

# **Electrodeposition and Characterization of Manganese Coatings**

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Manganese coatings of high quality are electrodeposited on steel substrates from simple sulfate solutions with addition of ammonium sulfate. Potentiodynamic scans and galvanostatic experiments are used to study manganese electrodeposition in a wide range of pH and current density. The effect of these variables on the microstructure, crystallography, mechanical, and corrosion-resistance properties of manganese deposits are investigated. It is found that ammonium sulfate enhances the reduction reaction of the manganese ion and provides a buffering effect. Two types of manganese deposits can be obtained depending on current density: crystalline films (type I, body-centered tetragonal  $\gamma$ -Mn) at low current density and amorphous films (type II) at high current density. Bright manganese films with (002) preferential orientation are electrodeposited at low pH. Type I structures show recrystallization at room temperature with phase transformation; the rate of phase transformation from  $\gamma$ -Mn to  $\alpha$ -Mn (body-centered cubic) follows a Johnson-Mehl-Avrami kinetics. Crystalline films obtained at relatively high current density and low pH tend to have higher phase transformation rates. Amorphous films show good corrosion resistance both in acidic sodium sulfate/ borate and sodium chloride electrolytes.

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Electrodeposited coatings of manganese (Mn) or Mn alloys potentially combine good sacrificial corrosion protection with adequate tribological behavior and suitable mechanical properties for coating steel products.<sup>1.4</sup> Despite this interest, few investigations have been concerned with a detailed study of the electrodeposition of pure Mn metal and the structure and properties of its deposits. This is probably due to the very low potential of Mn in aqueous solutions  $(E_0(\text{Mn}^{2+}/\text{Mn}) = -1.18 \text{ V}_{\text{SHE}})$ , which renders Mn the most electronegative metal that can be electrodeposited from aqueous solutions, leaving a narrow processing window available for optimization of the deposition process.

Although manganese electrowinning has been an industrial process since 1930, recent literature on the electrodeposition of manganese and the relationship between its physical properties and processing conditions is rather sparse. Dean's book<sup>5</sup> provides an excellent survey of the status of manganese electrowinning technology up to 1952, and Brenner's book<sup>1</sup> offers an exhaustive review of manganese and Mn alloy electroplating up to 1960. Early literature focused on electrowinning and consequently studied mainly the effect of bath composition, pH, current density, etc., on current efficiency, coating appearance, and power consumption.<sup>6-10</sup> Manganese could be electrodeposited from both sulfate and chloride solutions, with or without additives. A current efficiency of up to 60-70% and both ductile gamma manganese (body-centered tetragonal, bct, or more precisely, centered tetragonal<sup>11</sup>) and brittle alpha manganese (body-centered cubic, bcc) could be obtained under different conditions. The ductile metal was found to recrystallize to the brittle form at room temperature, the transformation being complete in about 14 days.<sup>12</sup> This phenomenon was ascribed to the high hydrogen content of electrolytic Mn.<sup>13</sup> The phase transition kinetics was investigated through the evolution of electrical resistivity with time.<sup>12</sup> By using modern electrochemical techniques, more recent papers14-18 examined the influence of processing conditions on manganese electrodeposition.

In this paper, the electrodeposition of Mn from ammonium sulfate electrolytes at pH 1.7-7.5 and current density from 30 to 330 mA/cm<sup>2</sup> is studied. Morphological, chemical, structural characterization, and open-circuit potential measurements were further used to characterize the properties of the deposits. In order to attempt stabilization of ductile gamma manganese, the phase transformation kinetics and its dependence on current density and pH were investigated. This work provides a range of processing conditions for the

production of high-quality Mn deposits, which could be taken as a starting point in the development of viable processes for the electrodeposition of various Mn alloys.

#### Experimental

The electrodeposition experiments were carried out in a threeelectrode, two-compartment prismatic cell. The counter electrode was a platinum foil placed in the same compartment as the working electrode, and covered by a diaphragm to avoid the contamination of solution following formation of manganese oxides. The saturated calomel reference electrode (SCE) was in a different compartment, separated from the working electrode by a Luggin capillary mounted on a syringe barrel. The same cell was used for potentiodynamic scans and galvanostatic electrodeposition. The experiments were performed, and potential/current curves as well as galvanostatic transients were recorded, using an EG&G PAR A273 potentiostat/ galvanostat.

