

CHAPTER V

Effect of conditions of deposition on the structure of electro-deposited manganese

The effect of cathodic current density and pH of catholyte on the structure of manganese deposit obtained has been studied. Increase in current density from 5 to 30 amps/sq dm prevents the formation of gamma manganese from pure solutions and an amorphous brittle manganese containing about 550 cc of hydrogen per 100 gm is obtained. The hardness of this amorphous deposit is similar to that of alpha manganese. In presence of sulphur dioxide, deposits obtained at low pH values of catholyte show a crystalline pattern of alpha manganese instead of the amorphous deposits obtained in the early stages of deposition from the same solution at high pH values.

Introduction

The present established process^{1,2} for the production of electrolytic manganese consists in the electrolysis of a solution with a composition of 33 gm of manganese as manganese sulphate, 135-50 gm of ammonium sulphate and 0.1 gm of sulphur dioxide per litre of electrolyte in a double compartment cell between stainless steel cathodes and lead silver anodes, with arrangement for flow of electrolyte, at a catholyte pH of 7.8-8.2, temperature of 30-35°C and a cathodic current density of 4.8 amps/sq dm. Such electrolysis results in hard brittle alpha manganese deposits with a current efficiency of 65 per cent.

Dean¹ obtained ductile gamma manganese in absence of sulphur dioxide from the same electrolyte and, according to Dean, with all other conditions of deposition remaining the same, current efficiency in deposition of gamma manganese falls off after few hours in the absence of SO₂ but may be maintained for 48 hours or more with SO₂ addition when alpha manganese is the deposition product. In a series of comparable 48 hour tests, Dean³ obtained a current efficiency of 60.2 per cent with sulphur dioxide with a sulphide content of 0.02-0.04 per cent in the metal, and 42.1 per cent in the absence of sulphur dioxide with a sulphide content of 0.002 per cent in the metal. Dean is of opinion that the commercial process depends on the transformation of the metal to the alpha form as it is deposited and that this transformation is brought about by certain compounds of sulphur in the electrolyte.

Subsequent detailed study by Schlain and Prater⁴ conclusively proved that the presence of SO₂ or colloidal sulphur in the electrolyte results in brittle alpha modification of manganese and, in the absence of sulphur dioxide or colloidal sulphur, deposits of ductile gamma manganese can be obtained on copper cathodes with current efficiencies of 62-72 per cent on 5-12 hours run. The gamma manganese thus obtained completely transforms to alpha manganese in about 10 days at a room temperature of 32°C (ref 5).

Bell⁶, in her studies on the electroplating of manganese on aluminium, mild steel and copper to a thickness of 0.0015", examined the structure of manganese deposits by X-rays immediately after plating and found only presence of alpha manganese which had hardness between 550 and 725 DPN. X-ray patterns failed to reveal the presence of gamma manganese in any of the deposits, though according to Bell, there were no sulphur compounds present in the electrolyte. Further, when sulphur dioxide was intentionally added, the resulting deposits were much less adherent and seemed to be more brittle than those deposited from sulphur-free electrolytes. Bell had used a current density of 23-27 amps/sq dm

and had used electrolytic manganese flakes in the anolyte to make up the manganese content of the bath.

Recently, there had been some considerable work in USSR on phase-transformations in electro-deposits of manganese^{7,8,9}. Moiseev and Popova^{7,8} have used manganese ammonium sulphate electrolyte with or without addition of glycerol (20 cc per litre) for deposition of manganese on cathodes of copper, silver and iron. The deposition was conducted at a constant current density of 30 amps/sq dm and at a pH of 3.8-4. The thickness of the deposits varied from 10 to 60 microns. The current density of 30 amps/sq dm corresponded to the maximum amount of hydrogen in the deposit (570 and 770 cc/100 gm without and with glycerol respectively). According to Moiseev, X-ray patterns of deposits from solutions without the addition of glycerol, on silver cathodes to a thickness of 10 microns in some cases revealed lines characteristic of gamma modification. These gamma deposits were highly unstable and transformed irreversibly to the alpha form in 6-10 hours. Small additions of glycerol to the electrolyte accelerated the transformation or completely suppressed the formation of gamma manganese.

