However, the reasons why thick chromium coatings are difficult to obtain in Cr(III) baths have not been fully clarified.

The purpose of this work was to examine the effect of solution chemistry on the quality of Cr deposit and to find optimum plating conditions for chromium electrodepositon from Cr(III) bath containing both sodium formate and urea as complexing agents.

2. Experimental details

Chromium coatings were plated on steel containing 99.4% iron (Steel-3) in solution containing 0.3 M of $Cr_2(SO_4)_3\ 6H_2O$, 0.6 M of Na_2SO_4, 0.5 M of H_3BO_3, 0.2 M of $Al_2(SO_4)_3\ 18H_2O$, 0.5 M of NaF and additionally 0.4 M of HCOONa and 0.75 M of $(NH_2)_2CO$ as complexing agents. To study the effect of complexing agents on chromium electrodeposition the solutions without and with complexing agents were used. The pH of these solutions was adjusted to 2.0 ± 0.1 by addition of H_2SO_4 or KOH. The polarization measurements were conducted in a three-electrode electrochemical cell using a PI-50-1 potentiostat under potentiodynamic conditions with a potential scan rate of $10\ mV\ s^{-1}$ at a temperature of 20 °C. A saturated Ag/AgCl electrode was used as reference and Pt plate served as a counter electrode. The steel (99.4% purity) cathode was mechanically polished, degreased with a mixture of calcium and magnesium oxides, rinsed thoroughly, activated in a diluted (1:1) hydrochloric acid and then rinsed with deionised water. To study the properties of the Cr coatings the steel samples were plated at a current density (i_c) of 20 and 30 A dm^{-2} and a temperature of 50 °C. The quality of Cr deposits was assessed visually and by using an optical microscope. A light metallic deposit of good appearance and good adhesion was defined as a high quality deposit. The electrodeposition rate of Cr was determined gravimetrically.

Elemental analysis of coatings was carried out using X-ray photoelectron spectroscopy (XPS). Spectra were recorded by an ESCALAB MK-II spectrometer (VG Scientific, UK) using MgK_{α} anode radiation. The spectrometer had a base pressure of 1.33×10^{-7} Pa in the analyser chamber. For sputter etching the argon gas pressure was maintained at 5×10^{-3} Pa in the preparation chamber. Under these conditions the chromium phase can be etched at a rate of ~0.2 nm min^{-1}. The quantity of each element in at % was calculated from the area of the single peak. Empirical sensitivity factors of the elements were taken from [9] and the spectra recorded were compared with the standard ones. No less than five spectra were recorded for every element. The maximum accuracy of the method was 0.1 at %. A standard program was used for data processing. Bands were determined according to their energy, intensity, width, and shape.

The surface of Cr plated sample was examined by means of contact mode atomic force microscopy (AFM) on a scanning probe microscope Explorer (ThermoMicroscopes, USA). 50, 10 and 2μm scans in distinct areas of surface near the center of the specimen were performed collecting topography and internal sensor data. The most common statistical parameters R_a and R_{rms} (the average roughness deviation and the root–mean–square roughness deviation, respectively) were calculated from the topography data using SPMLab 5.01 software. The calculation of these parameters is shown in (1) and (2):

$$R_a = 1/N\sum_{i=1}^{N}|Z_i - \bar{Z}| \qquad (1)$$

$$R_{rms} = \sqrt{1/N\sum_{i=1}^{N}\langle Z_i - Z\rangle^2} \qquad (2)$$

Areas with erroneous data, noise spikes and noise lines were excluded before the calculations.

The infrared spectra were recorded as KBr discs using a Fourier transformation infrared spectrometer (Hartman & Braun, Canada) with 2 cm^{-1} scale resolutions in the region of wave numbers between 3600 and 400 cm^{-1}.

