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Microstructural aspects of manganese metal during its electrodeposition from sulphate solutions in the presence of quaternary amines

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ABSTRACT

In the present study investigation was made on the electrodeposition of manganese from sulphate solutions in the presence of quaternary amines TEABr, TPABr and TBABr. The concentrations of these additives were varied over a relatively broad range to evaluate their effect on the deposit morphology and preferred crystal orientations of the electrodeposited metal. TEABr resulted in bright and smooth manganese electrodeposits giving euhedral shape to the crystals with distinct triple junction points. TPABr also showed similar results at lower concentrations. However, TBABr resulted in the formation of dendritic growths with elongated poly-nodular crystals similar to that of Paragorgia corals having uniform multistep growths. The presence of these quaternary amines in the electrolyte causes polarisation of the cathode. TBABr being the strongest cathode polariser adsorbs strongly on the cathode resulting in poor deposit quality. TEABr was found to be the most efficient additive producing the desired quality manganese electrodeposit.

1. Introduction

Manganese metal is the last element in the electrochemical series having high electroreduction potential ($E^\circ = -1.18$ V vs SHE) that can be electrodeposited from aqueous solutions. The applications of manganese are mostly in the field of steel and alloy production. Manganese is an important constituent of today's steels. Steel contains at least 0.3% of manganese which improves hardenability and machinability of steel apart from increasing the yield by minimising the formation of iron pyrite.

The alloys of manganese with tin [1], zinc [2] and copper [3] have been found to exhibit high resistance towards corrosion. In spite of the wide use of the metal, a cost-effective technology for the production of the manganese needs to be developed. Extensive research has been conducted on the electrodeposition of manganese metal and its alloys since more than half a century ago [4,5]. Most of the literature has focused on the practical issues related to electrodeposition of manganese metal. Manganese has high electroreduction potential in aqueous solutions, its electrodeposition is very much sensitive to the presence of impurities, viz. Fe, Co, Ni, Cu, Zn, etc. in the solution. These impurities are very detrimental and lower the hydrogen overpotential and hence hydrogen evolution reaction becomes dominant causing a severe fall in the current efficiency of manganese electrodeposition [6]. Generally, manganese electrodeposition is carried out from sulphate and chloride electrolytes, but due to the negative impact provided by the chloride medium, viz. corrosive nature of the solution which ultimately requires expensive materials of construction, ventilation of cells to eliminate obnoxious fumes produced at anode [7], sulphate medium was selected for the present study. The electrodeposition was carried out using manganese sulphate with ammonium sulphate as an electrolyte mixture. The presence of ammonium sulphate prevents precipitation of manganese hydroxide and improves the conductivity of the solution [4,5]. In addition to this, the presence of ammonium sulphate improves manganese ion discharge ability and also imparts a buffering effect [8].

Scanty information is available in the literature on the effects of organic or inorganic additives on deposit surface morphology, current efficiency, and crystal orientations of electrolytic manganese metal. Hammerquist and Tenn [9] used thio-urea as an additive in the range of 0.005–0.06 g L^{-1} and got manganese metal deposits of

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60–68% current efficiency over a period of 24 h from sulphate bath containing ammonium sulphate. Gong and Zangari [8] reported the effect of current density and pH on microstructure of manganese deposits. They got sound and homogeneous deposits of manganese metal from pH 2 to 7 and below pH 2 discontinuous films are obtained. They also noticed a change in appearance of the deposits from silvery matte to silvery bright below pH 7. They studied the effect of current density on surface topography and got crystalline grains with good coverage at lower current density. Higher current density results in the formation of fibrous microstructure.

Additives (organic/inorganic) during electrodeposition are usually important due their effects on the growth and structure of the deposits. The promising benefits of additives include: brightening of the deposit, grain size reduction, reducing the tendency of tree formation, increasing the current density, promoting levelling, reducing stress and pitting, etc. [10].

Quaternary amines are found to be used as useful additives in the electrodeposition process [11–13]. The present study investigates the role of different quaternary amines, Tetra ethyl ammonium bromide (TEABr), Tetra propyl ammonium bromide (TPABr) and Tetra butyl ammonium bromide (TBABr), on the deposit morphologies, crystal orientations of the deposited manganese metals and polarisation behaviour of the cathodes.