The structure of freshly deposited manganese as per Moiseev was similar to an amorphous deposit caused by a non-uniform electron distribution among the manganese atoms and also on the displacement of atoms because of a higher hydrogen content. The characteristic feature of the X-ray pictures of deposits with or without addition of glycerol was one strongly diffused line with a large background of incoherent scattering and, according to Moiseev, separate strongly diffused lines all alike lead to the possible judgement that both the gamma phase and also the alpha phase developed during electrolysis. These deposits on heating to 125°C for an hour and a half reveal the pattern of alpha manganese. From his experiments, Moiseev concludes that the manganese formed by electrolysis, both directly and as a result of transformation from gamma modification, is an interstitial solid solution of hydrogen in the manganese lattice with a strong distortion of the lattice.

According to Moiseev^{7,8}, interesting changes occur in the structure of manganese deposits with the introduction of sulphur dioxide instead of glycerol to the electrolyte. The deposits obtained with 0.3 per cent sulphur dioxide at current densities of 17-25 amps/sq dm and at pH values of 2.3-3.0 showed clear crystalline structure of alpha manganese with a texture, while deposits obtained at current densities of 25-30 amps/sq dm and at pH values 3.8-4.2 showed only a pattern of amorphous body.

Sanzharovski¹⁰ agrees with Moiseev in that the properties of manganese deposits with sulphur dioxide changed with the pH value of the electrolyte. According to Sanzharovski, deposits obtained with

0.1-0.5 gm/l of sulphur dioxide in the electrolyte was alpha manganese but had internal stresses. But deposits obtained at $pH < 4$ was essentially alpha manganese ($8.894\text{\AA}$) and internal stresses were absent and the deposit had a texture. The axis and the orientation changed at different sulphur dioxide contents. Micro-hardness of the deposits had a maximum of 1000 kg/sq mm at 0.35 gm/l sulphur dioxide. The cathodic polarization increased on addition of sulphur dioxide.

Thus, the properties of the deposit in the presence of sulphur dioxide are altered by the change of polarization, inclusion of sulphur in the deposit and selective adsorption of sulphur on the growing borders of the crystals which influence the orientation of the growth. The following mechanism on the effect of sulphur dioxide on manganese electrolysis was suggested by Sanzharovski. Sulphur dioxide at $pH > 6$ does not exist in the solution because of extensive evolution of hydrogen on the cathode. At $pH \leq 6$, the sulphur dioxide effect is related to chemical reactions causing the formation of dendrites on the cathode to decrease and the current yield to increase. At $pH < 4$ the sulphur dioxide effect is related to the changes in the electrochemical reactions at the cathode.

Thus, it can be seen that the current density and pH of catholyte have some influence on the structure of deposited manganese. Perhaps the divergent view points of earlier workers can be traced to the different conditions of deposition employed by them. Hence, it was felt desirable to examine the structure of deposited manganese under different conditions of deposition, especially from the same concentration of the electrolyte but at different current densities and pH values.

Materials and methods

The electrolytic cell used and the mode of preparation of electrolyte were the same as described in Chapter III. For the deposition of manganese at high current densities and for back reflection studies of cathodes with deposited manganese, a small cell measuring $6.5 \times 6.5 \times 5$ cm was used. The arrangement of the cell as a whole was a complete replica of the bigger cell except that the size was reduced to about 1/8. A photograph of the cell is given in Fig. 5.I.

Results of experiments

The effect of increasing the current density from 5 to 30 amps/sq dm with the big cell on the structure and hydrogen content of manganese obtained has been given in Table 5.1.

