



# Influence of different electrolysis parameters on electrodeposition of $\gamma$ - and $\alpha$ -Mn from pure electrolytes – a review with special reference to Russian language literature



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## ABSTRACT

Recently an increasing interest in deposition of electrolytic Mn has been observed. Part of the experimental data published earlier (in the journals of the former Soviet Union), but unfamiliar to western researchers because of the inaccessibility of the literature is presented and compared. The following results were reported in these papers that were inaccessible to Western researchers: larger crystals of  $\gamma$ -Mn were obtained from chloride electrolytes than from sulfate electrolytes; the crystal structure of  $\alpha$ -Mn phase was observed by XRD when Mo  $K_{\alpha}$  radiation was used; the influence of Zn, Cd and Cu impurities on microhardness of Mn coatings was complex; successful deposition of  $\gamma$ -Mn was possible at temperature as high as 80 °C from “ultra pure” sulfate electrolyte containing ammonium ion; the phase of deposited Mn from pure electrolytes was influenced by the cathode-substrate, but increase in current density allowed eliminating the influence of the cathode-substrate leading to the deposition of  $\alpha$ -Mn coatings.

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## 1. Introduction

Recently an increasing interest in deposition of electrolytic Mn (Gong and Zangari, 2002; Gong et al., 2001; Wei et al., 2007) and influence of  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$  impurities on it has been observed (Gong and Zangari, 2003, 2004a, 2004b; Mangolini et al., 2004). The electrodeposited Mn coatings are divided into the I type (crystalline  $\gamma$ -Mn) and the II type (amorphous  $\alpha$ -Mn) ones, and some conditions of electrolysis have been presented by the authors of these articles. We think that the part of the experimental data is known and has been published earlier (in the journals of the former Soviet Union), but is unfamiliar to western researchers because of the absence of accessibility of the literature. Naturally, various hypotheses published earlier in those articles have been confirmed by the state-of-the-art instrumental methods that were unavailable in earlier times. For example, influence of oxide-hydroxide particles on electrodeposition of Mn has been visibly proved (Diaz-Arista and Trejo, 2006; Gong et al., 2001), an electrolysis method has been developed for the removal of deleterious components of catholyte solutions prior to manganese deposition (Wei et al., 2007) and etc. Later, aiming at the increased current efficiency of Mn coatings, decreased deleterious effects of the impurities, improved

mechanical and anticorrosive properties of the coatings, the additives of the VIA group elements S (Diaz-Arista and Trejo, 2006), Se (Fan et al., 2012; Li and Zhang, 2011; Sun et al., 2011; Wei et al., 2010) and Te (Galvanauskaitė et al., 2011; Sharma et al., 2004, 2007), started to be used in the manganese electrolytes.

Our goal was to introduce the researchers working in the area of Mn deposition to the research conducted earlier and, thus, to point to them the necessity to refer to the initial correct references.

## 2. Results and discussions

The following electrolysis factors influence electrolytic deposition of  $\gamma$ -Mn:

1. Aging of deposit and pH of electrolyte;
2. Current density  $j_c$ ;
3. Temperature of electrolysis;
4. Impurities in electrolyte;
5. Cathode employed.

### 2.1. Aging of deposit and pH of electrolyte

Transition  $\gamma$ -Mn  $\rightarrow$   $\alpha$ -Mn starts after 2 h of electrolytic deposition at room temperature (Vorozhko and Gamali, 1973) which was confirmed by the data in Table 1 (Gofman et al., 1967). The authors of these articles have indicated that the duration of the transition of the plastic  $\gamma$ -Mn phase to the solid  $\alpha$ -Mn phase depends very much on the purity of the metal and thickness of the coating. It was

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**Table 1**  
Kinetics of  $\gamma$ -Mn  $\rightarrow$   $\alpha$ -Mn transition after electrolysis.