2. Experimental details

2.1. Apparatus and material

Electrodeposition of manganese was carried out by means of an uninterrupted process in a three chambered electrolytic cell made of Perspex sheet with distinct cathodic and anodic chambers separated by means of a polypropylene diaphragm. Cathodic and one of the anodic chambers consists of inlet and outlet port for the flow of catholyte and spent electrolyte respectively. The flow of the feed solution and anolyte was controlled by using peristaltic pumps. A thermostatic water bath (Julabo, Germany) was used for maintaining the temperature of the electrolyte. Cathode and anode used for the electrolysis were made of SS 316 grade and Pb–Ag (1%) alloy, respectively and were kept at a distance of 2.5 cm from each other. Regulated direct current was supplied from a rectifier (Aplab, India) for carrying out the electrolysis.

2.2. Reagents

The electrolyte was prepared using analytical grade reagents from Merck Chem. Ltd., India using doubly distilled water. Manganese sulphate ($MnSO_4{\cdot}H_2O$), ammonium sulphate ($(NH_4)_2SO_4$) and sodium meta bisulphite ($Na_2S_2O_5$) were used for the preparation of electrolyte. Various organic additives (TEABr, TPABr, TBABr) were added to both the catholyte and feed electrolyte from the respective stock solutions. Ammonium hydroxide and sulphuric acid were used to correct the pH of the electrolyte.

2.3. Solution purification

Alkali, alkaline earth metals and aluminium if present in the solution will not hamper on cathodic efficiency and deposit morphology [6]. However, the presence of elements just like Fe, Co, Ni, Cu, Zn, etc. in the solution has an effect on the electrodeposition process to a greater extent and needs to be separated prior to the electrolysis. The impurities present in the stock solution above the admissible limit were separated as their insoluble sulphide using sodium sulphide as a precipitant. The concentration of these impurities in a stock solution containing $30\,g\,L^{-1}$ Mn before and after purification is shown in Table 1.

2.4. Electrode preparation

The cathode was first polished with 400 and 1200 grade silicon carbide paper to mirror like finish followed by washing with de-ionised water. It was then dipped in dilute HNO_3 for 30-min followed by washing with water. Then these cathodes were treated with sodium silicate and allowed to air dry. No specific treatment was carried out for the anodes. The dried cathode was then weighed prior to electrodeposition.

2.5. Electrolysis

All the electrodeposition experiments were conducted for 3 h duration. The concentration of manganese in the purified solution was analysed volumetrically by titration method. The impurities which are present in very trace amount were analysed by AAS (Perkin Elmer, Model No. AA200). The concentration of manganese in the feed solution and catholyte used for electrodeposition is $30\,g\,L^{-1}$ and $12\,g\,L^{-1}$ respectively. Both the solutions contain $120\,g\,L^{-1}$ of $(NH_4)_2SO_4$ and $0.475\,g\,L^{-1}$ sodium meta bisulphite. The cell voltage was recorded at an interval of 30 min. After electrodeposition the cathode was dipped in 0.1 N potassium dichromate solution and then washed thoroughly with water followed by drying in air. The cathode was then weighed to find out the current efficiency and energy consumption. The manganese metal flakes were then removed from the cathode with the help of a rubber mallet.

2.6. Deposit examination

A PANalytical diffractometer (PW 1830; Philips, Japan) was used to study crystallographic orientations of the manganese electrodeposits by X-ray diffraction (XRD) using Mo Kα radiation, $\lambda = 0.70932$ Å. The scans were recorded in the 2θ range 10–40°. The surface morphology of the electrodeposited manganese metals was analysed using a scanning electron microscope (SEM) (JEOL JSM 6510, Japan).

2.7. Polarisation behaviour

Linear sweep voltammetry (LSV) technique was employed to see the polarisation behaviour of the cathode in the presence and absence of these quaternary amines using Metrohm potentiostat/galvanostat model 128A. A conventional three-electrode glass cell was used to run these experiments. 316 stainless steel electrodes with an effective area of $1\,cm^2$ and a sheet of Pb–Ag (1%) alloy were used as working and counter electrodes, respectively. All the potentials were recorded with reference to a saturated calomel electrode (SCE). The linear scans were carried out in the potential range of -0.7 to -1.09 at scan rates of $10\,mV\,s^{-1}$.

3. Results and discussion

3.1. Digital images

The presence of quaternary amines (TEABr, TPABr and TBABr) in the cells during electrodeposition showed noticeable effect on the surface texture of the electrodeposited manganese metals. Fig. 1 shows the digital images of the electrodeposited manganese metals in the presence and absence of quaternary amines. The electrodeposited manganese metal obtained from additive free electrolyte was dull (Fig. 1a) to the naked eye and the surface of the deposit was uneven. It is interesting to see that introduction of TEABr in to the electrolytic bath resulted in a bright and smooth manganese electrodeposit (Fig. 1b). It was also seen