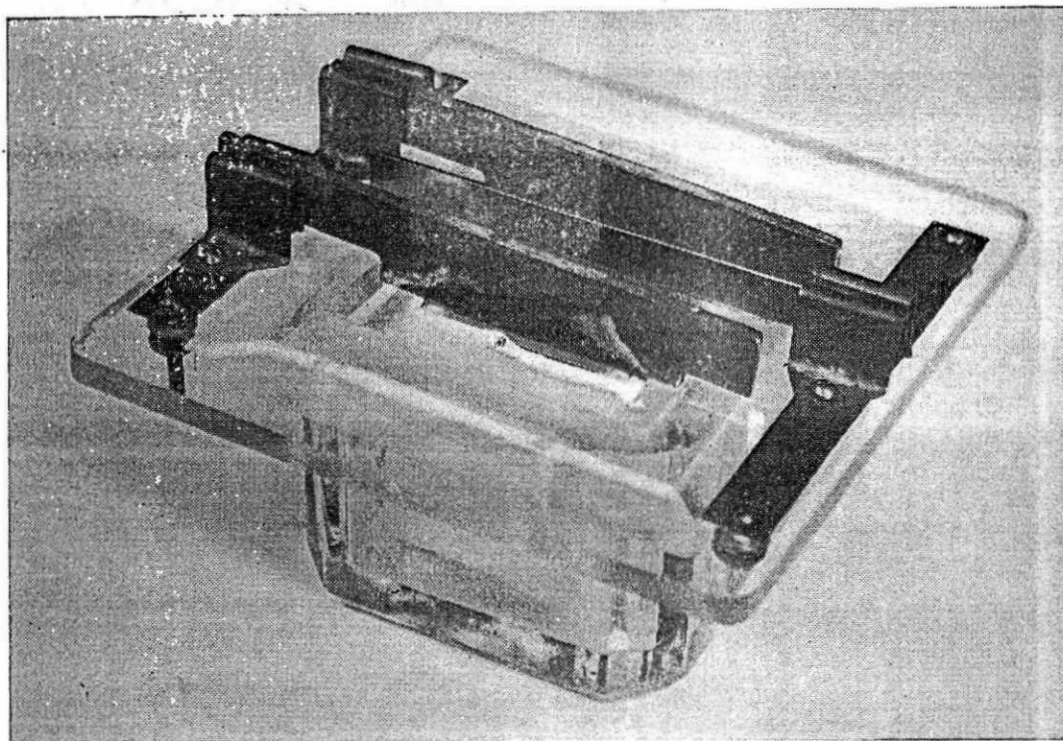


FIG. 5.I — ELECTROLYTIC CELL FOR BACK REFLECTION X-RAY STUDIES OF DEPOSITED CATHODE

Results of experiments with small electrolytic cell on the structure and hydrogen content of manganese deposits obtained at a cathodic current density of 30 amps/sq dm from pure solutions and in presence of addition agents, such as glycerol and triamylamine, have been given in Table 5.II.

Discussion of experimental results

Effect of current density — From Table 5.I, it is seen that, under the same experimental conditions, with increase in current density, the hydrogen content of the deposit increases. At and above 27 amps/sq/dm, from pure solutions of manganese and ammonium sulphate, instead of the coherent soft flexible gamma manganese, which is usually obtained at lower current densities, hard brittle manganese is obtained excepting at the top solution air interface portion where gamma manganese is obtained. With increase in current density from 5 to 27 amps/sq dm, the current efficiency of deposition falls down with a consequent increase in hydrogen evolution. These evolved hydrogen bubbles flock up to the solution air interface. This accumulation of hydrogen air bubbles, during its passage of escape from the cell at the solution air interface, block the passage of current with a resultant decrease in the current density and polarization

TABLE 5.I — CURRENT DENSITY, STRUCTURE AND HYDROGEN CONTENT

Pure solutions:

Composition of electrolyte: 65-70 gm of manganese sulphate per litre
135-40 gm of ammonium sulphate per litre

Big cell:

Stainless steel cathodes — Temperature of electrolysis: 35-45°C

Effective area of cathode : 8×6 cm; pH of initial solution: 5.5

CURRENT DENSITY amps/ sq dm	TIME OF DEPOSITION min	CURRENT EFFICIENCY %	HYDROGEN CONTENT cc/100 gm	STRUCTURE AND REMARKS	HARDNESS (DPN)
5	30	—	48.90	Gamma	—
18	30	58	106.00	do	—
10-20	45	48.79	—	Gamma-current increased from a cd value of 10 amps/sq dm to 20 amps/sq dm	—
27	30	21.47	—	Top portion 1 cm gamma which peels off later Bottom hard brittle manganese adherent to cathode	—
30	10	—	66.5 163.4	do { Alpha portion Gamma portion	788 137

Remarks — It is noticed that with increase in current density from 5 to 27 amps/sq dm, excepting at the top 1 cm solution air interface portion, at other areas of the cathode manganese with a hardness of 788, indicative of alpha structure, is obtained from pure solutions.

at the solution air interface because of which crystalline gamma manganese is obtained in that portion.

With increase in current density, the temperature of the electrolyte also increases. To keep the electrolyte at constant temperature, the feed electrolyte flow had to be increased by about 15 times. For a less consumption of electrolyte to keep the bath temperature same throughout the experiment, and also as the deposit with the cathode can be put for back reflection X-ray studies without any work on the deposit, a small cell with a submerged cathode area of 4×4 sq cm was further used for studies on high current density experiments. Above experiments with 30 amps/sq dm were repeated and confirmed with the small cell as seen from Table 5.II.

