

MANGANESE ELECTRODEPOSITION FROM UREA-RICH ELECTROLYTE

Mladen Vuruna¹, Mihael Bučko^{1*}, Ljubica Radović², Jelena B. Bajat³

¹Military Academy, University of Defense, P.J. Sturma 33, Belgrade, Serbia

²Military Technical Institute, Ratka Resanovica 1, Belgrade, Serbia

³Faculty of Technology and Metallurgy, University of Belgrade, P.O. Box 3503, Belgrade, Serbia

mbucko@tmf.bg.ac.rs

Pure manganese coatings were prepared on the steel (AISI 4340) electrode by a non-conventional electrodeposition method, in the presence of 8 mol dm⁻³ of urea as a plating additive. The influence of urea on the electrodeposition of Mn was investigated by cyclic voltammetry. The morphology of the coatings was studied by scanning electron microscopy (SEM), and their elemental composition by energy dispersive X-ray spectrometry (EDS). The results showed that the presence of urea in the solution increased the current efficiency for metal reduction for around 20%, and depending on the applied deposition potential, urea may act either as a complexing agent or through the adsorption mechanism. Moreover, urea improves the characteristics of Mn deposits, i.e. their adhesiveness, porosity, compactness, and appearance. Except for oxygen, as part of the Mn corrosion product at the coating surface, no carbon or nitrogen incorporation was detected in the deposits by EDS.

Keywords: urea; electrodeposition; Mn coating; morphology

ЕЛЕКТРОДЕПОЗИЦИЈА НА МАНГАН ОД ЕЛЕКТРОЛИТ БОГАТ СО УРЕА

Приготвени е филм од чист манган врз челична (AISI 4340) електрода со конвенционален метод на електродепозиција во присуство на 8 mol dm⁻³ уреа како адитив. Влијанието на уреата врз електродепозицијата на Mn беше испитувано со циклична волтаметрија. Морфологијата на филмот беше студирана со скенирачка електронска микроскопија (SEM), а елементарниот состав со енергетски дисперзивна спектрометрија со X-зраци (EDS). Резултатите покажаа дека присуството на уреа во растворот ја зголемува ефикасноста на струјата со намалување на металот за околу 20% и во зависност од потенцијалот на депозиција уреата може да дејствува или како комплексирачко средство или преку адсорпционен механизам. Исто така, уреата ги подобрува карактеристиките на депозитите на Mn, т.е. нивната адхезивност, порозност, компактност и изглед. Освен кислород како дел од корозивниот продукт на Mn на површината на филмот, со EDS не беа детектирани инкорпорирани депозити на јаглерод или азот.

Клучни зборови: уреа; електродепозиција; филмови од Mn; морфологија

1. INTRODUCTION

The production of pure manganese coating on a steel substrate may offer interesting practical uses, as shown by the following examples. Metallic manganese is used as an alloying element on a large scale in certain types of steel. Coatings of Mn as well as Mn-alloys with Cu, Zn, Ni or Co are

potentially useful as sacrificial coatings for protecting ferrous substrates against corrosion [1]. Furthermore, it has been recently reported [2] that when Mn coating is obtained on stainless steel, and post-annealed with the flow of nitrogen, the manganese nitride coating is formed, which significantly increases the corrosion resistance of stainless steel in NaCl medium. In another example [3], the

Mn and Co layers were sequentially deposited over stainless steel and annealed in oxidizing and inert atmospheres. In this manner, Co and Mn spinel phase oxides were prepared for application as coatings for interconnectors in solid oxide fuel cells.

The most common way of obtaining the Mn coating is electrochemical deposition – this process has been used for the last 80 years as the final step in the large scale production of metallic Mn from manganese ores [4]. Industrially, manganese is obtained on steel sheets by cathodic reduction of manganese sulfate or chloride, from water solution, along with corresponding ammonium salts. However, the standard reduction potential for Mn^{2+}/Mn is very negative (-1180 mV vs. SHE), so the reduction of Mn^{2+} to Mn is always accompanied by hydrogen evolution. Therefore, Mn electrodeposition is still technically very challenging due to a low current efficiency and the formation of rough and dendritic deposits [4].

The use of additives is key in the production of dense high-quality Mn metals at a high current efficiency, and so, various additives have been investigated for this purpose. Group VI element (S, Se and Te) compounds were reported as the most successful additives which increase the overpotential for hydrogen evolution, improve the leveling effect of the electrolyte and facilitate the crystallization of stable α -manganese; unfortunately, however, these compounds have a hazardous effect on the environment and also contaminate the manganese products [5]. Along with S, Se and Te compounds, many other additives, especially organic compounds, such as ammonium thiocyanate [1], carboxylic acid, glycerol, water-soluble polyacrylamide, guar gum and thiourea [6, 7], have been tested to improve manganese electrodeposition. However, there is little information about their performance.