Simple sulfate electrolytes with addition of ammonium sulfate were used. pH was adjusted by adding concentrated ammonium hydroxide or sulfuric acid. No attempt was made to control the pH during deposition, but pH was measured and, if necessary, adjusted, after each deposition experiment. The basic bath contained 0.59 M MnSO<sub>4</sub> and 1 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The solutions were prepared with analytical grade reagents and triply distilled water. All experiments were carried out at 25°C.

Manganese was plated on stainless steel 304 plates with an active surface area of 3 cm<sup>2</sup> ( $1.5 \times 2.0$  cm). The substrates were first mechanically polished with various grades of alumina powder papers and degreased with alkaline solution (23 g/L NaOH, 22 g/L Na<sub>2</sub>CO<sub>3</sub>, 10 g/L Na<sub>2</sub>SiO<sub>3</sub>(anhydrous), 10 g/L Na<sub>3</sub>PO<sub>4</sub>, 1 g/L sodium lauryl sulfate, 90-95°C, 3-5 min) and acetone. Subsequently, they were electropolished in concentrated phosphoric acid (85%) and pickled in mixed nitric (5%) and hydrochloric acid (25%) just before use.

The current efficiency was calculated from the weight gain of the sample. Surface morphology was examined by scanning electron microscopy (SEM) using a Philips XL30 instrument. Chemical analysis of the deposits was performed by energy-dispersive X-ray spectrometry (EDAX) attached to the SEM, while the incorporation of oxygen and the chemical states of Mn were studied by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis 165. Crystallographic structure was determined by X-ray diffraction (XRD) using a Philips APD 3520 diffractometer with Cu K $\alpha$  radiation. A Buehler Micromet microhardness tester (model 1600-6100) was employed to measure the microhardness of manganese films.

Corrosion resistance of the coatings was evaluated by monitoring the open-circuit potential of the deposits after immersion in  $0.5 \text{ M} \text{ Na}_2 \text{SO}_4 + 0.5 \text{ M} \text{ H}_3 \text{BO}_3$  (pH 3) or 2.5% NaCl (pH 3) solu-

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Figure 1. Potentiodynamic behavior of Mn 0.59 M at room temperature: (a) pH 3, with and without 1 M  $(NH_4)_2SO_4$ ; (b) with  $(NH_4)_2SO_4$ , at various pH values. Note the vertical log axis of the inset.

tions. The solutions were quiescent and no inert gas was used to purge the electrolyte. Morphology and chemical composition of the coatings after corrosion testing were evaluated to gain insight into the extent and nature of the corrosion process.

#### **Results and Discussion**

*Potentiodynamic behavior.*—The pH of the as-prepared electroplating solution was 3.7, which was adjusted in the range from 1.7 to 7.5 by addition of concentrated ammonium hydroxide or sulfuric acid. As pointed out by Dean,<sup>5</sup> the addition of ammonium sulfate to the manganese electrolyte can prevent precipitation of manganese hydroxides during electrodeposition as the pH increases and improves the conductivity of the solution. In addition, we observed a buffering effect of the ammonium sulfate at pH above 6 and below 3.5. In the presence of air, at high pH (7-9), the electrolyte was not stable unless sulfur compounds or other antioxidants were added, such as sulfur dioxide and hydroxylamine salts.<sup>5</sup> These substances, however, are generally undesirable from the viewpoint of corrosion protection; consequently, simple sulfate acidic electrolytes were preferred in this work.

Figure 1 reports the cathodic current/voltage curves for the Mn electrolyte, with and without addition of ammonium sulfate (Fig. 1a), and at various pH (Fig. 1b). The increase in current density below  $-1.5 V_{SCE}$  with addition of ammonium sulfate observed in Fig. 1a is due both to an increase in the discharging ability of Mn ions, as reported in Ref. 5, and to a decrease in the overpotential for hydrogen evolution.<sup>17</sup> As demonstrated by galvanostatic deposition, the presence of ammonium sulfate is essential to grow manganese coatings with good coverage. The increase in the slope of the curve



Figure 2. Effect of current density on current efficiency at pH 6.4, 0.59 M  $MnSO_4$  and 1 M  $(NH_4)_2SO_4$ .