TABLE 5.II — CURRENT DENSITY, STRUCTURE AND HYDROGEN CONTENT WITH ADDITION AGENTS

Composition of electrolyte: same as in previous Table

Small Cell:

Cathode — Stainless steel of effective area: 4×4 sq cm

Current density: 30 amps/sq dm

Time of deposition: 30 min

ADDITION AGENT, IF ANY/LITRE	CELL VOLTAGE	END TEM- PERATURE °C	FLOW OF ELECTRO- LYTE cc/min	CE %	HYDRO- GEN CONTENT cc/100 gm	STRUCTURE AND REMARKS
Pure solution	7.45	36	30	26.55	—	Vide Fig. 5.II for cathodes with deposited manganese. Top 1 cm gamma; rest amorphous, loose and brittle
+20 cc glycerol	7.5	36	30	30.61	581.3 (of amorphous deposit)	Top $\frac{1}{2}$ cm gamma; rest amorphous and slightly adherent
+0.11 gm tri- amylamine	7.4	36	30	—	—	do
Pure solution	7	43	20	—	—	do
do	6.9	56	10	—	—	do

Remarks — Experiments with 30 amps/sq dm have been repeated and confirmed with the small cell. The small cell was used as the deposit with the cathode can be put for back reflection X-ray studies directly without any work on the deposit.

The back reflection X-ray studies of the deposits, immediately after electrolysis, from pure solutions at a current density of 30 amps/sq dm, show that the top portion gives crystalline pattern of gamma manganese with the particle size of the deposit greater than that of the deposit obtained at lower current densities. The deposit of bottom portion does not give any back reflection pattern and in the powder photograph gives only a broad halo at a 'd' value of $2.087\text{--}2.139\text{\AA}$. The micro-hardness of the top deposit was 137 DPN, while that at the bottom was 788. The hydrogen content of the top deposit was 137.63 cc per 100 gm from a number of experiments while that of the bottom deposit was 550.75 cc per 100 gm. The hardness and the X-ray patterns indicate that, while the top portion is that of gamma manganese, the bottom portion is of alpha manganese, the grain size being far below the range to be diffracted by X-rays.

Fig. 5.II gives the photographs of the deposits with cathodes obtained at high current densities of deposition. Pictures 1 and 2 are at 10 and 30 minutes of deposition, respectively, from pure solutions of manganese ammonium sulphate without any addition agents. The hard alpha deposits obtained at the bottom portions are not very adherent, and from picture 1 it can be seen that, by 10 minutes of deposition, the deposit is found to crack. This cracked portion peels off from the cathode, floats on the electrolyte and redissolves. Sometimes at the peeled off portions even gamma manganese has been found to be deposited. It is further interesting to note from pictures 3 and 4 of Fig. 5.II, that on the portions of the cathode facing the glass tube bringing in the feed electrolyte to the bottom of the cell, gamma manganese is obtained similarly as on the top portion where the current is blocked by the accumulation of hydrogen.

Fig. 5.III shows the photographs of deposits obtained on a similar cathode which has been bent as in the picture. On the projected side, which is drawn nearer to the anode and where the current density is high, alpha manganese is obtained while, on the other side of the cathode, which is drawn away from the other anode and where the current density is low, gamma manganese is obtained. Under the experimental set up for manganese deposition and with so much of hydrogen, it is rather difficult to keep a uniform current density all through the surface area of the cathode even on plain electrodes at such high current densities of deposition. It is an interesting feature to be mentioned that at separate areas of one side of the cathode, alpha and gamma manganese can be obtained at high current densities of deposition but never during the whole of this investigation a mixture of alpha and gamma manganese together on the same area has been found. The gamma deposit at the top portion and against the glass tube on the cathodes peel off with passage of time while the deposit at other portions, which has not been peeled off during the course of experiment, remains adherent with the cathode with passage of time.

It is seen from Table 5.I that increase in current density to about 30 amps/sq dm increases the hydrogen content of the deposit to about 566 cc/100 gm. The deposit has a hardness of 788 DPN similar to that of alpha manganese. The X-ray patterns show only a broad halo at the low angle indicating that it is amorphous. This is to be compared with the initial deposit up to 10 minutes deposition from solutions containing sulphur dioxide when only amorphous deposit is obtained. It is well known¹¹ that increase in current density increases the cathode potential as does addition of sulphur or selenium as discussed earlier.