Time after electrolysis, h	Phase determined by XRD analysis
1–192	$\gamma$ + traces of $\alpha$
216	$\gamma$ + small amount of $\alpha$
240	$\gamma$ + bigger amounts of $\alpha$
264	$\gamma$ + fairly big amounts of $\alpha$
288	Equal amounts of $\gamma$ and $\alpha$
336–360	$\gamma$ + constantly increasing amounts of $\alpha$
360–456	Mainly $\alpha$ , small amounts of $\gamma$
450–528	Gradually decreasing amounts of $\gamma$ .
	No $\gamma$ detected after 528 h.

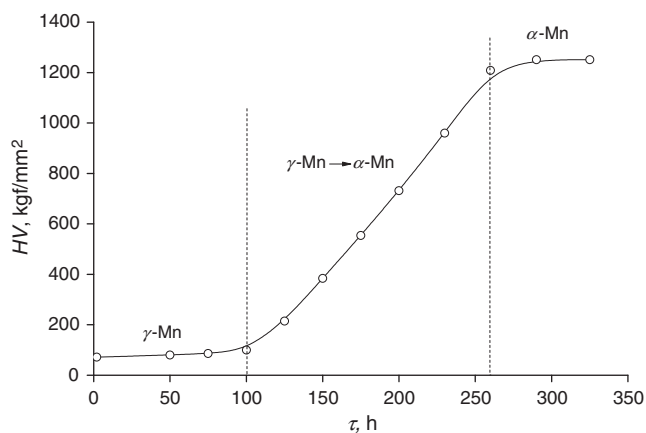
concluded that the plastic  $\gamma$ -Mn phase can be preserved for 188–240 h (7–10 days) with no change in its plasticity. The observation has been confirmed later (Gong and Zangari, 2002; Mangolini et al., 2004), and the kinetics of  $\gamma$ -Mn  $\rightarrow$   $\alpha$ -Mn transition according to Johnson–Mehl–Avrami equation was found out and indicated that 15 days were needed for the full recrystallization.

pH of the electrolyte, from which Mn is deposited, has strong influence on the kinetics of  $\gamma$ -Mn  $\rightarrow$   $\alpha$ -Mn transition. It has been found (Agladze et al., 1986), that, when thickness of  $\gamma$ -Mn coatings deposited at pH 2.5 and 7.5 is the same, kinetics of  $\gamma$ -Mn  $\rightarrow$   $\alpha$ -Mn transition is much faster for  $\gamma$ -Mn deposited at pH 2.5. The complete transition of  $\gamma$ -Mn to  $\alpha$ -Mn for the Mn coatings deposited at pH 7.5 lasts 4 days longer.

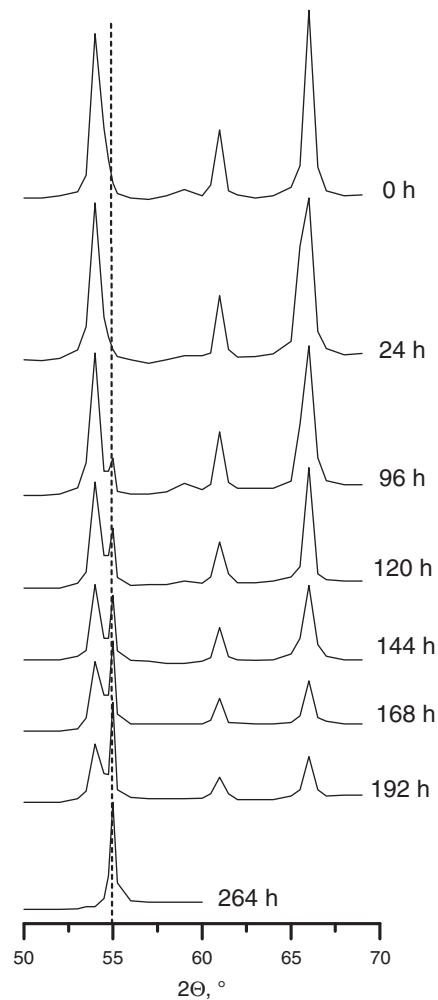
Kinetics of  $\gamma$ -Mn  $\rightarrow$   $\alpha$ -Mn transition was confirmed by investigation of microhardness and XRD analysis (Belinskij et al., 1975) (Figs. 1–2). A plot of the intensity of the intrinsic peak at  $2\theta = 55^\circ$  versus time (Fig. 2) gave the S-shaped curve similar to the one in Fig. 1. It has been established that change of microhardness with time for coatings obtained in ammonium sulfate electrolytes containing 2–9 g/l impurity of  $F^-$  ion (Ivanova and Kladnickaja, 1981) is different from the one prepared from pure ammonium sulfate electrolytes (Fig. 3). At  $j_c = 0.1$ – $0.25$  A/cm<sup>2</sup> coatings of ductile  $\gamma$ -Mn were obtained. Their hardness was 90–100 kgf/mm<sup>2</sup> and it remained constant for a long time (this period was 3–4 times longer than in the case of ammonium sulfate electrolytes, when coatings were deposited at 0.05 A/cm<sup>2</sup>) (Belinskij et al., 1975).