with addition of ammonium sulfate may indicate a different mechanism for Mn and/or hydrogen reduction. The scan rate has little influence on the potentiodynamic behavior until a relatively high overvoltage is attained, where a low scan rate yields a higher current density at the same overpotential. This is contrary to the common trend of voltammetric measurements and can be explained as follows: as the potentiodynamic scan proceeds, the stainless steel cathode would be completely covered by manganese at lower potentials when the scan rate is lower. Manganese has a higher catalytic activity for  $Mn^{2+}$  discharging and a slightly higher overpotential for H<sup>+</sup> discharging than stainless steel, <sup>17,19</sup> causing observation of a larger current. This effect was confirmed by galvanostatic depositions.

At all pH values investigated, Mn(II) discharge is accompanied by hydrogen evolution. At pH 2-3 a lower overvoltage for hydrogen evolution is observed (Fig. 1b). The consequent increase of hydrogen evolution and the fast dissolution of the Mn coating in acid solutions limit the practical pH range for deposition above these values. A manganese electrodeposition peak can be seen around  $-1.7 V_{SCE}$ , corresponding to a current density of about 25-30 mA/cm<sup>2</sup> (see inset in Fig. 1b; note the log scale of the vertical axis). To summarize, the Mn(II) ion discharging reaction is accompanied by hydrogen evolution at all pH values, while ammonium sulfate increases manganese ion discharging ability and provides a desirable buffering effect at pH 2-3.5 and 6-7.

Galvanostatic electrodeposition.—The manganese deposits were grown galvanostatically at a temperature of 25°C, with current density varying in the range 30-330 mA/cm<sup>2</sup> and pH from 1.7 to 7.5. Deposition was carried out without stirring of the electrolyte, for a time duration calculated to obtain a 10  $\mu$ m thick deposit according to Faraday's law, assuming 100% current efficiency and the deposits in the tetragonal  $\gamma$ -form ( $\rho = 7.20$  g/cm<sup>3</sup>). The actual current efficiency was calculated from the weight gain of the cathode. The results are reported in Fig. 2 as a function of current density for fixed pH 6.4. The highest current efficiency is about 60% at the current density of 65 mA/cm<sup>2</sup>. This is very close to the results reported by Dean<sup>5</sup> at pH 8.2-8.4. At low current densities, the efficiency of manganese deposition is affected by self-dissolution of the film. Because both hydrogen ion discharging

$$2\mathrm{H}^+ + 2\mathrm{e} \to \mathrm{H}_2^{\uparrow}$$
 [1]

and manganese dissolution

$$Mn + 2H^+ \rightarrow Mn^+ + H_2 \uparrow$$
 [2]

contribute to hydrogen evolution, the hydrogen evolution rate is high and the manganese deposition rate appears low. A sharp fall of



Figure 3. Effect of pH on current efficiency (current density 65 mA/cm<sup>2</sup>), 0.59 M  $MnSO_4$  and 1 M  $(NH_4)_2SO_4$ .

current efficiency when current density was increased from 65 to 150 mA/cm<sup>2</sup> was also observed, in agreement with both earlier<sup>5</sup> and recent results<sup>16,18</sup> in sulfate and chloride solutions. Various reports indicate different values of this transition current density, which might be due to the different deposition conditions employed.

For aqueous electrolytes containing  $MnSO_4$  and  $(NH_4)_2SO_4$ ,  $Mn^{2+}$  can exist in the forms  $[Mn(H_2O)_6]^{2+}$ ,  $[Mn(NH_3)_{x=1-6}]^{2+}$ , or  $[Mn(H_2O)_{6-n}(NH_3)_n]^{2+}$ .<sup>20-22</sup> Due to the presence of the high-spin 3d<sup>5</sup> manganese(II) ion, all these compounds are octahedrally coordinated and possess zero ligand field stabilization energy.<sup>20</sup> Therefore, the complexes formed in this system are unstable. It was also proposed<sup>22</sup> that  $Mn^{2+}$  discharge could take place through the following mechanism when  $NH_3$  is present

$$[Mn(H_2O)_{6-n}(NH_3)_n]^{2+} + xH_2O$$
  

$$\leftrightarrow [Mn(H_2O)_{6-n+x}]^{2+} + nNH_3$$
[3]