Heating this amorphous deposit at 125°C for one hour in a vacuum of 10^{-3} mm of Hg gives a clear crystalline pattern of alpha manganese.

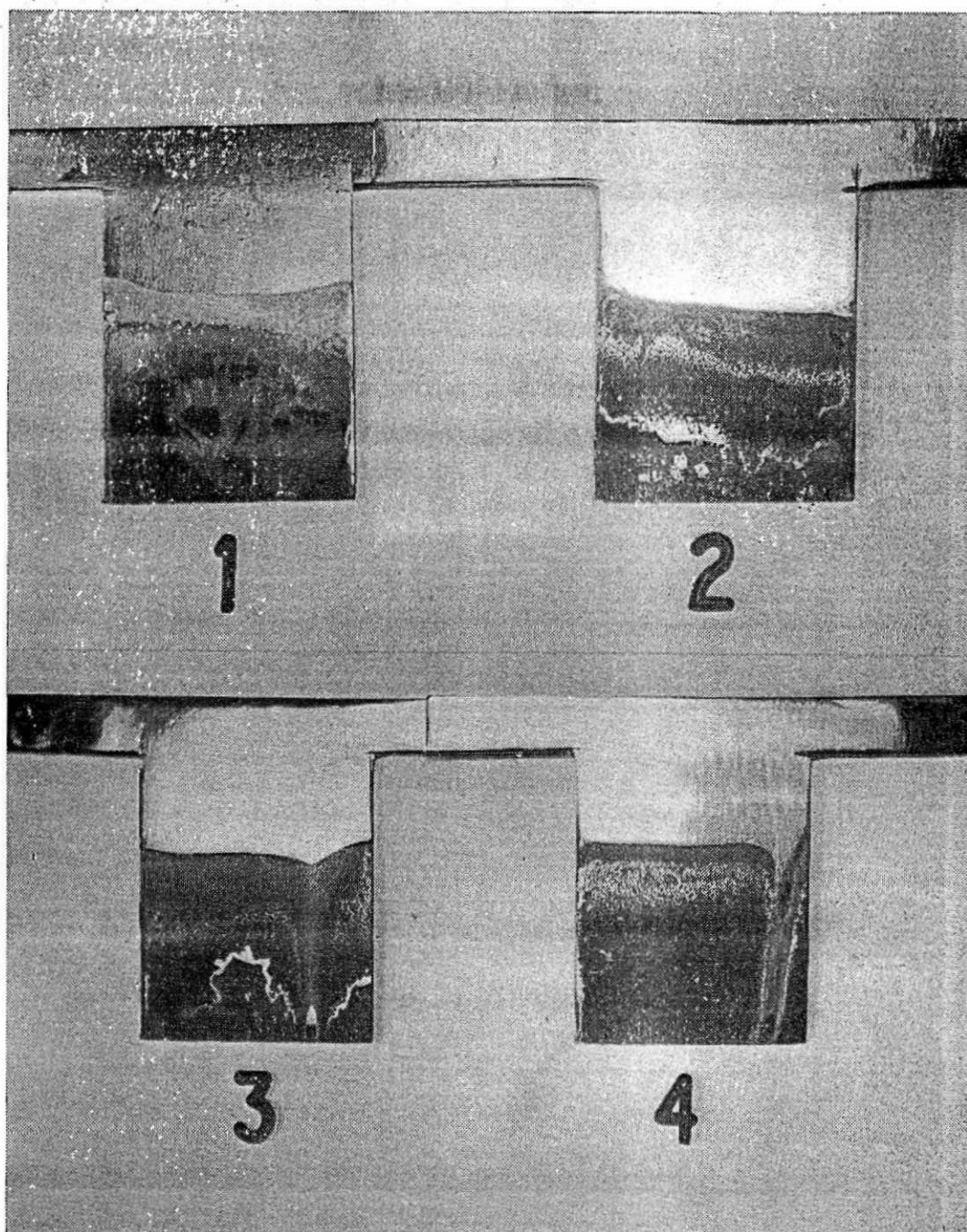


FIG. 5.II — CATHODES WITH DEPOSITED MANGANESE OBTAINED AT HIGH CURRENT DENSITIES

1. From pure solutions at 10 min of deposition
2. From pure solutions at 30 min of deposition
3. Same as above — other side
4. On addition of glycerol — 30 min of deposition