3. Results and discussion

The voltammograms recorded on steel and Cu in both Cr(III) baths without and with complexing agents (Figure 1) show no current until the electrode potential reaches −0.64 V, then the current increases with the potential sweep. This value agrees with the potential for the onset of reduction of Cr(III) to Cr(II) [6]. The current increases more dramatically in bath containing complexing agents for both Fe and Cu cathodes. In the absence of complexing agents the current increases slowly until the electrode potential reaches about −1.3 V and then increases dramatically. The curves show the erratic current response when the potential is more negative than −1.65 V, which may be due to hydrogen evolution. Inhibition of the cathodic process observed in the absence of complexing agents (curves 1, 3) suggests the formation of some inactive species in diffusion layer. Adsorption of these species into the crystal growth site of the metal is believed to cause the loss of metallic quality. For example, electrode surfaces corresponding to curves 1 and 3 in Figure 1 were covered with a thin layer of dark substance, whereas the electrode surfaces corresponding to curves 2 and 4 were covered with a thin layer of light chromium.

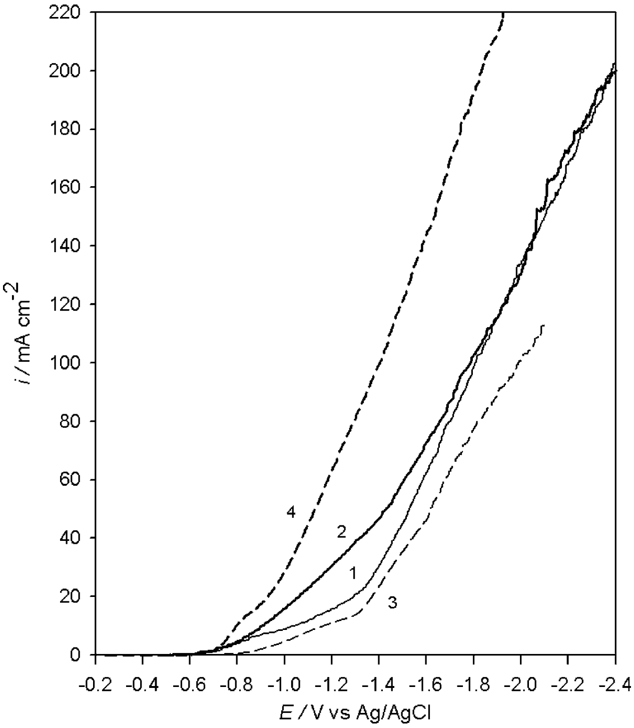


Fig. 1. Cathodic polarization curves for steel (1, 2) and Cu (3, 4) electrodes recorded in the base Cr(III) electrolyte (1, 3) and in formate-urea bath (2, 4). pH 2.0, temperature 20 °C, potential scan rate 10 mV s^{-1}.

The effect of complexing agents on Cr electrodeposition was studied in Cr(III) bath containing sodium formate alone and in bath containing both sodium formate and urea. It was found that the current efficiency (CE) of Cr in Cr(III) bath containing both HCOONa and $(NH_2)_2CO$ was twofold higher than that in bath containing HCOONa alone. The optimum concentrations of complexing agents in the electrolyte are 0.4 M HCOONa and 0.75 M $(NH_2)_2CO$. The working lifetime of the electrolyte containing HCOONa alone is very short and the maximum thickness of Cr

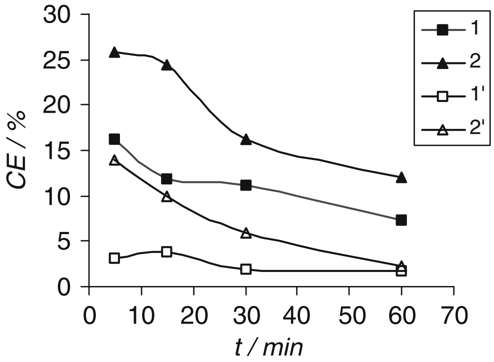


Fig. 2. CE of Cr obtained in the formate-urea electrolyte (1, 2) and in the base Cr(III) electrolyte (1′,2′) at 20 A dm^{-2} (1 and 1′) and 30 A dm^{-2} (2 and 2′). Temperature 50 °C.

