



Electrodeposition of manganese metal from sulphate solutions in the presence of sodium octyl sulphate



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ABSTRACT

In the present paper the effects of anionic surfactant sodium octyl sulphate (SOS) on the electrodeposition of manganese from sulphate solutions were studied. It was observed that addition of SOS increases the current efficiency and hence decreases the energy consumption during electrodeposition of manganese. High quality manganese deposits with smooth and compact surfaces were deposited on 316 grade stainless steel substrate in the presence of SOS. The concentration of this anionic surfactant was varied over a relatively broad range to assess its effect on current efficiency, energy consumption, crystallographic orientations and deposit morphology of the electrodeposited manganese metal. The addition of SOS increased the cathodic efficiency of manganese metal from 59% to 67% when $20 \text{ mg} \cdot \text{L}^{-1}$ SOS was introduced into the electrolytic bath. X-ray diffraction studies revealed that (330,411) planes are the most preferred planes of crystal growth during manganese electrodeposition at a current density of $500 \text{ A} \cdot \text{m}^{-2}$ resembling alpha-manganese irrespective of the concentration of additive. Scanning electron micrographs showed smooth, bright and uniform deposit morphologies when manganese was electrodeposited in the presence of $20 \text{ mg} \cdot \text{L}^{-1}$ SOS. Linear sweep voltammetry showed polarisation of the cathode indicating additive adsorption on it.

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1. Introduction

Manganese plays an indispensable contribution in steel making and is one of the most important metals in an industrial economy. Manganese enhances the solubility of nitrogen in the matrix at higher temperatures, which will lead to lower probability of nitride formation during thermal treatment. It is estimated that about 90% of all manganese consumed worldwide goes into the steel industry as an alloying element for steel production alone which makes manganese the fourth most used metal (Manganese: The Fourth Most Used Metal in the World, 2014).

Most of the literatures on manganese electrodeposition reported the effect of bath composition, electrolyte pH, current density, nature of the electrodes etc. on cathodic current efficiency, energy consumption and quality of the deposited metal (Jacobs, 1946; Bradt and Oaks, 1937; Sengupta, 1993). Very little information is available which articulates on phase analysis and the microstructure of the deposited metal. Due to the low electro-reduction potential ($E^0 (\text{Mn}^{2+} / \text{Mn}) = -1.18 \text{ V Vs SHE}$) of manganese it is difficult to electrodeposit the metal with high cathodic current efficiency (CE). Therefore, to obtain very high CE and better deposit quality, the electrolyte must be free from impurity

metal ions such as Co, Ni, Cu, Zn, Fe, etc. (Harris et al., 1977). Some researchers tried to increase the current efficiency of electrolytic manganese metal by introducing compounds of selenium in the form of selenious acid (H_2SeO_3) or selenium dioxide (SeO_2) (Ilea et al., 1997; Radhakrishnamurthy and Reddy, 1977). Sun et al. (2011) have reported that Se(IV)O_2 reduces to Se(0) during manganese electrodeposition and then adsorbs on the cathode. The formation of $\alpha\text{-MnSe}$ on the cathode is a key factor in increasing the CE. The kinetics of reduction of manganous ion without SeO_2 slows down due to the unavailability of efficient crystallisation centres (Fan et al., 2012). However incorporation of selenium or its compounds lowers the quality of the manganese metal resulting in products with metal purity of about 99.7% Mn and selenium contamination of about 0.15%. On the other hand selenium-free manganese metal has a purity of at least 99.9% and is safe and eco-friendly (Lemly, 2004; Selenium free, 2014). About 75% of the world's manganese is currently made using the selenium addition method in order to cut production costs and maximize the net profit. But selenium and its compounds have hazardous effect on the environment and selenium pollution has resulted in a global environmental safety issue. Hence, alternative route for the electrodeposition of manganese metal with high current efficiency and better deposit quality is the need of the day. As an alternative to selenium, attempt was made by Galvanauskaitė et al. (2011) who used tellurium compounds during manganese electrodeposition and reported that the presence of tellurium in the electrolytic

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solution decreased the CE. Recently, Griškonis et al. (2014) studied the effect of Te (VI) at higher temperature and reported that the CE increased from 37 to 71% when the temperature of the bath increased from 20 to 80 °C. He also reported that the manganese metal was associated with phase changes from mix α -Mn & β -Mn to brittle α - and then to very hard β -form with increasing temperature. Hammerquist and Tenn (1951) initiated the introduction of organic additive to the electrolyte prior to electrolysis with an aim to increase the cathodic efficiency. He reported that introduction of thiourea to the electrolytic bath increased the CE to about 68% with a plating cycle not less than 24 h.

Electrolytic manganese metal can be obtained from both sulphate and chloride electrolytes with and without additives. However, the corrosive nature of the chloride solutions which require expensive materials of construction and evolution of obnoxious fumes at the anodes makes the process disadvantageous for manganese electrodeposition (Jacobs and Churchward, 1948). Hence, in general electrodeposition of manganese metal is carried out from sulphate baths. Further the presence of ammonium sulphate in the bath prevents precipitation of manganese hydroxide, improves both manganese ion discharge ability and the conductivity of the solution, and also imparts buffering effect (Oaks and Bradt, 1936; Bradt and Oaks, 1937).