Effect of current density in presence of addition agents in the electrolyte — Table 5.II presents the effect of addition of 30 cc glycerol per litre of electrolyte or 0.11 gm per litre of triamylamine to the electrolyte at high current densities of deposition. Picture 4 of Fig. 5.II shows the cathode

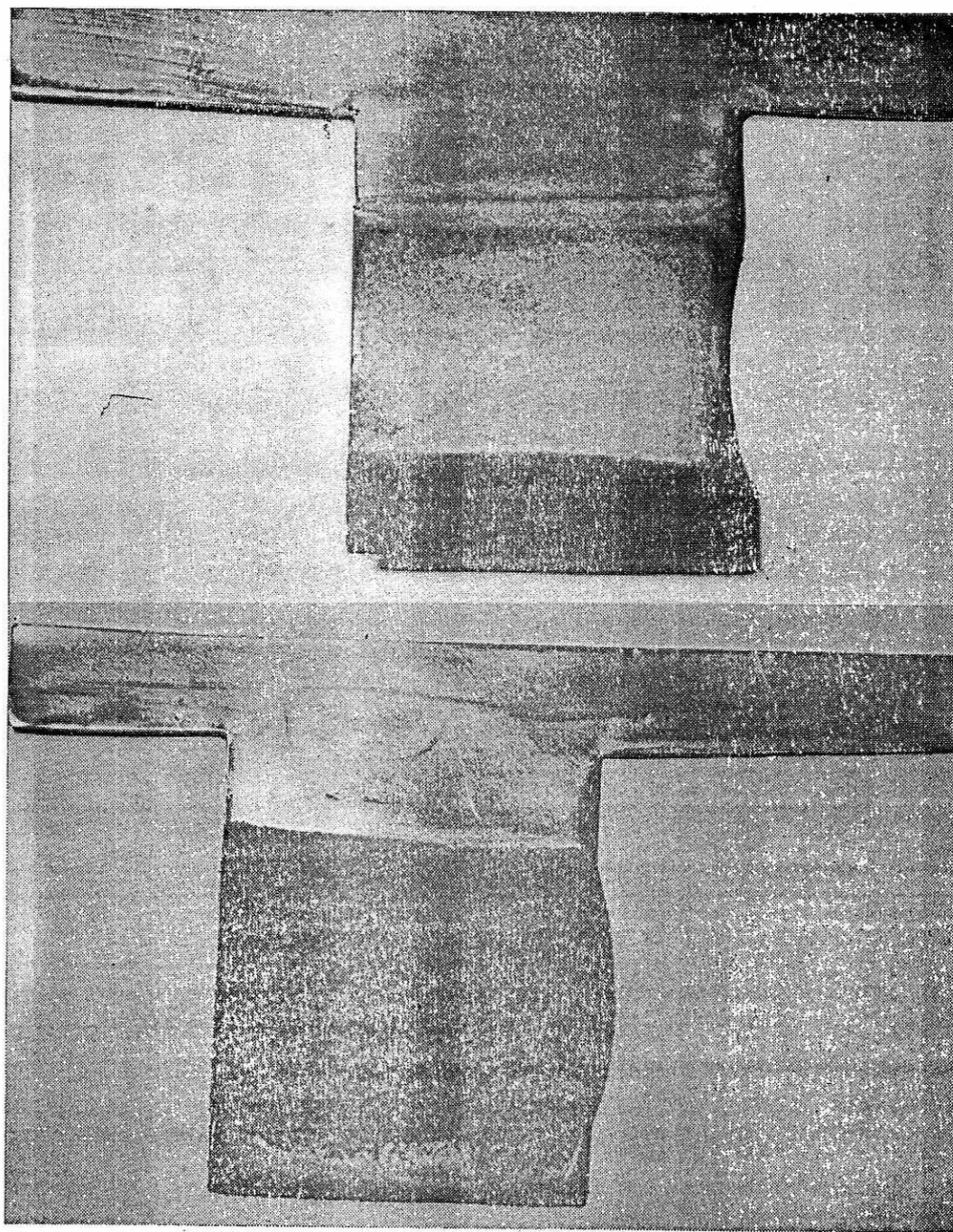


FIG. 5.III — THE TWO SIDES OF A BENT CATHODE WITH DEPOSITED MANGANESE FROM PURE SOLUTIONS AT HIGH CURRENT DENSITIES

obtained in presence of glycerol. Even on addition of 30 cc per litre of glycerol, the deposits at the top portion of the cathode and in the area facing the feed inlet tube are of gamma manganese which peel off with passage of time. The deposits at other parts are found to be amorphous as in the case obtained from pure solutions at high current densities. The efficiency of deposition with glycerol is 4 per cent higher

than that obtained from pure solutions and the amorphous deposit was more adherent and contained 581 cc of hydrogen per 100 gm. Other than these, no other significant change was found to be brought about by the addition of glycerol to the electrolyte.