coating is about 2– 3 μm, whereas a thick coating (about 30μm) of good quality may be obtained in bath containing the optimum concentrations of both formate and urea. It is known [6] that the electrodeposition of Cr occurs in bath containing formate ions due to the formation of $[Cr(H_2O)_5(HCOO)]^{2+}$ and may be presented through the following reactions:

$$[\mathrm{Cr(H_2O)_5(HCOO)}]^{2+} + e^- \rightarrow [\mathrm{Cr(H_2O)_5(HCOO)}]^{+} \quad (3)$$

$$[\mathrm{Cr(H_2O)_5(HCOO)}]^{+} + 2e^- \rightarrow \mathrm{Cr} + 5\mathrm{H_2O} + \mathrm{HCOO^-} \quad (4)$$

Some of $[Cr(H_2O)_5(HCOO)]^{+}$ complexes may diffuse to the bulk of the solution and decompose to stable $[Cr(H_2O)_5]^{2+}$ ions and $HCOO^-$. Accumulation of Cr(II) particles (catalysts for an olation reaction) in the diffusion layer may be responsible for collapse of the deposition rate. Therefore, it was impossible to obtain the coating with a thickness of more than 2–3 μm. According to the literature data $[Cr(urea)_n(H_2O)_{6-n}]^{3+}$ complexes are responsible for the acceleration of Cr electrodeposition in formate-urea bath [2].

Figure 2 shows that CE of Cr in Cr(III) bath without complexing agents (curves 1′,2′) is much lower than that in formate-urea bath (curves 1,2). It should be pointed out that Cr deposits obtained in the absence of organic compounds possessed poor quality and were very thin (about 2– 3 μm). Thick Cr coatings (about 30 μm) of good quality were obtained in bath containing 0.4 M of sodium formate and 0.7 M of urea. It is seen that CE of Cr decreases for both base and formate-urea baths with increase in electrolysis time from 5 to 60 min per workpiece. According to the literature data [1, 2, 10] the decrease in CE of Cr during electrolysis may be related to the appearance of stable and inert oligomeric species. It is suggested that sodium formate and urea do not completely stop but only delay the process of formation of such species.

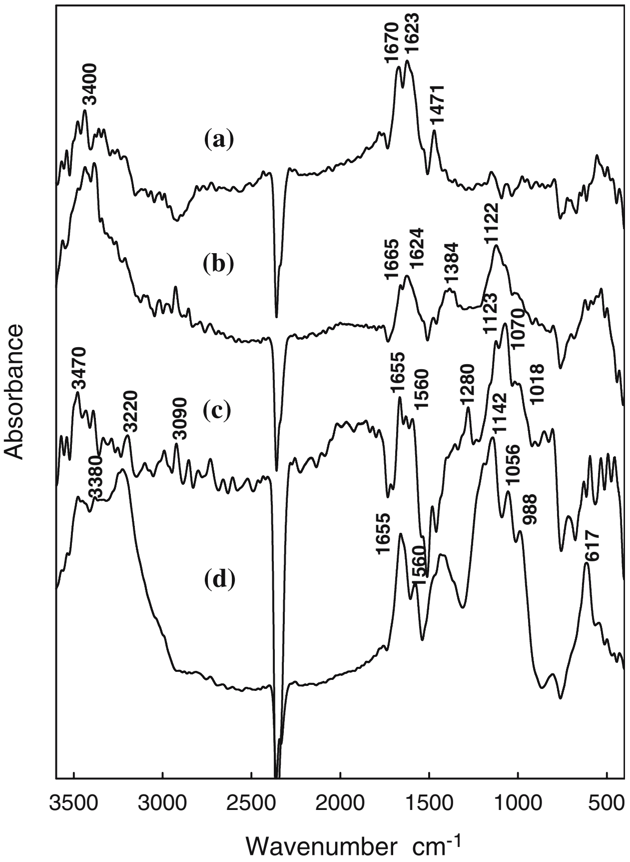
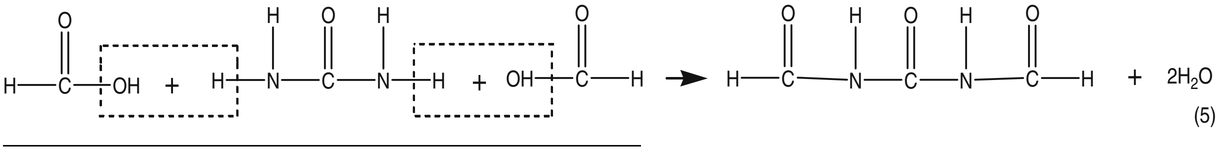