In the present study, the influence of urea, $(\text{NH}_2)_2\text{CO}$, on manganese electrodeposition from an acidic sulfate solution, was investigated by cyclic voltammetry. The morphology and elemental composition of the Mn deposits were analyzed using scanning electron microscopy (SEM).

Urea was reported as an additive in the electrodeposition of other metals, for instance Pt arrays [8], Cr–Co alloys [9], bright Cu deposition [10], Zn coating [11], etc. It may act as a leveling agent [10, 11] due to the selective adsorption of urea molecules on the specific crystal planes of metal electrode [8, 12], but it is also a complexing agent for metal ions [9]. Earlier, a saturated water solution of urea oxalate was used as an electrolyte for the electrodeposition of Mn, as well as metals which were difficult to deposit from aqueous baths (tech-

netium and actinium) [13]. Also, urea may be a part of non-aqueous electrolytes for metal electrodeposition, such as an organic solution of 3 mol dm^{-3} urea in DMSO [14] or an ionic liquid composed of urea and choline chloride in a molar ratio of 1:2 [15].

A different approach to metal electrodeposition was applied in the present work, as urea was added at a high concentration (8 mol dm^{-3}) to the aqueous solution, so it did not behave only as an additive, but also as a supporting electrolyte; however, pure urea in water behaves as a weak electrolyte, and with an increase of urea concentration, conductance even slightly falls off [16]. Urea is an economically affordable compound, produced on an industrial scale, and it is very soluble in water ($108 \text{ g}/100 \text{ ml}$ at 20°C). Dissolved in water, it is neither acidic nor alkaline.

2. EXPERIMENTAL SECTION

The electrodeposition of Mn coatings and the electrochemical experiments were performed using a sulfate electrolyte containing 1.0 mol dm^{-3} $(\text{NH}_4)_2\text{SO}_4$ and 0.2 mol dm^{-3} MnSO_4 , pH 5.50. Two types of solutions were prepared to examine the effect of urea on the Mn deposition process: the first solution contained the above ingredients, and in the second solution, urea was added at a concentration of 8 mol dm^{-3} . The electrolytes were prepared with analytical grade reagents and double distilled water.

The substrates for all experiments were steel (AISI 4340) panels with an active surface area of 3.57 cm^2 . Prior to each experiment, the steel surface was prepared using abrasive emery papers of the following grades: 600, 1000 and 1200, and then degreased in a saturated solution of NaOH in ethanol, pickled with 2 mol dm^{-3} HCl for 30 s and finally rinsed with distilled water.

A three-electrode cell arrangement was used for both the voltammetric studies and Mn electrodeposition, at the temperature of 25°C , without stirring. The reference electrode was a saturated calomel electrode (SCE) mounted in a Luggin capillary. All potentials in this paper refer to this electrode. The counter electrode was a platinum plate with surface area of 3 cm^2 . The working and counter electrodes were separated by a polyester membrane with dimensions of $3 \times 4 \text{ cm}$, with the aim of preventing Mn^{2+} oxidation products (anodic sludge) to diffuse from anode to the cathodic surface. The initial composition of anodic and cathodic cell compartments was the same, and one aliquot of both was used for coating one sample, after which the solution was discarded.

The Mn coatings were electrodeposited from solutions with and without urea, galvanostatically at current densities (c.d.s) in the range of 20 – 90 mA cm⁻², using a PAR M173 galvanostat as the power supply. The deposition time was chosen to obtain layers of 10 μm thickness, verified by a coating thickness measuring instrument Dualscope MPOR.

The cyclic voltammetry (CV) experiments were performed with IR correction by using a ZRA Reference 600 potentiostat, Gamry Instruments. The CV curves were carried out by scanning the potential within -1500 mV to -400 mV vs. SCE, starting from the rest potential.

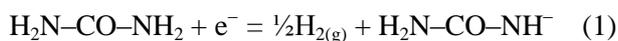
Surface morphology of the coatings was examined by scanning electron microscopy, SEM Jeol JSM 6610LV. Chemical analysis of the deposits was performed by an attached energy dispersive X-ray spectrometer (SEM/EDS).

3. RESULTS AND DISCUSSION

3.1. Voltammetric study

To determine the effect of urea on the reduction of Mn(II) and H₂O at steel electrode, we carried out voltammetric studies in the potential range between -1500 and -400 mV_{SCE}, in different solutions.