Moiseev and Popova⁸ have studied the deposition of manganese, from pure solutions of manganese and ammonium sulphate with or without addition of glycerol, to a thickness of 10-60 microns on cathodes of copper, iron and silver at a cathode current density of 30 amps/sq dm. According to them also, the characteristic feature of the X-ray photographs of the deposits obtained from the above two baths is that, in its appearance, it is similar to the one from the amorphous substances, namely a strongly diffused line and a large background of incoherent scattering. The amorphous nature, as per Moiseev⁸, is caused by a non-uniform electron distribution among the manganese atoms and also on the displacement of atoms because of a higher hydrogen content.

The result of high current density experiments in this work agrees with that of Moiseev^{7,8} and Gorbunova⁹ in that at high current densities an amorphous deposit with close similarity to alpha manganese (as seen from the hardness values) is obtained. But according to them^{7,8} "gamma form of manganese was obtained in the deposit 10 microns thick on silver base from the bath without the addition of glycerin. At room temperature it passes over to alpha form of manganese in 6-10 hours". The gamma manganese obtained in this investigation did not change over to alpha manganese in 6-10 hours time as reported by Moiseev. At room temperature it took about 5 days for half completion of transformation¹². Presumably, a close proximity of the deposit of gamma and alpha manganese on the same surface of the cathode (as also found in the course of this investigation), depending upon the current density at the area, might have led them to arrive at their conclusion. Further, glycerin did not have any effect on the structure of deposited manganese. At low current densities, addition of glycerol did not effect in any way the smooth formation of coherent gamma manganese from pure solutions. At high current densities, from pure solutions, gamma manganese is obtained with or without glycerol only at those areas where the current density is lowered with consequent decrease in polarization.

Effect of pH of catholyte in presence of sulphur dioxide on the structure of deposited manganese — The alpha manganese deposits prepared in presence of sulphur dioxide at low pH values of catholyte, viz at pH 2, are found to be very bright and adherent compared to the dull and easily detachable deposits obtained at alkaline pH values, viz at pH >7. Similarly, deposits obtained at higher temperatures are more bright and adherent than the deposits obtained at low temperatures¹³. With increase in temperature of electrolysis, the stress has been found to be

decreased¹⁴ which explains the better adherence obtained at higher temperatures of electrolysis. Likewise, the deposits obtained at alkaline pH values of the catholyte have been found to have high internal stresses due to occlusion of hydroxide¹⁵. Thus, the better adherence of the deposit obtained at low pH values of catholyte can be interpreted as due to the absence of, or due to minimum stress in the deposits. According to Sanzharovski¹⁰ in the manganese deposits obtained at pH values less than 4, internal stresses were absent.

The manganese deposits obtained in presence of sulphur dioxide at various pH values show different characteristics. At pH values around 2, the deposits even after 2 minutes of deposition show the crystalline pattern of alpha manganese all through the surface, while the deposits obtained at pH values greater than 7 show amorphous nature in the initial stages of deposition.

In acidic condition, the electro-chemical reduction of sulphur dioxide takes place in the following order^{16,17}.

	E° volts (298°K)
$\text{H}_2\text{SO}_3 + 4\text{H}^+ + 4\text{e}^- = \text{S} + 3\text{H}_2\text{O}$	+0.45
$2\text{H}_2\text{SO}_3 + 2\text{H}^+ + 4\text{e}^- = \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O}$	+0.40
$\text{H}_2\text{SO}_3 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{SO}_2 + \text{H}_2\text{O}$	+0.40
$\text{S} + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{S}$	+0.141
$2\text{H}_2\text{SO}_3 + \text{H}^+ + 2\text{e}^- = \text{HS}_2\text{O}_4^- + 2\text{H}_2\text{O}$	-0.08

It is seen that in acid medium, the electro-chemical reduction of sulphur dioxide can easily take place to sulphur, hydrogen sulphide, thiosulphates and dithionates. It is known¹⁸ that when H_2S is passed, usually slowly and periodically, into a solution of H_2SO_3 , a milky solution results, which contains colloidal sulphur, hydrogen sulphide, thiosulphate, sulphite and considerable quantities of polythionic acids. In electro-deposition of manganese at low pH values and at sulphur dioxide contents >0.3 gm per litre, similar milky solution has been often observed. This indicates that with sulphur dioxide in the electrolyte, hydrogen sulphide is formed at low pH values of catholyte.