The use of anionic surfactants during electrodeposition of non-ferrous metals is not new (Tripathy et al., 1997; Mohanty et al., 2009). SOS has also been used during electrodeposition of manganese dioxide from acidic manganese sulphate solutions (Biswal et al., 2015). These surfactants are used in order to increase the CE, decrease EC and to obtain better deposit morphology (Tripathy et al., 1997; Mohanty et al., 2009; Biswal et al., 2015). Anionic surfactants usually contain polar and solubilising groups like carboxylates, sulphonates, sulphates and phosphates. Among these compounds, the alkyl sulphates containing eight or more carbon atoms are often used as anionic surfactants (Schwartz and Perry, 1963).

As the use of surfactants in electrodeposition of non-ferrous metals looks promising and has not been assessed for manganese electrodeposition, the present study uses sodium octyl sulphate to improve the electrodeposition characteristics of manganese metal from sulphate solutions.

2. Experimental

2.1. Apparatus and material

Electrodeposition of manganese metal was carried out in continuous mode using a three chambered electrolytic cell made of Perspex with distinct cathodic and anodic chambers separated by polypropylene diaphragms. Cathodic and one of the anodic chambers consist of inlet and outlet ports for the flow of catholyte and spent electrolyte respectively using a peristaltic pump. A thermostatic water bath [Julabo, Germany] was used to maintain the temperature of the electrolyte. A stainless steel (316 grade) sheet was placed between two Pb–Ag (1%) alloy anodes and the distance between anode to cathode was kept at 2.5 cm. A regulated power supplier [Aplab, India] was used as a source for DC current to carry out the electrodeposition process.

2.2. Reagents

The sulphate bath was prepared from analytical grade reagents from Merck Chem. Ltd., India using doubly distilled water ($6.21 \mu\text{Sm}^{-1}$). Manganese sulphate, ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) and sodium meta-bisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) were used for the preparation of the bath electrolyte. Sodium octyl sulphate (Sigma-Aldrich, India) was used as an anionic surfactant and added to catholyte and feed electrolyte at various concentrations ($\text{mg} \cdot \text{L}^{-1}$) to investigate their effects on manganese electrodeposition. Diluted solutions of ammonia and sulphuric acid

were used for pH adjustment of the electrolyte. The pH of the catholytes and that of the feed solutions was maintained at 7.0 and 3.0 respectively.

2.3. Electrode preparation

The cathode was first polished with 400 and 1200 grade silicon carbide paper to mirror like finish followed by washing with doubly distilled water. The cathode was then dipped in dilute HNO_3 (10% v/v) for 30 min followed by washing with water. Then the cathode was treated with sodium silicate (5%) and allowed to air dry. No specific treatment was carried out for the anodes. The dried cathode was then weighed prior to electrodeposition.

2.4. Electrolyte preparation

The cathodic reduction potential of manganous ion is very high hence requires a very high pure solution for its electrodeposition from an aqueous solution. Elements like Fe, Co, Ni, Cu, Zn, etc. require to be removed prior to the electrolysis. However, the presence of alkali, alkaline earth metals and aluminium in solution does not affect the manganese electrodeposition process. The synthetic manganese sulphate used for this purpose contains Co and Ni beyond their tolerance limits which need to be separated. Sodium sulphide was used as a precipitant to precipitate these elements as their respective insoluble sulphides. The concentrations of these impurities in the stock solution containing $30 \text{ g} \cdot \text{L}^{-1}$ Mn before and after purification are shown in Table 1. It can be noted that after purification all the elements are present well below the tolerance limit.

2.5. Electrolysis

All the electrodeposition experiments were conducted for 3 h duration at a current density of $500 \text{ A} \cdot \text{m}^{-2}$. The concentration of manganese in the purified solution was analysed volumetrically by titration method. The impurities which were present in very trace amount were analysed by AAS (Perkin Elmer, Model No. AA200). The concentrations of manganese in the feed solution and the catholyte used for electrodeposition were $30 \text{ g} \cdot \text{L}^{-1}$ and $12 \text{ g} \cdot \text{L}^{-1}$ respectively, which means approximately $18 \text{ g} \cdot \text{L}^{-1}$ of manganese, has been stripped from the feed solution. The plating rate of manganese metal was kept at $\sim 2.95 \text{ g} \cdot \text{h}^{-1}$ so that the concentration of manganese in the catholyte remained constant throughout the process. Both the solutions contain $120 \text{ g} \cdot \text{L}^{-1}$ of $(\text{NH}_4)_2\text{SO}_4$ and $0.475 \text{ g} \cdot \text{L}^{-1}$ 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 and air dried. The cathode was then weighed to find out the cathodic 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

X-ray diffraction (XRD) patterns were measured with PANalytical diffractometer (PW 1830; Philips, Japan) within $2\theta = 10^\circ$ to 80° using

Table 1
Required solution purity for manganese electrodeposition, $[\text{Mn}^{2+}]$: $30 \text{ g} \cdot \text{L}^{-1}$

Element	Before purification, ($\text{mg} \cdot \text{L}^{-1}$)	After purification ($\text{mg} \cdot \text{L}^{-1}$)	Maximum admissible ^a ($\text{mg} \cdot \text{L}^{-1}$)
Cu	1.061	0.319	5.0
Ni	4.56	0.566	1.0
Co	35.06	0.393	0.5
Zn	0.906	0.359	20.0
Fe	1.190	0.722	10.0
Na	1.645	456	Not reported

^a Ilea et al. (1997).

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