Fig. 3. FT-IR spectra obtained for: urea (reagent) solution (a), Cr coating of poor quality (b), Cr coating of good quality (c) and the formate-urea electrolyte (d).

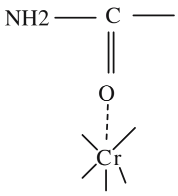
To identify the species in the studied formate-urea electrolyte FT-IR spectra for both electrolyte and deposit were recorded (Figure 3). The deposit was analysed after coating removal from the plated sample. For comparison, the spectrum obtained for the urea is shown in Figure 3a. The spectrum recorded for Cr(III) formate-urea bath (Figure 3d) has the bands at 1560 and 1655 cm^{-1} due to bending vibrations (δ) and at 3220 cm^{-1} due to stretching vibrations (v) which are characteristic of the amido-group (–NH—CO–) [11]. The IR spectrum for Cr coating of good quality has the bands at 1560, 1655, 3090 and 3220 cm^{-1} (Figure 3c), which points to the presence of (–NH—CO–) group in the deposit. These data suggest that the secondary ligand containing carbamidic groups was formed in the Cr(III) formate-urea electrolyte. The following reaction was considered as possible:



$$\mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH} + \mathrm{H{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}H} + \mathrm{OH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H} \rightarrow \mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H} + 2\mathrm{H_2O}$$

(5)

It is supposed that a newly formed secondary ligand with carbamidic groups (amidate) may replace one or more H_2O molecules in $[Cr(H_2O)_6]^{3+}$ complexes to form active chromium–carbamid complexes $[Cr(carbamid)_n(H_2O)_{6\text{-}n}]^{3+}$. It is known [2] that urea may form the active $[Cr(urea)_n(H_2O)_{6\text{-}n}]^{3+}$ complexes where Cr(III) is coordinated with oxygen of carbamidic group [11]:



(6)

It may be assumed that the ratio $[Cr(carbamid)_n(H_2O)_{6\text{-}n}]^{3+}/[Cr(urea)_n(H_2O)_{6\text{-}n}]^{3+}$ in the solution depends on the complexing power and concentration of both secondary and original ligands. A gradual loss in the deposit quality and a drop in the deposition rate after some period of electrolysis (about 25 A h l^{-1}) may be related to the change in chemistry of the electrolyte. It was found that a worsening quality of Cr coating is related to the appearance of dark suspension in the electrolyte and a simultaneous increase in pH. The IR spectra recorded for both suspension and spent solution show the bands at 1624, 1592, 3472.7 and 3386 cm^{-1} (Figure 3b), which may be attributed to the presence of NH_2—CO– group, whereas the bands characteristic of NH vibrations in carbamidic group are absent. The IR spectrum for Cr coating of poor quality also shows the bands, characteristic of NH vibration in urea.

IR spectrum recorded for Cr coating of good quality (Figure 3c) shows the peaks of hydroxyl groups at around 3470 cm^{-1} (ν vibration) and at 1280 and 1070 cm^{-1} (δ vibration). The presence of hydroxides in the outer layer of Cr coating is also seen from XPS data. In particular, the Cr2p peak at 577.3 ± 0.1 eV is assigned to $Cr(OH)_3$.