## 2.2. Current density

Investigation of electrolytic deposition of Mn from sulfate (Janickij et al., 1967) and chloride (Vorozko et al., 1972) electrolytes has revealed that deposition of poorly crystalline Mn (II type (Gong and



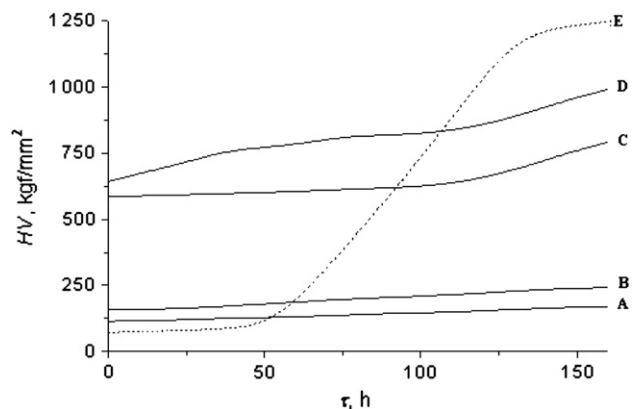
**Fig. 1.** Microhardness of electrolytically pure  $\gamma$ -Mn versus time in its transformation to  $\alpha$ -phase. Bath composition (g/l):  $MnSO_4 \cdot 5H_2O - 100$ ;  $(NH_4)_2SO_4 - 50$ . Current density  $j_c = 0.05$  A/cm<sup>2</sup> (Belinskij et al., 1975).



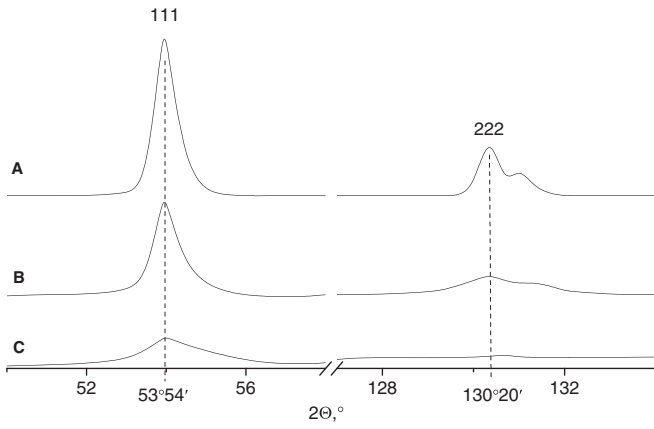
**Fig. 2.** XRD patterns of  $\gamma$ -Mn  $\rightarrow$   $\alpha$ -Mn transition. Bath composition (g/l):  $MnSO_4 \cdot 5H_2O - 100$ ;  $(NH_4)_2SO_4 - 50$  (Belinskij et al., 1975).

Zangari, 2002, 2004a; Gong et al., 2001), i.e. amorphous Mn coating) is possible only at high values of  $j_c$  (Fig. 4).