On the other hand in alkaline medium^{16,17}

	E° volts (298°K)
$2\text{SO}_3^{2-} + 3\text{H}_2\text{O} + 4\text{e}^- = \text{S}_2\text{O}_3^{2-} + 6\text{OH}^-$	-0.58
$2\text{SO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- = \text{S}_2\text{O}_4^{2-} + 4\text{OH}^-$	-1.40

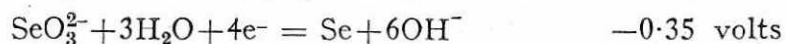
the electrochemical reduction of sulphur dioxide yields thiosulphate and dithionate ions and the incorporation of sulphur in the deposit should depend mainly on the chemical decomposition and/or formation of colloidal or precipitated sulphur.

The different characteristics of the deposit obtained at low and high pH values may be dependent upon the cathodically reduced sulphur and the formation of H_2S in acid medium and colloidal or precipitated sulphur in alkaline medium. To summarize them, it is found

<i>Acid medium</i>	<i>Alkaline medium</i>
Cathodically reduced sulphur and H_2S formation	Colloidal or precipitated sulphur
Very bright deposit	Dull black deposit
Low stress	High stress
Low efficiency of deposition	High efficiency of deposition

It is felt that the strength of bond between manganese and sulphur may be greater with a result that the adsorption of colloidal particles on the surface in the case of alkaline medium and their effect on discharge of metal ions are both greater. Hence, the formation of manganese sulphur bonding makes a weakening effect on manganese-manganese bonding. This may explain the amorphous characteristics of the deposits together with other properties like easy strippability of the deposits obtained at alkaline pH values.

In acid medium, the formation of bright crystalline deposit might be dependent upon cathodically reduced sulphur and the formation of hydrogen sulphide and its direct inhibitive action on the re-combination of hydrogen atoms. According to Smialowsky²¹ in the case of catalytic poisons P, S, As, Se, Te and Bi the formation of a volatile hydride is decisive for the poisoning effect and for the increased ability of hydrogen to penetrate into the cathodic metal. The fact that in alkaline medium, selenite ions yield cathodically reduced selenium



and that, on addition of selenious acid to the electrolyte even at alkaline pH values, even after 1 minute of deposition, gives crystalline pattern of alpha manganese, as seen earlier, shows that cathodically reduced sulphur or selenium and formation of hydrogen sulphide or selenide might be responsible for the deposition of the initial deposit in crystalline pattern. However, how the cathodically reduced sulphur or hydrogen sulphide directly brings about the initial deposition of manganese in crystalline pattern is not clearly understood and needs further investigation.

According to Vagramyan^{19,20} the solubility of hydrogen in metal in the course of electro-deposition may also result from the direct inclusion

of hydrogen ion into the lattice in the form of a proton as distinct from the inclusion of adsorbed atom. The experimental results showing a higher hydrogen content from acid as compared with alkaline solutions do indicate the possibility of such proton inclusion of hydrogen into electro-deposits.

Conclusions

At cathodic current densities above 27 amps/sq dm, instead of gamma manganese, amorphous brittle manganese containing about 550 cc of hydrogen per 100 gm is obtained from pure solutions. The X-ray pattern of this deposit is similar to that obtained in the initial stages in presence of sulphur dioxide at alkaline pH values. The hardness of this amorphous deposit is similar to that of alpha manganese. Heating this amorphous deposit at 125°C in a vacuum of 10^{-3} mm of Hg, when part of the hydrogen is liberated, gives clear crystalline pattern of alpha manganese.

In presence of sulphur dioxide, deposits obtained at pH values around 2 show crystalline pattern of alpha manganese instead of the amorphous deposits obtained up to 10 minutes of deposition at alkaline pH values of catholyte. The crystalline and amorphous nature of the deposits at various pH values of catholyte have been explained on the basis of electro-chemical and chemical reduction of sulphur dioxide at different pH values.

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