Figure 1 presents the CV curves obtained with a potential scan rate of 20 mV s⁻¹ in (NH₄)₂SO₄ solution, containing urea and MnSO₄, or without them. Since Mn deposition is always accompanied with hydrogen evolution reaction (HER) [4], the first experiments were carried out in blank solutions without Mn²⁺ (Fig. 1a). It can be seen that no significant current is recorded at the cathodic scan until -1070 mV, the value corresponding to the onset of HER, and then the current steadily increases with the potential sweep. However, comparison of the two curves in Fig. 1a shows that the starting overpotential for H₂O reduction is for about 50 mV lower in the presence of urea. The first explanation for this result could be that an additional electrochemical process occurs, *i.e.* that urea is reduced together with HER. It was reported earlier [17, 18] that hydrogen evolution resulted from the electrochemical reduction of urea, according to the reaction:



However, these reports relate to urea-based melts and the temperatures from 70 to 140°C; what is more, urea reduction was indicated by a cathodic current peak [17]. Therefore, we assumed that the reaction (1) did not happen in our case, due to the

absence of any peak. Instead, it is assumed that the water reduction process at low overpotential is slightly catalyzed with the addition of urea in the solution, although there are no published data on practical use of urea as an additive in water electrolysis. Nevertheless, it is seen in Figure 1a that the *j*-*E* slope for urea-assisted HER process is lower compared to the slope of the curve recorded without urea. As a result, at potentials more negative than -1390 mV_{SCE}, the water reduction in the solution containing urea is slower compared to the urea-free solution.

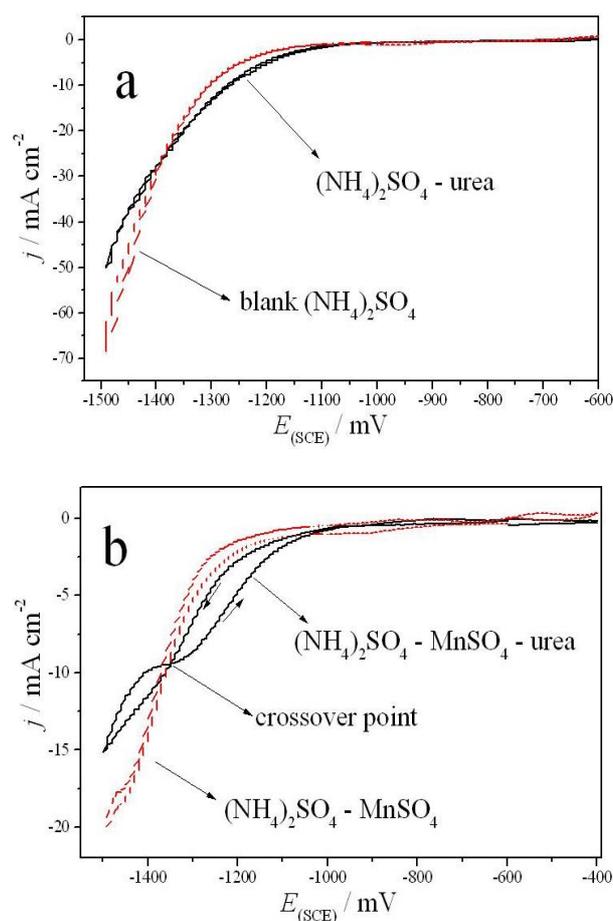


Fig. 1. Influence of urea on cyclic voltammograms recorded on steel electrode at 20 mV s⁻¹, without stirring. The electrolyte composition is denoted in diagrams, where the concentrations are 1 mol dm⁻³ (NH₄)₂SO₄, 0.2 mol dm⁻³ MnSO₄ and 8 mol dm⁻³ urea.

When Mn²⁺ ions are present in the solution containing urea (Fig. 1b), the first current onset occurs again at -1070 mV, and the voltammograms recorded towards the negative potentials are the same shape as those observed in the absence of Mn²⁺ ions (Fig. 1a). This suggests that the Mn²⁺/Mn reduction is masked, and the main process at the working electrode is HER, as in previous cases [19]. However, during the revers-

ing sweep in the solution with urea, a current crossover between cathodic branches is observed. At a more cathodic potential region than the crossover point, current in the backward sweep is lower than in the forward sweep, probably due to the decreased concentration of Mn^{2+} ions on the electrode surface as a result of the deposition process, or due to the intensive adsorption of urea molecules. On the other hand, in the potential range that is more positive than the crossover point, the current in the backward sweep is higher than during the forward sweep. This indicates an easier Mn^{2+}/Mn reduction and HER process at the freshly formed manganese film, as compared to the bare steel surface electrode [20]. In other words, the crossover of voltammogram branches in the solution with urea gives evidence that this compound is beneficial for manganese nucleation and growth [20].

It is clear from Figures 1a and 1b that at the potentials more negative than -1390 mV, the cathodic current density of the voltammograms recorded in the presence of urea is lower than that of the curves recorded without urea. This behavior is in accordance with the voltammetric investigation of the majority of organic additives (for example [1, 10]), where a supplementary overvoltage for both the HER and metal ion reduction is usually observed, due to an adsorbed layer of additive molecules on the electrode surface [21].