According to the authors of (Gamali et al., 1974; Vorozko et al., 1972), the structure of the poorly crystalline Mn is a solid solution obtained when hydrogen penetrates into deformed crystal lattice of  $\alpha$ -Mn. This assumption was confirmed by the hydrogen charged coatings of Mn: 240 cm<sup>3</sup>/100 g in  $\alpha$ -Mn (Agladze et al., 1970; Dhananjayan, 1970a) and only 30 cm<sup>3</sup>/100 g in  $\gamma$ -Mn (Agladze et al., 1970).



**Fig. 3.** Microhardness of manganese deposits versus time. Current density, A/cm<sup>2</sup>: A – 0.1; B – 0.25; C – 0.50; D – 1; E – 0.05 (Ivanova and Kladnickaja, 1981).



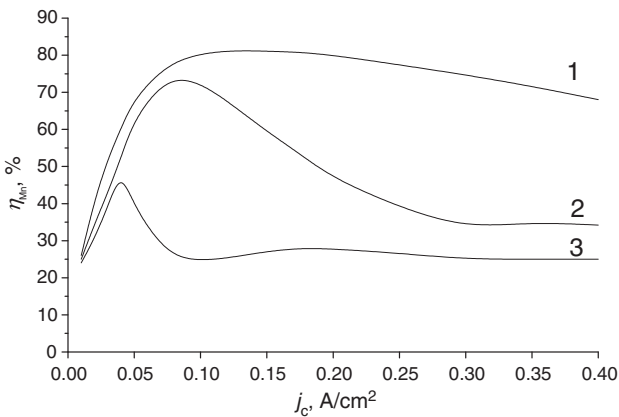
**Fig. 4.** Influence of current density on the change of the interference lines (111) and (222) to the XRD patterns of  $\gamma$ -Mn deposits (Fe  $K_{\alpha}$  radiation). Bath composition (g/l):  $MnCl_2$  – 252,  $NH_4Cl$  – 121; pH 5.6. Current density,  $A/cm^2$ : A – 0.1; B – 0.5; C – 0.8 (Vorozhko and Gamali, 1973).

XRD analysis has shown that one diffraction peak is characteristic to the coatings of the faintly expressed Mn, which were analyzed using Fe  $K_{\alpha}$  radiation (Fig. 4). The same results were obtained when Cu  $K_{\alpha}$  radiation was used (Sulcius, 1982). The crystal structure of  $\alpha$ -Mn phase was observed (Vorozhko et al., 1972) when Mo  $K_{\alpha}$  radiation was used. This indicates the presence of the fine-grained structure and large inner stress. These factors are responsible for the very broad diffraction peaks when long-wave radiation is used (Fe, Cr or Cu).

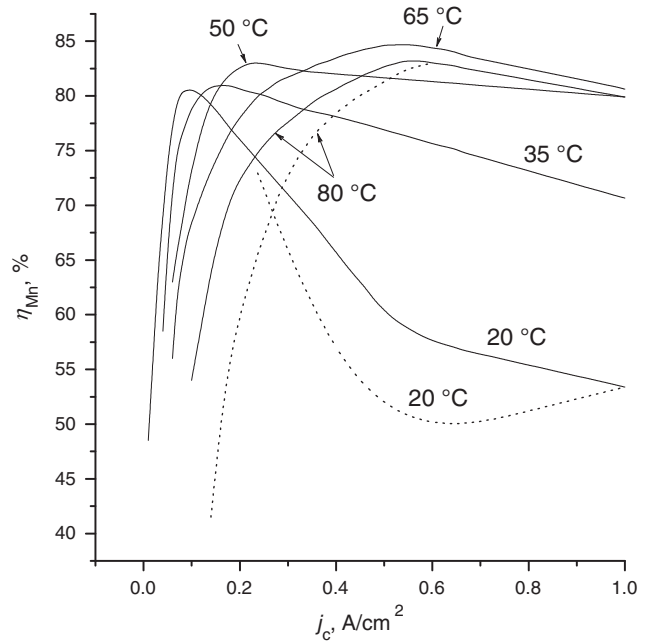
Moreover, it has been determined (Gofman et al., 1967), that larger crystals of  $\gamma$ -Mn are obtained in chloride electrolytes than in sulfate electrolytes. The typical dependence of Mn current efficiency on  $j_c$  in chloride electrolyte is depicted in Fig. 5.

