Investigation of electrochemical co-deposition of zinc and molybdenum from citrate solutions

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ABSTRACT

The co-deposition of molybdenum with zinc from citrate electrolytes was studied. Cyclic voltammetry with rotating disc electrode experiments and potentiostatic deposition in coulostatic conditions were carried out in order to analyse the mechanism of electrodeposition of molybdenum with zinc. The results of voltammetric studies indicate Zn and Mo interaction during the electrodeposition process. The electrodeposits were characterised by wavelength dispersive X-ray fluorescence (WDXRF), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Possibility of Zn–Mo alloy layers electrodeposition from citrate solutions was confirmed. The molybdenum content in metallic components (Zn–Mo alloy/compound or Mo) on the surface of deposit was close to 70% of the total molybdenum amount. The mechanism of the co-deposition of molybdenum with zinc has been proposed. It was found that the reaction of molybdenum deposition is limited by the presence of adsorbed Zn(I)-citrate ions, which are formed in the outer-sphere charge transfer mechanism. Further reduction processes are related to the formation of adsorbed mixed Zn(I)–Mo(VI)–citrate complexes, then reduced to metallic molybdenum and metallic zinc during a complicated, multi-stage process.

1. Introduction

Zinc–molybdenum alloys are of interest as environmentally benign corrosion protective coatings. They can be attractive especially as replacement materials for toxic cadmium coatings and for zinc coatings with Cr(VI)-based conversion layers, hence the RoHS EU directive restricts the use of cadmium and hexavalent chromium. Hexavalent chromium may have genotoxic effects, which may lead to carcinogenesis. Conversely, hexavalent molybdenum is much less toxic and it has no genotoxic effects. The addition of molybdenum also has a great effect on the corrosion behaviour of zinc [1–3] and zinc alloys [4–6]. It is commonly known that the addition of molybdenum improves abrasion hardness, toughness and corrosion resistance of alloys [7]. The electrodeposits of zinc-molybdenum showed unusually good corrosion resistance [1–3], similar to that of the electrodeposits from zinc–cobalt–molybdenum [4–6] and zinc–nickel–molybdenum alloys [4,5]. The plating from these alloys proved to last about two to six times longer than Zn plating, as judged from the occurrence of red rust, by salt spray test [4].

There are great differences in the melting and boiling temperatures of zinc and molybdenum, therefore the formation of Zn–Mo alloys is difficult by conventional thermal methods. Electrodeposition can be considered as the best way to obtain such alloys. Electrodeposition is already applied successfully to the production of protective Ni–Mo coatings [8,9], electrocatalytic CoMo alloys [10,11], CoMo and CoNiMo magnetic materials [12,13], etc.

It is known that molybdenum cannot be electrodeposited in a pure state from an aqueous solution. It requires the presence of another metal, which causes molybdenum codeposition. This mechanism of the electrodeposition of alloys is described by Brenner as induced co-deposition [14]. Various hypotheses have been proposed to explain the process of induced co-deposition of molybdenum with the formation of intermediate products [10,15–26]. In all of these theories, iron-group metals play important role, because they may act as catalysts in the formation of intermediate products. Myers, in 1940, initially suggested that the induced codeposition of molybdenum is related to the phenomenon of the formation of an iron-group metal hydroxide layer on the cathode. This layer acts as a membrane, which can be penetrated by molybdate ions. Otherwise, only hydrogen would be discharged [15]. Ernst et al. presented another hypothesis. According to this, Mo first forms oxides or hydroxides, which can be then reduced to Mo by hydrogen in the presence of iron-group metal [16,17]. Fukushima et al. [18,19] supported and developed this hypothesis, stating that atomic hydrogen adsorbed on the deposited iron group element induces the

reduction of intermediate molybdenum oxides or hydroxides to metallic molybdenum. This model suggests that there is an upper limit of molybdenum content in the deposited alloy. Next, Chassaing et al. [20] studied Ni–Mo alloy electrodeposition in citrate electrolytes. They proposed the mechanism by which intermediate molybdate anions and nickel cations present in the electrolyte are reduced by hydrogen forming an Ni–Mo alloy. However, the results of Podlaha et al. [21–23] contradict the participation of hydrogen in the induced deposition of molybdenum and show that the concentration of molybdenum can be achieved above theoretical upper limit proposed by Fukushima [18]. This model proposes that the iron-group metal ions induced the molybdate reduction by forming a molybdenum–ferrous intermediate, which adsorbs on the cathode and is then reduced to metallic molybdenum. After this, Gomez et al. [24,25] analysed the first stages of Co–Mo and Co–Ni–Mo induced electrodeposition. It was found that molybdenum oxides are formed as a first step in the induced co-deposition of molybdenum with cobalt and nickel. This is consistent with the model described by Podlaha et al., which Gomez developed to include the intermediate species, which adsorb on the cathode. They are composed of molybdenum oxides and iron-group metal ions. The research of Subramania et al. [10] is also in line with the model that involves in the alloy formation, the adsorbed intermediate species consisting of molybdenum oxides and iron group metal ions, which undergoes reduction to Mo. However, this work suggests that, at extreme cathodic potentials, in alkaline solutions, the hydrogen formation contributes to the reduction of molybdate ions to molybdenum oxides. More recently, Esteves et al. [26] showed that the adsorbed ferrous intermediates may act as inducing species in the co-deposition of a CoNiMo alloy, rather than mixed intermediates consisting of molybdenum oxides and iron group complex ions as previously stated.