IR spectra also show the bands at around 1120 and 620 cm^{-1} that are characteristic of the sulphate anions. The shift of these bands may be related to structural modification in Cr(III) complexes. These may be the stable μ-sulphato-bridged oligomeric species that are formed during electrolysis and impair the quality of deposit.

The XPS spectra recorded for Cr coating of good quality show N1s peak at 400.7 eV (Figure 4) that may be attributed to a NH bound (amidic group) in organic ligand [12, 13].

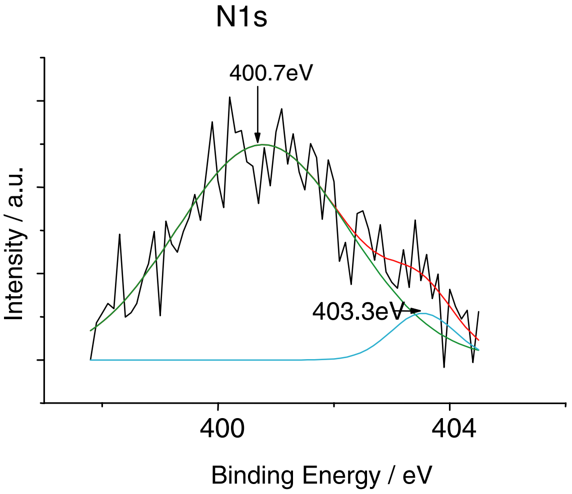


Fig. 4. XPS spectra for N1s recorded on the surface of Cr coating.

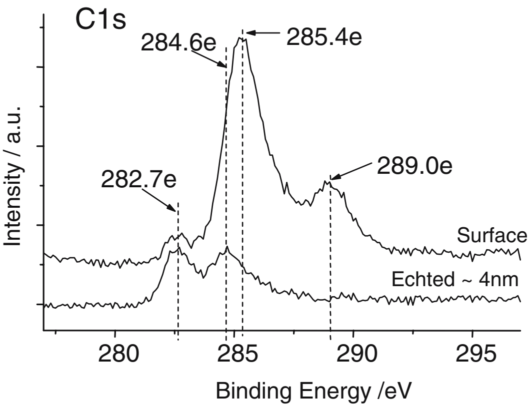


Fig. 5. XPS spectra for C1s recorded for Cr coating before and after sputtering by argon ion bombardment in a depth of 4 nm.

The XPS spectra recorded in the depth of Cr coating (Figure 5) show three carbon peaks for the outer layer (at 282.7, 285.5 and 289 eV) and only two C1s peaks (at 282.7 and 284.4 eV) for the inner layers (4 nm in depth). The peak at 282.7 eV corresponds to metal-carbon bond [9, 14, 15], the second C1s peak may be attributed to the C—C bound [16] and the peak at 289 eV may be assigned to organic ligands adsorbed on the coating surface. The data obtained correlate with those published in [9].

The AFM images of the deposits with a thickness of 5, 10 and 20 μm are shown in Figure 6. The sample 5 μm thick (Figure 6a) possesses a fine grained structure with some dispersed growth nodules (the chromium dispersoids). The size of crystallites increases with increase in thickness of the coating and the agglomerates formed by dispersoids are distinctly seen in the deposit with a thickness of about 20 μm (Figure 6c). It is supposed that the formation of nodules occurs at the initial stages of deposition. The coatings deposited at 30 A dm^{-2} (Figure 6d) have a more fine-grained structure without dispersoids in comparison with those deposited at 20 A dm^{-2} (Figure 6c). The smaller grain size may be conditioned by progressive nucleation during electrodeposition (the formation of numerous new nucleation sites). Nodules are no longer formed and a fine- and smooth-grained structure is formed. The comparison of AFM images (Figure 6) with the data in Table 1 suggests that the roughness increases with coating thickness and decreases with the current density.