2.3. Temperature of electrolyte

It has been established that successful deposition of  $\gamma$ -Mn is possible at temperature as high as 80 °C (Janickis et al., 1986). "Ultra pure" electrolyte, which was purified by long time electrolysis until deposition of Mn on Al cathode started at  $j_c = 0.07$ – $0.1$  mA/cm<sup>2</sup>, was used. Bath composition was the following:  $MnSO_4 \cdot 5H_2O$  (200 g/l) and  $(NH_4)_2SO_4$  (150 g/l). Pt sheet electrolytically covered by a layer of  $\gamma$ -Mn was used as a cathode-substrate. The modification of Mn was investigated by microhardness and XRD analysis. It has been found (Fig. 6), that maximum of current efficiency shifts toward higher  $j_c$  values and loses its sharpness with increasing temperature. Mn has been deposited as



**Fig. 5.** Typical dependence of Mn current efficiency versus current density. Bath composition (g/l): 1 –  $MnCl_2$  – 63,  $NH_4Cl$  – 214, pH – 6.15; 2 –  $MnCl_2$  – 31.5,  $NH_4Cl$  – 214, pH – 6.15; 3 –  $MnCl_2$  – 63,  $NH_4Cl$  – 214,  $NH_3$  – 68. In all cases: 0.5 g/l of  $NH_2OH \cdot HCl$  (Gamali et al., 1974).



**Fig. 6.** Current efficiency of Mn versus current density using the activated cathode. Dotted lines – non-activated cathode (Janickis et al., 1986).

metastable  $\gamma$ -phase at the given temperature and lower  $j_c$ . The increase of  $j_c$  leads to deposition of the stable  $\alpha$ -Mn (Table 2).

Increasing of temperature extended the region of  $\gamma$ -Mn deposition considerably towards the higher  $j_c$  at 80 °C and up to  $j_c = 1.2$  A/cm<sup>2</sup> only  $\gamma$ -Mn deposited. In the medium region of  $j_c$  values, i.e. while simultaneous deposition of both modifications of Mn occurred, considerable fluctuations of the current efficiency were observed. They were avoided by preliminary activation of the cathode by current corresponding to maximum current efficiency at the given temperature. Moreover, such activation of the cathode increased the current efficiency in this region of  $j_c$  by 10–20%.

2.4. Impurities in electrolyte

The presence of the impurities of different metals in the electrolyte of manganese plating influences voltamperometric characteristics of the process and current efficiency (Mantell and Ferment, 1966). Influence of Zn, Cd (Belinskij, 1983; Belinskij et al., 1975), Fe, Co, Ni (Agladze and Basmanova, 1975; Agladze et al., 1975), Cu, Ag and Be (Janickij et al., 1978) impurities was investigated. It has been concluded that the main reason for decreasing current efficiency of Mn electrodeposited from electrolytes containing impurities is formation of dispersed precipitate on the cathode irrespective of their origin. The values of the deposition potential of these metals-impurities are lower than the one of Mn.

Impurities, which influence a modification of the deposited Mn, are divided into two groups (Belinskij et al., 1975):

- 1) The ones that stabilize phase of  $\gamma$ -Mn deposited on cathode (Cu, Ni, Co, Zn, Ge, Ga);
- 2) The ones that influence deposition of  $\alpha$ -Mn phase (Se, S, Cd, Cr, etc.).

**Table 2**  
Current density regions of Mn phase deposited on an activated electrode.

Phase	Temperature, °C				
	20	35	50	65	80
$\gamma$	0.3 A/cm <sup>2</sup>	0.4 A/cm <sup>2</sup>	0.5 A/cm <sup>2</sup>	0.7 A/cm <sup>2</sup>	1.2 A/cm <sup>2</sup>
$\gamma + \alpha$	0.3–0.5 A/cm <sup>2</sup>	0.5–0.7 A/cm <sup>2</sup>	0.7–1 A/cm <sup>2</sup>	0.7–1 A/cm <sup>2</sup>	–
$\alpha$	0.7–1 A/cm <sup>2</sup>	1 A/cm <sup>2</sup>	–	–	–