To sum up, it can be said that it is relatively easy to deposit molybdenum from aqueous solutions together with ferrous metals forming an alloy. Nevertheless, the addition of an appropriate complexing agent is necessary and has an effect on quality of the coatings. Work by Eliaz and Gileadi [27] presents a detailed review of all the above-mentioned theories concerning induced co-deposition of molybdenum. It is indisputable that this is a complex, multi-step process, which has not been sufficiently understood so far.

Furthermore, the deposition of metallic molybdenum alone from aqueous electrolytes was demonstrated recently by Morley et al. [28]. Thick layers of metallic molybdenum were obtained from a solution containing a very high concentration of acetates (up to 10 M). It was also proved that co-deposition of molybdenum with zinc was possible, but the maximal content of molybdenum was significantly lower than in deposits of molybdenum with iron group metals. Myers [15] first noted that it is possible to co-deposit Mo with Zn from a pyrophosphate bath. The deposits thus obtained contained about 4% of Mo and 6% of O. The co-deposition of Zn–Mo coatings from the bath based on nitrilotriacetic acid was described elsewhere [2,3]. In this case the deposit contains 0.6–0.8 wt.% of molybdenum. In a previous investigation, Kazimierczak and Ozga [29] studied the electrodeposition of Sn–Zn–Mo layers from citrate electrolytes. Accordingly, the results of voltammetric studies and chemical profile analysis indicate some connections between electrodeposition of Zn with Mo. However, the mechanism of the electrochemical deposition of molybdenum from aqueous electrolytes without a ferrous element has not so far been described as well, as the oxidation state of molybdenum additives in Zn–Mo coatings are not unequivocally determined.

The purpose of this work was to analyse the mechanism and kinetics of the induced co-deposition of molybdenum with zinc from aqueous citrate solutions, and characterisation of surface of obtained alloy layers.

Table 1
Chemical composition of electrolytic baths used.

No.	Electrolyte composition + 0.5 g/dm³ PEG[a] + 0.05 g/dm³ SDS[b], pH = 5		
	$C_6H_5Na_3O_7\cdot 2H_2O$ (M)[a]	$ZnSO_4\cdot 7H_2O$ (M)	$Na_2MoO_4\cdot 2H_2O$ (M)
A1	0.65	0.16	0
A2	0.65	0.16	0.02
A3	0.65	0.16	0.05
A4	0.65	0.16	0.10
A5	0.65	0.16	0.15
A6	0.65	0.16	0.20
A7	0.65	0.16	0.24
A8	0.65	0.16	0.30
B1	0.55	0.16	0.24
C1	0.45	0.16	0.24
D1	0.35	0.16	0.24
E1	0.25	0.16	0.02
E2	0.25	0.16	0.04
E3	0.25	0.16	0.06
E4	0.25	0.16	0.08
E5	0.25	0.16	0.12
E6	0.25	0.16	0.16
E7	0.25	0.16	0.24
F1	0.25	0.08	0.02
F2	0.25	0.12	0.02
F3	0.25	0.20	0.02

[a] Denoted in text as Na_3HCit (where $Cit = C_6H_4O_7$).
[b] PEG-3000, polyethylene glycol 3000 (molecular mass between 2700 and 3300).
[c] SDS, dodecyl sulphate sodium salt.

2. Experimental

The Zn–Mo alloys were electrodeposited electrochemically from citrate electrolytes. The chemical compositions of the electrolytes are given in Table 1. The solution pH was adjusted to 5.0 by the addition of sulphuric acid. All electrochemical measurements were carried out in a 50 cm³ cell, in a system with a rotating disc electrode to ensure constant and controlled hydrodynamic conditions. The measurements were performed in a three-electrode cell, by means of potentiostat PGSTAT302N. A low-carbon steel disc or copper disc was used as a working electrode (surface area 2.83 cm²). Copper electrodes were chemically polished using a mixture of concentrated nitric, acetic and phosphoric acids (1:1:1) in the ambient temperature. Steel electrodes were chemically polished using a solution of oxalic acid and 30% solution of hydrogen peroxide (mixture of 14 cm³ oxalic acid 100 g/dm³ with 2 cm³ 30% H_2O_2 and 40 cm³ H_2O in 40 °C). A platinum sheet (2 cm²) was used as the counter electrode. The working electrode potentials were referred to the saturated calomel electrode (SCE) and were corrected for ohmic drop (CI method). The mechanism of electrodeposition was studied by cyclic voltammetry, with the copper disc as a working electrode. The electrodeposition of the alloy was conducted in the potentiostatic and coulostatic conditions on copper and steel substrates. The surface composition of deposits at different analytic depth was determined by Wavelength Dispersive X-ray Fluorescence (WDXRF) and X-ray Photoelectron Spectroscopy (XPS). The electronic states of elements in the alloy were analysed by XPS. The XPS measurements were performed with a hemispherical analyser (SES R4000, Gammadata Scienta) using Al Kα (1486.6 eV) radiation. The power of the X-ray source was 200 W. All spectra were fitted with a Voigt function (a composition 70/30 of Gaussian and Lorentzian function) in order to determine the number of components under the spectrum envelope. The morphology of the selected coatings was studied by SEM technique. The WDXRF analysis was determined with a Rigaku Primini spectrofluorimeter using scintillation counters (LiF1 crystal). The SEM analysis was performed using a JEOL JSM-7500F Field Emission Scanning Electron Microscope equipped with Oxford Instruments. The current efficiencies and partial polarisation curves were determined on