Contrary, at potentials more positive than -1390 mV in the case of urea addition, as shown in Figure 1, both reduction processes are facilitated. To explain this result, an analogy with chromium electrodeposition can be made. According to the literature, urea has been used as a complexing agent in the reduction of Cr(III) ions to Cr, in order to increase current efficiency. Namely, it is known that $[\text{Cr}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ species are quite stable and inert, so they are heavily reduced at the cathode, but urea forms active $[\text{Cr}(\text{urea})_n(\text{H}_2\text{O})_{6-n}]^{3+}$ complexes which are reduced more easily [22, 23]. Therefore, the observed influence of urea on Mn reduction in this work could be explained through the formation of complex salts like $[\text{Mn}(\text{urea})_3(\text{H}_2\text{O})_{6-3}]^{2+}$ and $[\text{Mn}(\text{urea})_6]^{2+}$ which are well documented [24]. On the contrary, the role of 8 mol dm^{-3} urea in increasing the rate of HER is not easy to explain and it requests further research, also because we could not find any report regarding the catalytic or inhibiting activity of urea towards water reduction. Nevertheless, the explanation could be the complexation of water molecules as for the Mn^{2+} ions, because H_2O -urea complex species have been also reported [25].

Very weak oxidation peaks are observed in the anodic branch of CV curves (Figs. 1a and 1b). Similar behavior has been reported in [1], where the lack of peak related to manganese dissolution was attributed to the instability of the manganese deposits, which are easily dissolved in acidic media. In order to obtain more intensive peaks which can be distinguished from the baseline, higher scan rates may be applied [26], as shown in Figure 2.

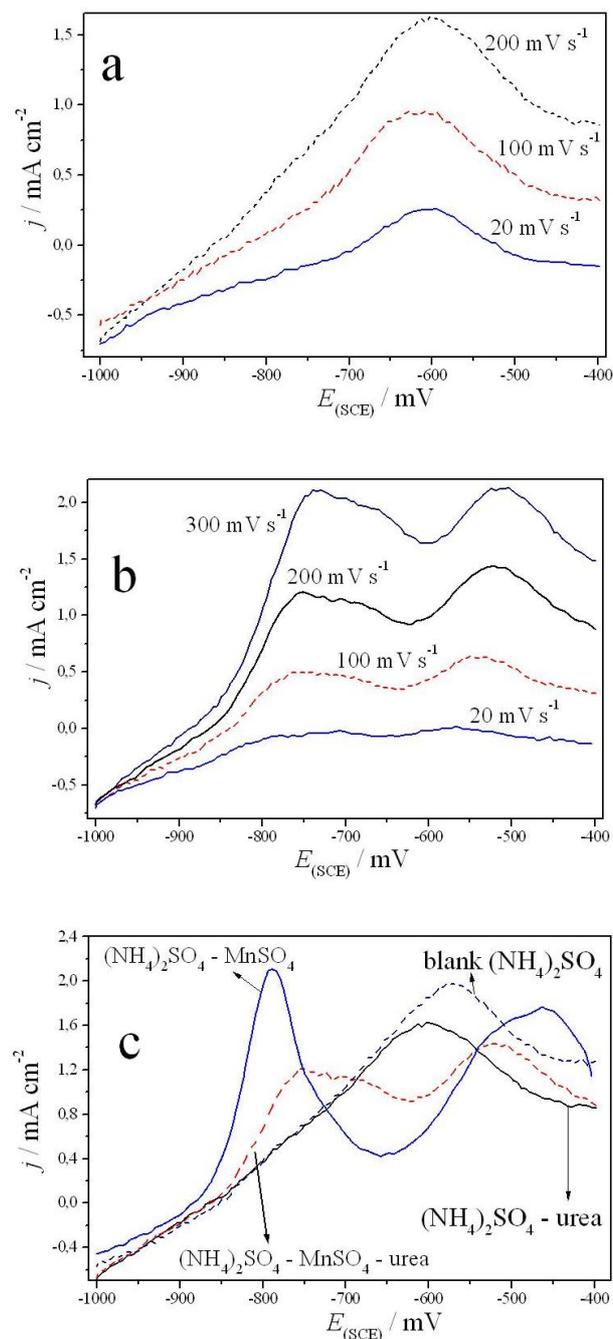
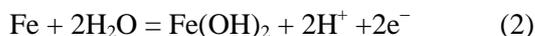


Fig. 2. Anodic part of voltammograms (a) obtained at various scan rates in $(\text{NH}_4)_2\text{SO}_4$ -urea solution; (b) obtained at various scan rates in $(\text{NH}_4)_2\text{SO}_4$ - MnSO_4 -urea solution; and (c) obtained at 200 mV s^{-1} in four different solutions, on a steel electrode without stirring

The voltammograms obtained in Mn^{2+} -free solution, with or without urea, show one anodic peak at around -600 mV (Fig. 2a), which can be attributed to the pre-oxidation or pre-passivation of steel to form the $\text{Fe}(\text{OH})_2$ deposit layer according to the reaction [27]:



On the contrary, when Mn^{2+} ions are added to the solution, two separate anodic peaks appear (Fig. 2b), which may correspond to the dissolution of manganese (at around -750 mV) and probably its oxides and/or hydroxides (at around -500 mV), as already reported in an earlier work [28].