The influence of Zn, Cd and Cu impurities on microhardness of Mn coatings is complex (Fig. 7) (Belinskij et al., 1975). When 0.30–0.34% of Zn and Cu are present in Mn coatings, microhardness of Mn increases 1.5–2.0 times in comparison with the pure Mn. The further increase of the amount of Zn in Mn coatings leads to the slight decrease of microhardness, which becomes constant when there are 0.4% of Zn. Microhardness of Mn reaches its maximum value of 318 kgf/mm<sup>2</sup>, when there are 0.18% of Cd. Manganese loses its plasticity, becomes more brittle. Increase of the amount of Cd more than 0.18% leads to the marked decrease of microhardness. According to the authors, this heavy increase of microhardness of Mn coating in the presence 0.18% of Cd in it can be related to the rise of  $\alpha$ -Mn, whose microhardness is greater than that of  $\gamma$ -Mn. XRD analysis showed that the distinctive peaks of  $\alpha$ -Mn were absent in the spectra of the freshly deposited coatings in the presence of 40 mg/l Cd in sulfate electrolyte. However, the distinctive peak of  $\alpha$ -Mn was observed already after 24 h (Fig. 8). Whereas, after 24 h the distinctive peak of  $\alpha$ -Mn was not observed in the spectra of pure Mn coatings, i.e. in the absence of Cd (Fig. 2). In the opinion of the authors, crystallization centers of fine-grained phases of  $\alpha$ -phase, which is undetectable under Fe K $\alpha$  radiation, form in the freshly deposited Mn when Cd is present. They increase microhardness of  $\gamma$ -Mn and it becomes brittle. Furthermore, according to the authors, crystallization rate of  $\alpha$ -Mn from those centers is considerably higher than the rate of  $\gamma$ -Mn  $\rightarrow$   $\alpha$ -Mn transition.

### 2.5. Nature of substrate

Phase of deposited Mn from pure ammonium sulfate/chloride electrolytes (for example, MnSO<sub>4</sub>·5H<sub>2</sub>O – 100 g/l; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> – 50 g/l) is also influenced by the cathode-substrate. Influence of Pt, Fe, Cu, Ag, Al (Dhananjayan, 1970b; Janickij et al., 1968) on deposition of Mn was investigated (Fig. 9). As seen from Fig. 9,  $\gamma$ -Mn coatings with high current efficiency were obtained on Pt, Fe and Cu, when  $j_c$  was up to 0.2 A/cm<sup>2</sup>. Whereas, low current efficiency was obtained on Ag and Al at the same values of current density; the coating deposited was fine-grained and

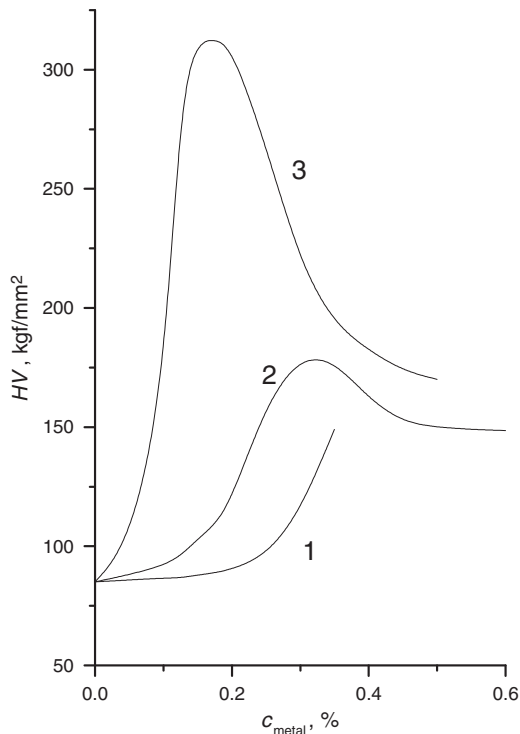


Fig. 7. Dependence of microhardness of Mn on metallic impurities: 1 – Cu; 2 – Zn; 3 – Cd (Belinskij et al., 1975).