$$[Mn(H_2O)_{6-n+x}]^{2+} + 2e \to Mn + (6 - n + x)H_2O \quad [4]$$

Due to the relative instability of the possible Mn<sup>2+</sup> complexes, as current density increases from 65 to 150 mA/cm<sup>2</sup>, it is unlikely that the dissociation of these complexes becomes the rate-determining step of Mn<sup>2+</sup> discharge. It is more probable that Mn<sup>2+</sup> discharging is limited by the diffusion of  $Mn^{2+}$  complexes to the cathode surface.<sup>16</sup> When such limiting current is attained, any further increase of current density would only increase the H<sup>+</sup> discharging rate, decreasing the current efficiency and eliminating the H<sup>+</sup> adjacent to the cathode surface. The buffering effect of  $(NH_4)_2SO_4$ could stabilize the pH near the cathode only to a limited extent. With increasing current density the hydroxyl ion concentration at the interface would increase to such a high level that large amounts of manganese hydroxide would precipitate and be incorporated into the growing deposit, increasing the apparent current efficiency as current density goes above 150 mA/cm<sup>2</sup> (Fig. 2). Incorporation of Mn hydroxides at high current density was confirmed by XPS analysis, as discussed in the next section.

Current efficiency *vs.* pH at a fixed current density of 65 mA/cm<sup>2</sup> is plotted in Fig. 3. Current efficiency is relatively stable at above 70% from pH 2 to 6. Current efficiency decreases below pH 2, at which the high electrolyte acidity and the increased H<sup>+</sup> discharging rate induce higher Mn dissolution rate and lower relative Mn deposition rate, respectively. From pH 2 to 4,  $Mn^{2+}$  exists predominantly as  $[Mn(H_2O)_6]^{2+}$ , and at pH 4 to 6 as  $[Mn(H_2O)_{6-n}(NH_3)_n]^{2+}$ , *n* increasing with pH.<sup>20-22</sup> Above pH 6.5, in the presence of air, the bulk electrolyte becomes gradually unstable due to the precipitation of manganese hydroxide  $[Mn(OH)_2]$ . Its oxidation product



**Figure 4.** High-resolution XPS spectra of manganese coatings in the O 1s and Mn 2p energy windows: (top) type I, 65 mA/cm<sup>2</sup> and (bottom) type II, 330 mA/cm<sup>2</sup>.

 $MnO(OH)_2$  also makes the solution unclear and lowers current efficiency, which is detrimental to manganese deposition.

Microstructure and composition of the coatings.-Adherent manganese deposits of good quality are generally obtained by this process. At current densities from 30 to 100 mA/cm<sup>2</sup>, coatings are silvery matte in appearance, compact, uniform, and continuous; these deposits are indicated in the following discussion as type I. Typical microhardness of as-deposited type I coatings is 147 Knoop hardness number (KHN), using a load of 200 gf on a 40 µm thick film obtained at the current density of 65 mA/cm<sup>2</sup>. The depth of indent is about 11% of the deposit thickness. On the other hand, black, glossy, and even more compact films (which are called type II in the following discussion) are formed at current densities above 150 mA/cm<sup>2</sup>. Microhardness of type II deposits is typically 487 KHN, using a load of 200 gf on 40 µm thick films obtained at the current density of 330 mA/cm<sup>2</sup>. The depth of indent is about 6.3% of the deposit thickness. At current densities between 100 and 150  $mA/cm^2$  a transition between type I and type II films is observed; occasionally the two microstructures are present in the same sample, with type I observed at the center area and type II at the edges.

The chemical states and composition of typical type I and type II coatings were examined by EDAX and XPS depth profiling. Although EDAX seems to indicate that both types of films are pure Mn and do not contain other impurities, XPS analysis gives more accurate results. Figure 4 shows high-resolution XPS scans of the Mn 2p and O 1s regions for the two types of films at different depths. For type I films, the Mn:O (atom %) ratio changes from 51:49 near the surface (after etching five cycles, about 10 nm deep) to 85:15 at the interior (after etching 40 cycles, about 80 nm deep). By deconvoluting the O 1s peak using three components (corresponding to water, oxide, and hydroxide),<sup>23</sup> the existing forms of oxygen could be quantified. Analyzing the Mn 2p peaks with the charge neutralizer on to avoid sample charging effects, Mn oxidation states could be determined. Near the surface, manganese is almost exclusively in the form  $Mn^{2+}$  to  $Mn^{4+}$ , probably as  $MnO_x(OH)_{2-x}$  (x = 0-2), while in the bulk of the deposit, Mn is mostly present as Mn<sup>0</sup>. For type II coatings, composition and chemical states do not depend on depth. Mn is mostly in the +2 and +3 valence states. Elemental manganese content is as low as 6-8 atom %. XPS results thus confirmed the depositing mechanism for the proposed type II coatings.