As a summary, Figure 2c illustrates the anodic part of voltammograms obtained in four different solutions, at 200 mV s^{-1} . Although the peak positions slightly evolve according to the solution composition, generally, one may conclude that the voltammograms in Mn^{2+} -free solution show one peak corresponding to the steel corrosion, while those obtained with Mn^{2+} ions exhibit two peaks related to Mn dissolution. It is also clear in both cases that the peak intensity is lower when urea is added to the solution, *i.e.* urea in this case acts as a dissolution inhibitor, which is in accordance with the previous literature [29]. For this reason, it is not feasible to estimate a current efficiency for Mn deposition by calculating the total charge of the anodic and cathodic current peaks in Figures 1 and 2.

In order to better understand the influence of urea on both Mn^{2+} reduction and HER, a current efficiency (*CE*) for metal deposition at various current densities was calculated from the mass gain of the cathode, and the results are shown in Figure 3. In both plating baths, the manganese electrodeposit did not cover the entire substrate surface for current densities lower than 20 mA cm^{-2} . At higher *c.d.s.*, the current efficiency of the Mn electrodeposition reaction steadily increased to 65% (without urea) and 84% (with urea) at 40 mA cm^{-2} , and it was on a high level at *c.d.* values up to 60 mA cm^{-2} . At the *c.d.s.* higher than 60 mA cm^{-2} , the current efficiency decreased, reaching a value of 22% for 90 mA cm^{-2} in the bath without urea. Such a decrease in current efficiency after reaching certain critical *c.d.* is a consequence of limited diffusion of Mn^{2+} species to the cathode, so any further increase in *c.d.* above 60 mA cm^{-2} only increases the HER [30].

The *CE* dependence on *c.d.*, characterized with maximum at certain *c.d.* range, as observed in Figure 3, is typical of Mn electrolysis from aqueous solution, since a HER may occur at a more positive potential than Mn^{2+} reduction. However, the posi-

tion of *CE* maximum varies with substrate type, plating bath composition, and temperature [4].

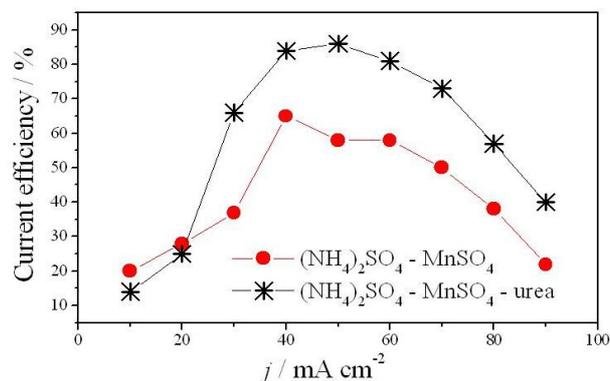


Fig. 3. Current efficiency versus current density for Mn deposition with and without urea in the plating bath.

Figure 3 shows higher plating efficiency for an urea containing bath, which is probably related to the formation of active $\text{Mn}(\text{II})$ -urea complexes, since the complexation may enhance metal deposition in several ways. Firstly, it is seen that the difference in *CE* between the non-urea and the urea bath is more expressed at higher *c.d.s.*, *i.e.* at higher rates of both Mn^{2+} reduction and HER. When the HER exceeds a certain rate, the *pH* increase in the near cathode layer enables the formation of $\text{Mn}(\text{OH})_2$ species and its oxidation product $\text{MnO}(\text{OH})_2$, and they may inhibit Mn reduction and decrease *CE* [19]. Therefore, it may be proposed that Mn-urea complexes prevent the formation of Mn hydroxo-compounds and increase the *CE* in this manner. Furthermore, it was suggested that at high *c.d.s.*, when diffusion to the cathode becomes an important step in the reduction mechanism, some ligands may improve Mn reduction if the diffusion coefficient of $[\text{MnL}_n(\text{H}_2\text{O})_{6-n}]^{2+}$ species is higher than for the $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ species [30]. Finally, urea as an organic molecule, may increase the plating *CE* by selectively adsorbing on active sites of the growing deposit, thus preventing aggregation of the newly generated Mn atoms into dendrites [8], as confirmed by SEM characterization in the following section.