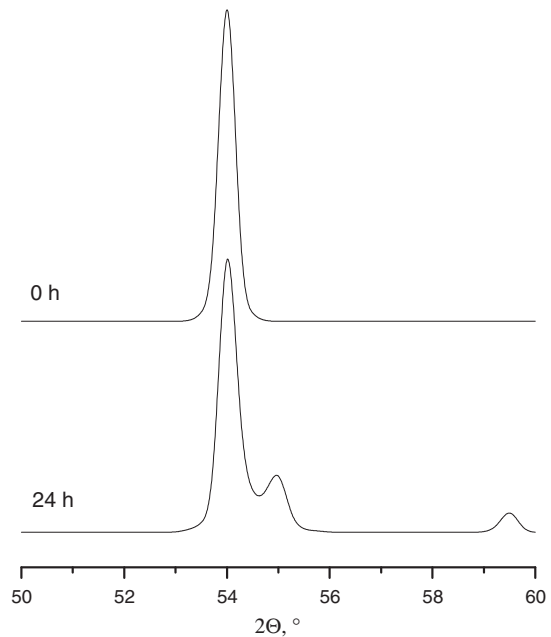


Fig. 8. XRD patterns of electrolytic  $\gamma$ -Mn obtained from sulfate electrolyte containing 40 mg/l Cd (Belinskij et al., 1975).

only rare big  $\gamma$ -Mn crystals were seen on the surface of the cathode. Increase in current density allowed eliminating the influence of the cathode-substrate leading to the deposition of  $\alpha$ -Mn coatings. It was found that  $\gamma$ -Mn did not deposit on the  $\alpha$ -Mn cathode-substrate from the pure electrolytes (Gamali, 1963; Vorozko, 1977). These results were confirmed by Dhananjayan (1970b), which reported that  $\gamma$ -Mn deposited on the  $\alpha$ -Mn cathode-substrate only in the presence of S or Se compounds in electrolyte.

### 3. Conclusions

The following conclusions can be made:

- Larger crystals of  $\gamma$ -Mn are obtained from chloride electrolytes than from sulfate electrolytes.
- The crystal structure of  $\alpha$ -Mn phase was observed when Mo K $\alpha$  radiation was used.

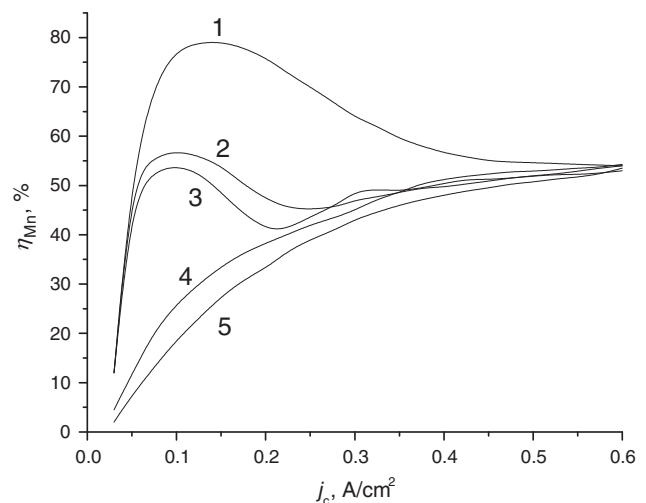


Fig. 9. Dependence of current efficiency on current density and cathode-substrate: 1 – Pt; 2 – Fe; 3 – Cu; 4 – Ag; 5 – Al (Janickij et al., 1968).

- The influence of Zn, Cd and Cu impurities on microhardness of Mn coatings is complex.
- Successful deposition of  $\gamma$ -Mn is possible at temperature as high as 80 °C from “ultra pure” sulfate electrolyte containing ammonium ion.
- Phase of deposited Mn from pure electrolytes is influenced by the cathode-substrate, but increase in current density allowed eliminating the influence of the cathode-substrate leading to the deposition of  $\alpha$ -Mn coatings.

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