SEM surface micrographs of samples prepared at current density 30-330 mA/cm<sup>2</sup>, pH 6.4, are shown in Fig. 5. Regularly shaped



Figure 5. SEM surface micrographs of manganese electrodeposited at various current densities and pH 6.4.

crystalline grains with apparent grain size in the range 3-6 µm are formed at the current density from 30 to 100 mA/cm<sup>2</sup> (type I deposits). Good coverage can be obtained already at low current density (30-40 mA/cm<sup>2</sup>); these films are composed of small (about 3  $\mu$ m) and uneven grains (Fig. 5, 30 mA/cm<sup>2</sup>). The relatively low grain size may be induced by the comparatively large hydrogen evolution rate. The grain size increases to about 6  $\mu$ m at 60 mA/cm<sup>2</sup>, where current efficiency is maximum, then decreases gradually as current density goes up to 100 mA/cm<sup>2</sup> (Fig. 5, 30-100 mA/cm<sup>2</sup>). The latter trend is reasonable on account of the current density dependence on nucleation rate. Between 100 and 150 mA/cm<sup>2</sup> a transition between the type I and II deposits is observed. The corresponding films are not continuous (Fig. 5, 120 mA/cm<sup>2</sup>), indicating difficult nucleation or poor adhesion of the type I structure in the presence of type II, which incorporates a large amount of Mn hydroxide precipitates. As current density increases above 150 mA/cm<sup>2</sup>, initially a globular structure and then a very fine-grained fibrous microstructure (50-100 nm  $\times$  100-500 nm), randomly oriented (Fig. 5, 200 mA/cm<sup>2</sup>) or aligned perpendicularly to the substrate (Fig. 5, 250

 $\rm mA/cm^2)$  are observed. The black and glossy appearance is probably due to the fibrous microstructure.

Manganese films were also electrodeposited at different pHs, from 1.7 to 7.5, at 65 mA/cm<sup>2</sup> current density (where type I deposits are obtained). SEM surface micrographs of the resulting deposits are shown in Fig. 6. Sound and homogeneous deposits can be obtained from pH 2 to 7. Below pH 2, discontinuous films are obtained as a consequence of strong hydrogen evolution and Mn dissolution. As pH decreases from 7, appearance of the deposits changes gradually from silvery matte to silvery bright, the transition taking place from pH 4 to pH 3. This corresponds to a transition of the microstructure from clearly defined small grains to large grains, seemingly faceted or composed of several subgrains (Fig. 6, pH 6.1-3.0). As the concentration of  $[Mn(NH_3)_x]^{2+}$  complexes increases with pH, a smaller grain size at higher pH could be due to the increasing overvoltage for metal reduction, as shown in Fig. 1b. $^{21,24}$  The grains formed at low pH are separated by sharply contrasted boundaries, while inside each grain, a lamellar structure oriented along a specific direction is observed (Fig. 6, pH 2.1). This microstructure is a pos-





Figure 6. SEM surface micrographs of manganese electrodeposited at different pH values, current density 65 mA/cm<sup>2</sup>.

sible reason for the brightness of these deposits.<sup>24</sup> The latter microstructure is textured, as confirmed by XRD characterization in the following section.

Crystallographic structure and phase transformation.—XRD was performed to determine the crystalline structure of the deposits. XRD patterns ( $\theta$ -2 $\theta$  scans) of the deposits obtained at different current densities are shown in Fig. 7. At pH 6.4, pure  $\gamma$ -Mn is obtained at current density from 30 to 100 mA/cm<sup>2</sup> (type I). With increasing current density, the main diffraction peaks become broader, indicating a decrease in grain size or a transition to an amorphous structure (type II). This observation is in agreement with microstructural evidence from SEM micrographs and can be explained in terms of large



Figure 7. XRD patterns of as-deposited Mn films at pH 6.4. Note the broadening of the  $\gamma$ -Mn diffraction peaks with increasing current density.

amounts of impurities codeposited with the metal, which are known to greatly inhibit crystal growth.<sup>24</sup> No  $\alpha$ -Mn could be observed for the freshly deposited coatings at all current densities observed. Small diffraction peaks due to a  $\gamma$ -Mn<sub>2</sub>O<sub>3</sub> phase are observed. The formation of  $\gamma$ -Mn<sub>2</sub>O<sub>3</sub> could be attributed to the high chemical activity of freshly deposited manganese.