3.2. Effect of urea on the morphological properties of Mn coating

The effect of urea in the plating electrolyte on the formation and distribution of the manganese agglomerates formed on the steel substrate was investigated by SEM. Microphotographs were taken for deposits obtained at *c.d.s.* in the range of 40 – 60 mA cm^{-2} , which were the ones with the highest current efficiency. The time of deposition was adjusted to produce $10 \mu\text{m}$ thick coatings.

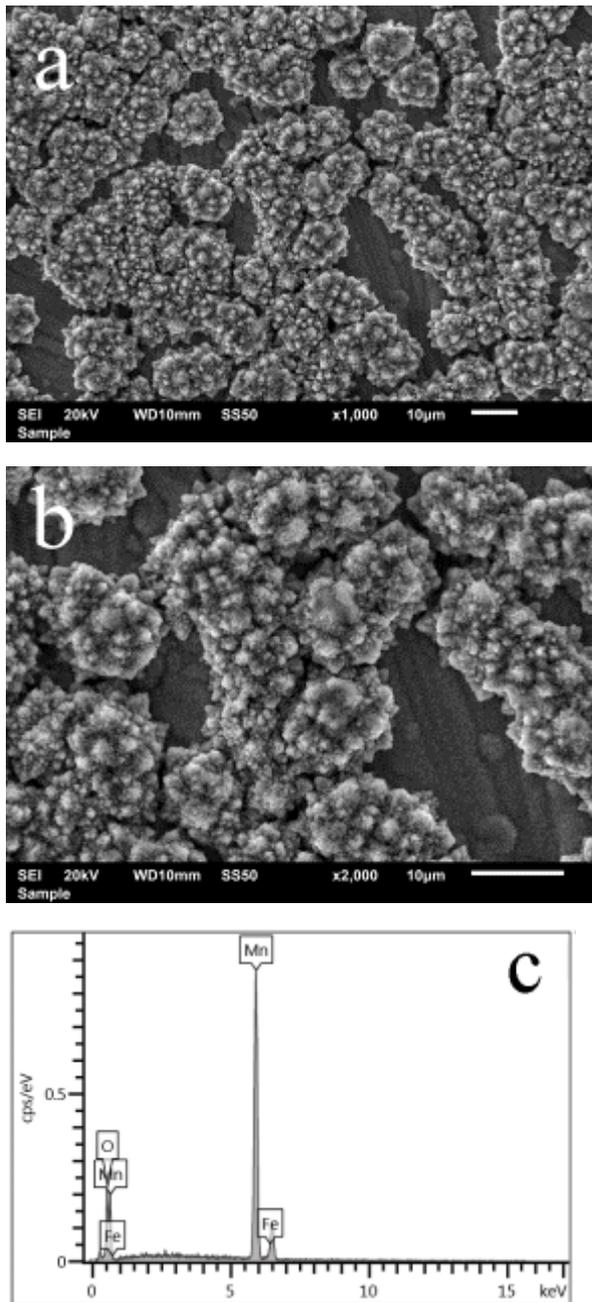


Fig. 4. The SEM microphotographs (a, b) and the EDS diagram (c) for manganese coating electrodeposited at 40 mA cm^{-2} from the bath without urea

Figures 4a and 4b show the deposit obtained at 40 mA cm^{-2} in the absence of urea. The manganese growth produces a surface with high roughness on the macroscopic scale and the formation of porous deposits. The flower-like clusters, having different sizes, are dispersed all over the steel surface, and pores between them even reach the substrate. When a longer deposition time was applied, to make coatings thicker than $10 \mu\text{m}$, the deposits peeled off.

In contrast, in the presence of urea (Figs. 5 a, b and 6 a, b), non-dendritic coatings with good

adherence were obtained. The growth of Mn crystallites perpendicular to the surface was inhibited and they spread across the surface as smooth oval-shaped agglomerates to produce deposits which were rather flat and dense on the microscopic scale. Therefore, these results suggest that urea functioned as a leveling agent. However, there are still small differences between the coatings obtained at different *c.d.s* in the presence of urea. The agglomerates formed at higher *c.d* (Fig. 6) are less uniform in size, and they possess spot-like pores, probably due to the more intensive hydrogen evolution at the growing deposit [31]. Also, the coatings obtained at 40 mA cm^{-2} were white and semi-bright in appearance, while those produced at higher *c.d* were dull, as affirmed by the naked eye.