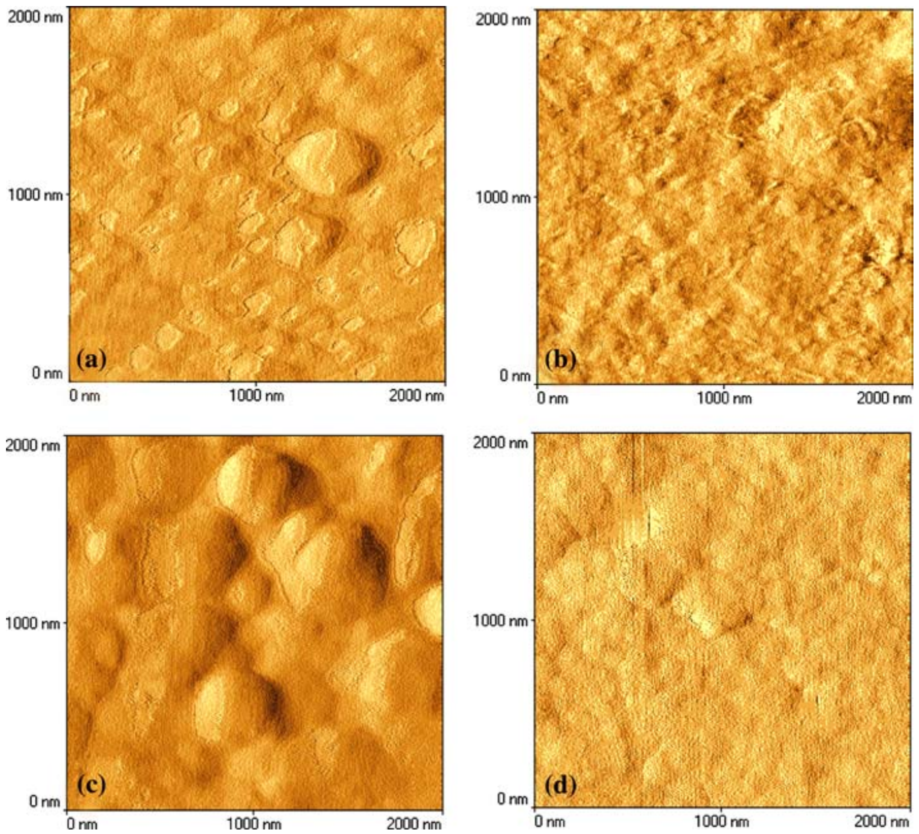


Fig. 6. Photographs of Cr deposited in the formate-urea electrolyte at $i_c = 20$ A dm^{-2} (a–c) and $i_c = 30$ A dm^{-2} (d). The thickness of the coating: 5 μm (a), 10 μm (b, d), 20 μm (c).

Table 1. The average roughness deviation (R_a) and the root-mean-square roughness deviation (R_{rms}) obtained for Cr coatings deposited in Cr(III) formate-urea bath

Complexing agents/M	i_c/A dm^{-2}	Thickness of coating/ μm	R_a/nm	R_{rms}/nm
0.75 M $(NH_2)_2CO + 0.4$ M NaCOOH	20	5	1.5469	2.0078
		10	2.2292	2.8886
		20	3.9171	5.1146
0.75 M $(NH_2)_2CO + 0.4$ M NaCOOH	30	10	1.2804	2.1100

4. Conclusions

This work provides a new insight into the interaction of urea with formate ions during chromium electrodeposition in a sulphate-based Cr(III) solution. The FT-IR spectra have shown that Cr coating of good quality may be obtained only in those cases when the secondary ligand with a carbamidic group predominates over urea in the electrolyte. This suggests that chromium electrodeposition occurs due to the formation of active chromium–carbamid complexes $[Cr(carbamid)_n\ (H_2O)_{6\text{-}n}]^{3+}$. These complexes delay the formation of the stable oligomeric species and thus provide a prolonged working lifetime of the Cr(III) bath.

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