Room-temperature recrystallization with phase transformation is observed for the type I microstructure, with the ductile  $\gamma$ -Mn gradually transforming to brittle and hard  $\alpha$ -Mn as shown in Fig. 8. This confirms the results reviewed in Ref. 1, although in our case no purification of the electroplating bath was necessary to obtain the  $\gamma$ -phase. Microhardness of type I deposits increased during the transformation from 147 KHN to 583 KHN as the atomic fraction of  $\alpha$ -Mn increased (Fig. 9). For type II coatings, both XRD (Fig. 10) and microhardness (Fig. 9) do not show any significant changes. On account of the overlapping of the main peaks of  $\alpha$ -Mn (411) and  $\gamma$ -Mn (101), a quantitative analysis to determine the proportion of the  $\alpha$  and  $\gamma$  phases and the preferential orientation of the films would be unreliable.<sup>16</sup> We roughly estimated the relative fraction of the  $\alpha$  and  $\gamma$  phases by two methods: (i) calculation of the relative intensity of the  $\alpha$  (411) and  $\gamma$  (101) peaks, and (*ii*) monitoring the variation of microhardness with aging time. With regard to the latter method, by assuming that the hardness of the coating is given by a weighed average of the hardness of the two phases, hardness should be a reliable estimate of the volume ratio of the two phases. By using both methods it was found that the phase transformation kinetics closely followed the standard Johnson-Mehl-Avrami equation

$$f = 1 - \exp(-kt^n)$$

where *f* is the volume fraction transformed, *t* is time, *k* is a constant, and *n* is the Avrami exponent.<sup>25</sup> The results are shown in linearized form  $\log_{10} \ln(1/(1 - f) vs. \log_{10} t)$  in Fig. 11, together with data of electrical resistance *vs.* time taken from Ref. 12. All the linear fits

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Figure 8. XRD patterns taken at various time intervals after deposition, showing the phase transformation of  $\gamma$ - to  $\alpha$ -Mn. Electrodeposition at pH 6.4 and current density 65 mA/cm<sup>2</sup>.

gave correlation coefficients above 96% and yielded Avrami exponents of 3.3-3.5. For a polymorphic transformation, that is with no change of composition, and for a nucleation and growth process, the theory predicts an Avrami exponent of 3 for an instantaneous, 3D nucleation and growth process, or an exponent of 4 for a progressive, 3D nucleation and growth process. An exponent between 3 and 4 is more realistic, as both instantaneous and strictly progressive nucleation are idealized models. Such values of the Avrami exponent can be interpreted in terms of a transformation starting at definite defect sites, with a nucleation rate decreasing with time as the number of available sites decreases.

The transformation rates are dependent on the growth conditions of the Mn deposits. Type I deposits obtained at high current density



Figure 9. Microhardness vs. aging time at room temperature for type I and II Mn deposits.



Figure 10. XRD patterns at different aging times for type II films electrodeposited at pH 6.4 and current density 300 mA/cm<sup>2</sup>. Note the constant width of the main diffraction peak.

exhibit higher transformation rates than those obtained at low current density (Fig. 12). This cannot be explained on the basis of microstructural data, assuming that grain boundaries are preferential sites for nucleation of the new phase. In fact, the grain size and grain boundary density of the samples grown at 30 mA/cm<sup>2</sup> are comparable with those of 100 mA/cm<sup>2</sup> samples, and comparable transformation kinetics should be expected in the two cases. This implies that defects other than grain boundaries are responsible for the transformation. Gamali *et al.*<sup>26</sup> proposed an explanation for the observed dependence of transformation kinetics on current density in biphasic  $\alpha + \gamma$  deposits obtained at high current densities. In the region of the limiting current density for manganese deposition, the  $\gamma$ -Mn lattice structure is highly distorted due to hydrogen incorporation, and nuclei of the  $\alpha$ -Mn modification are formed preferentially in the stressed, high-energy regions. This line of reasoning seems to be applicable also to our case, though no  $\alpha$ -Mn can be detected by XRD of freshly deposited samples (Fig. 7). According to Ref. 24, the reduced hydrogen diffusing into the deposit while plating is responsible for the internal stresses by causing a temporary lattice expansion in the deposited metal. During deposition hydrogen can diffuse into the base metal as well as back into the electrolyte. At the