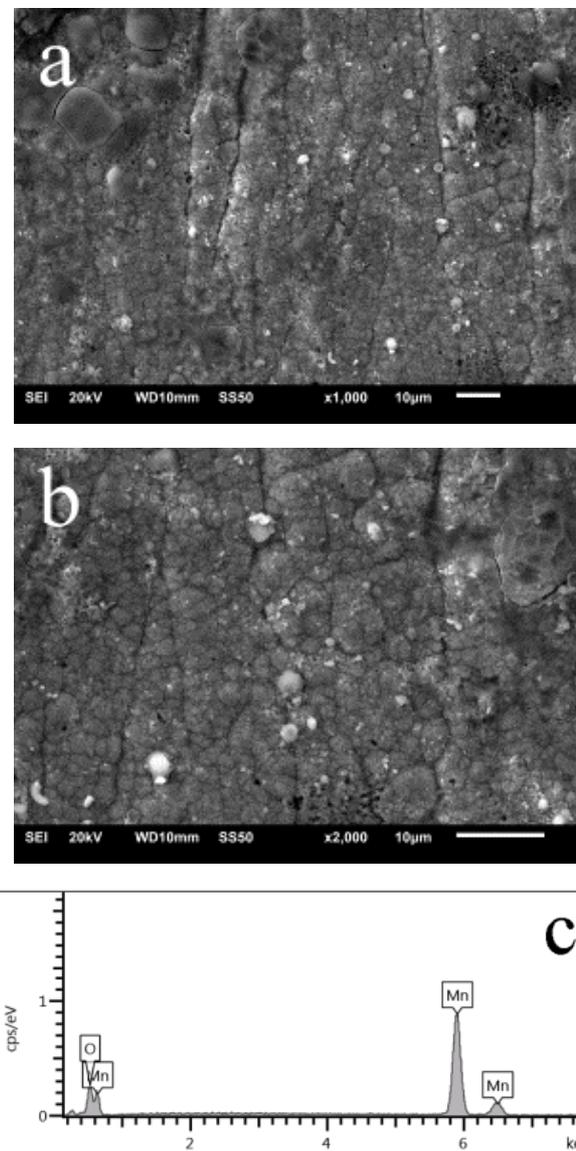


Fig. 5. The SEM microphotographs (a, b) and the EDS diagram (c) for manganese coating electrodeposited at 40 mA cm^{-2} from the bath with urea

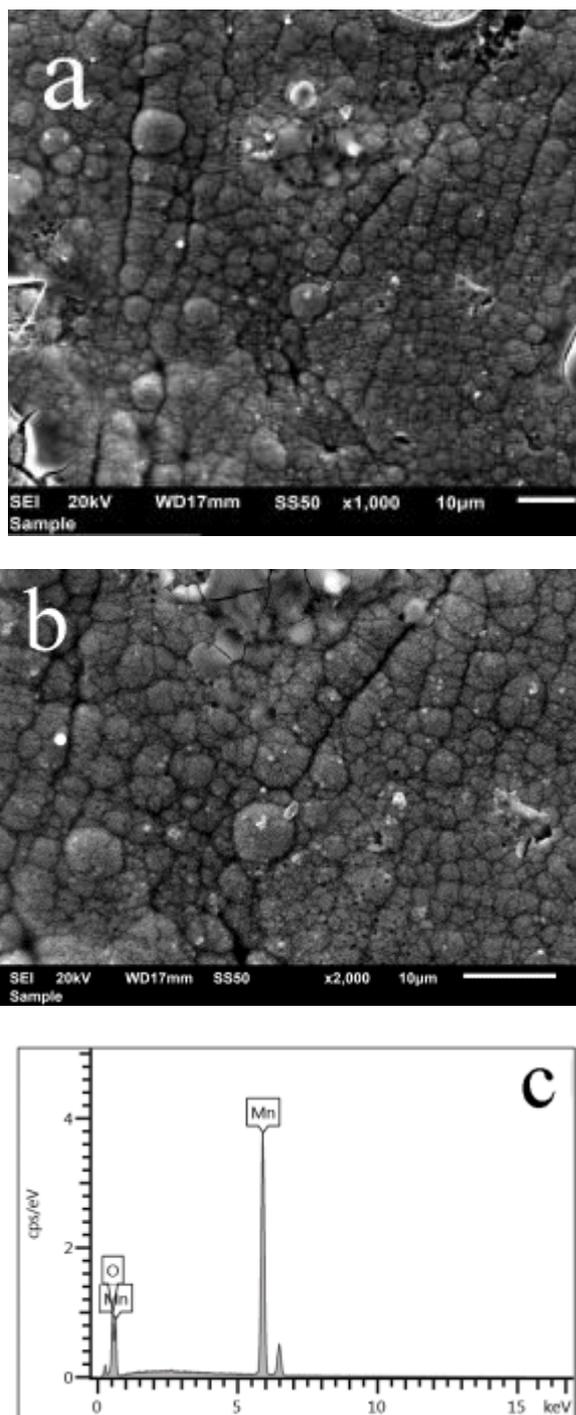


Fig. 6. The SEM microphotographs (a, b) and the EDS diagram (c) for manganese coating electrodeposited at 60 mA cm^{-2} from the bath with urea