**Figure 11.** Linearized plot of the relationship between the volume fraction of  $\gamma$  phase transformed (*W*) and aging time (*t*). Linear fits give *K* and *n* values from microhardness, XRD, and resistivity<sup>12</sup> data. From microhardness:  $K = 10^{-19.9}$ , n = 3.42; from XRD data:  $K = 10^{-19.2}$ , n = 3.36; from resistivity data:  $K = 10^{-20.79}$ , n = 3.47.

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Figure 12. XRD patterns of type I films obtained at various current densities, after 7 days. The rate of phase transformation increases with current density.

end of the deposition process, however, any hydrogen present in the lattice beyond the solubility limit diffuses out of the metal; consequently, its lattice shrinks and tensile stresses arise. A large amount of hydrogen is evolved during Mn electrodeposition, and it is reasonable to assume that the hydrogen content in manganese deposits is always at its saturation level<sup>13</sup> and does not change with current density. The lattice shrinkage and the strain energy of the Mn lattice would thus be related to the amount of supersaturated hydrogen temporarily incorporated during electrodeposition, which increases with current density. The difference in stored strain energy may thus account for the difference in the phase transformation kinetics. The observed shift of the  $\gamma$ -Mn diffraction peaks to higher angles (lower lattice parameters) with increasing current density (Fig. 7) can be related to this effect.

The crystalline structure of manganese electrodeposited at various pH values at a fixed current density of 65 mA/cm<sup>2</sup> was also examined by XRD ( $\theta$ -2 $\theta$  scan). The results are shown in Fig. 13. The deposits obtained at low pH (less than 3.7) exhibit a strong (002) preferential orientation, as do those obtained at pH 7.0. Figure 14 shows the relative intensity,  $I_r$ , of the diffraction peaks of  $\gamma$ -Mn as a function of pH. The relative intensity is defined as<sup>27</sup>



Figure 14. Relative integrated intensities of the diffraction peaks for asdeposited  $\gamma$ -Mn as a function of pH.

$$r_{r}^{i} = \frac{I'/I_{0}^{i}}{\frac{1}{n}\sum (I^{i}/I_{0}^{i})}$$

-i / -i

where  $I^{i}$  and  $I_{0}^{i}$  represent experimental and standard<sup>28</sup> integrated peak intensities of each main peak, respectively, and *n* is the number of the peaks considered. For a randomly oriented specimen, the relative intensity of each peak should be equal to 1. For a certain reflection *i*, a  $I^{i}_{r}$  value larger than 1 indicates that the corresponding crystallographic direction is preferred, while a value lower than 1 shows that the corresponding orientation is "preferentially avoided." <sup>29</sup> Figure 14 shows that the extent of preferential orientation of (002) presents a minimum around pH 4.5 and increases at high and low pH values.

Evaluation of the phase transformation kinetics of samples obtained at different pH (Fig. 15) showed that Mn deposits obtained at lower pH undergo a faster phase transformation than those obtained at higher pH. This could also be explained by internal stresses induced by hydrogen incorporation in the Mn film. Hydrogen discharge rate at low pH increases, and consequently, higher internal stresses would be developed and larger strain energy may be stored in manganese coatings obtained at low pH.



Figure 13. XRD patterns of as-deposited Mn at the current density of  $65 \text{ mA/cm}^2$  and various pH values. Note the change of the (002) peak intensity with decreasing pH.



**Figure 15.** XRD patterns of electrodeposited Mn grown at different pH after 4 days. The rate of phase transformation is higher at lower pH.



Figure 16.  $E_{corr}$  vs. time plots for electroplated manganese immersed in (a) 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub> at pH 3.0 and (b) 2.5% NaCl at pH 3.0.

To summarize, a  $\gamma$  to  $\alpha$  phase transformation takes place upon aging at room temperature in crystalline but not in amorphous deposits. The transformation can be slowed down by electrodepositing at low current density and high pH.

*Corrosion-resistance measurements.*—Corrosion tests were performed in sodium sulfate/borate and chloride electrolytes on both type I and type II coatings. The test samples were about 6 µm thick.

Figure 16 shows plots of corrosion potential  $E_{\rm corr}$  vs. time for type I and II manganese deposited at pH 6.4, 65 and 330 mA/cm<sup>2</sup>, respectively. The corrosion performance of the two types of coating is very different. In the sodium sulfate/borate system (Fig. 16a), taking  $E = -1.6 V_{\rm SCE}$  as the corrosion potential  $E_{\rm corr}$  of manganese (this plateau corresponds to manganese dissolution from the substrate) and  $E = -0.8 V_{\rm SCE}$  the voltage observed when dissolution is completed, the performance of the amorphous coating is much better.  $E_{\rm corr}$  of amorphous coatings in fact increases gradually toward the value of the substrate, while the change in  $E_{\rm corr}$  for the crystalline coatings is more abrupt and takes place after a shorter time.

In the sodium chloride solution (Fig. 16b), corrosion resistance of both coatings seems to be better, as  $E_{\rm corr}$  remains below  $-1 V_{\rm SCE}$ in the time investigated. The surface of the coatings after the corrosion test was analyzed by SEM and EDAX (Fig. 17). The morphology of amorphous coatings observed after a 21,600 s test appears to be less deteriorated than that of crystalline coatings observed after a test of duration 10,800 s. In the former case (Fig. 17b), no substrate area is exposed as evidenced by EDAX. Furthermore, a layer with an apparent composition of MnO<sub>2</sub> is formed on the coating surface, as confirmed by XPS data, which could slow corrosion kinetics.



**Figure 17.** SEM micrographs of manganese coatings after corrosion testing in 2.5% NaCl at pH 3.0: (a, left) type I, after 10,800 s immersion and (b, right) type II, after 21,600 s immersion.

This oxide surface appears black and dull, and in some cases it was already formed on the as-plated samples, as indicated by XPS analysis. Such oxide-hydroxide film could act as a passive film capable of maintaining the galvanic potential while acting as a kinetic barrier for corrosion processes. This behavior may be similar to that of some steels, when iron in the presence of certain alloying elements can form Fe-hydroxides, which provide stable passive films.

For comparison, 1  $\mu$ m thick cadmium coatings electroplated on steel from commercial electrolytes were tested in the same solutions, and results are shown in Fig. 18. In sodium sulfate/borate solutions the transition time of cadmium is longer but comparable to that observed for Mn coatings. Sacrificial protection in chloride solutions, however, seems to last much longer for Mn coatings.

### Conclusions

Manganese coatings of high quality can be electroplated from sulfate solutions with addition of ammonium sulfate. Ammonium sulfate improves manganese ion discharging ability and provides a buffering effect.

Current density has an important influence on current efficiency, appearance, microstructure, crystal structure, and corrosion resistance of manganese deposits.  $\gamma$ -Mn (bct, type I) can be formed at current densities from 30 to 100 mA/cm<sup>2</sup>, while amorphous coatings (type II), containing large amounts of oxyhydroxides, can be



Figure 18.  $E_{corr}$  vs. time plots for electroplated cadmium (thickness 1  $\mu$ m) in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub> at pH 3.0 and 2.5% NaCl at pH 3.0.

formed at higher current densities, above 150 mA/cm<sup>2</sup>. Roomtemperature recrystallization of type I samples is observed, with phase transformation from  $\gamma$ -Mn (bct) to  $\alpha$ -Mn (bcc); the kinetics of this transformation follows the Johnson-Mehl-Avrami equation. Transformation kinetics is slower for samples grown at low current density and high pH. Type II deposits do not exhibit phase transformation at room temperature for a relatively long period and have better corrosion resistance than type I ones in both acidic sodium sulfate/borate and acidic sodium sulfate solutions.

Electrolyte pH affects the microstructure of the coatings. An increasing (002) preferential orientation is observed at low pH, where bright films are obtained. pH values in the range from 2 to 6 do not obviously affect current efficiency or corrosion resistance of the coatings.

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