To sum up, the SEM analysis provides evidence that the addition of 8 mol dm^{-3} urea in the plating electrolyte improves the morphological properties of Mn deposits, such as increased adhesion, smoothness, uniform coverage, and white appearance. These differences might be ascribed to the adsorption action of urea molecules at the active sites of Mn coating [8, 10] and to the change

in the electrodeposition mechanism caused by the Mn-urea complex species formation [30]. In a commercial manganese production, the Mn deposit gradually becomes rougher and more dendritic with increasing deposition time, resulting in a lower current efficiency. Therefore, the Mn electrolysis industry is constantly seeking new additives which would ensure smooth and compact deposition and have a minimum contamination of the Mn coating [6].

3.3. Effect of urea on the chemical composition of Mn coating

In order to examine the purity of electroplated manganese, the elemental composition of the coatings was determined by EDS. Typical EDS diagrams for deposits obtained at different *c.d.s.*, with or without urea, are shown in Figs. 4–6 together with SEM images, and the data are presented in Table 1. Besides Mn, around 6 wt. % of oxygen was detected at the surface of all coatings, but this is a regular observation for manganese, because a layer of manganese oxides and/or hydroxides (30 to 50 nm) naturally forms on electrodeposited Mn coatings [1, 30]. It is known from earlier research [19, 30, 32] that much higher oxygen content (60 wt. % and more) is present in Mn deposits when Mn oxides/hydroxides are included in the coating during the electrodeposition process. Therefore, it may be concluded that under the conditions applied in the present work, oxygen-free Mn deposits are obtained.

Table 1

EDS elemental composition of manganese coatings electrodeposited at different current densities

Deposition conditions	wt. % Mn	wt. % O	wt. % Fe
40 mA cm^{-2} without urea	92	6	2
40 mA cm^{-2} with urea	94	6	0
60 mA cm^{-2} with urea	93	7	0

Nevertheless, Table 1 shows that at the sample deposited in urea-free electrolyte at 40 mA cm^{-2} , EDS detected around 2 wt. % Fe from the substrate, despite the fact that the coatings were $10 \mu\text{m}$ thick. This finding is in agreement with SEM microphotograph (Fig. 4a) which has shown that the Mn coating was porous and the pores reached to the substrate.

It should be emphasized in this section that no carbon or nitrogen was detected in the deposits, although a high concentration of urea was involved in the electrodeposition process. This is in agreement with the report from B. Bozzini *et al.*, who thoroughly investigated the influence of thiourea, $(\text{NH}_2)_2\text{CS}$, on the electrodeposition of Zn-Mn alloys [33]. Thiourea differs from urea only in a sense that the carbon atom is double-bonded to sulfur, instead of an oxygen atom, and the cathodic reduction of thiourea gives urea along with Zn^{2+} and Mn^{2+} reduction. However, the XPS analysis in this research [33] did not show the presence of S, C or N in the deposits. On the contrary, Cr deposits obtained by Cr(III) electrodeposition in the presence of urea, may contain considerable amounts of organo-metallic compounds with amide- and carboxylic-groups, chromium carbides or nitrides, as a consequence of the reduction of the organic ligand from the inner coordination sphere of the chromium complex [9]. Therefore, although it was concluded in the electrochemical section that urea enhances Mn and Cr deposition in a similar way, the elemental analysis of the deposits proves that there are still differences in the urea-assisted reduction mechanism of these two metals.

4. CONCLUSION

This work offers a new method for manganese electrodeposition from aqueous solution, where an organic substance is added in high concentrations (8 mol dm^{-3}) in order to improve the deposition process and deposit characteristics. Urea was chosen as a high-concentration additive, having already been used as an ionic liquid and organic solution in metal electrolysis. Electrochemical analysis has shown that at lower overpotentials, urea facilitates both the hydrogen evolution reaction and Mn^{2+} reduction, probably through the complexation phenomenon, while at potentials more negative than $-1390 \text{ mV}_{\text{SCE}}$, these processes are inhibited as a result of urea adsorption on the working electrode. However, it was pointed out that the current efficiency for metal deposition is higher in average for 20% in the urea-containing bath, and the highest efficiency was measured in the current density range between 40 and 60 mA cm^{-2} .

The most distinct effect of urea was observed by SEM analysis of the coatings' morphology, where it was shown that without the additive, a porous coating is formed, with flower-like agglomerates which are detached at longer deposition times. In contrast, the Mn samples obtained with urea are smooth, compact, with oval-shaped ag-

glomerates, and for the deposition current density of 40 mA cm^{-2} have white and semi-bright appearance. The chemical analysis shows that Mn deposits formed in this work, regardless of the urea presence in the plating electrolyte, do not contain inclusions with oxygen, carbon or nitrogen atoms.

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