

CHAPTER III

Nature and growth of electro-deposits of manganese

The nature and growth of electro-deposits of manganese on substrates of alpha manganese, gamma manganese, copper, stainless steel and aluminium from pure solutions with no addition agents and with addition agents of sulphur dioxide or selenious acid have been studied. It has been shown that a flash layer of amorphous manganese is initially deposited from pure solutions fitting in or resembling that of alpha manganese over which gamma manganese begins to build up in absence of reducible sulphur or selenium compounds. In presence of sulphur dioxide, the amorphous nature continues to build up to an increasing thickness over which a crystalline pattern of alpha manganese is obtained. It has been further shown that the substrate has a directing influence only in the first few atomic layers of the deposit and beyond that, with all other conditions of deposition remaining the same, on the same and similarly prepared substrates, gamma and alpha manganese can be prepared with an addition of 0.1 gm/l of SO_2 or H_2SeO_3 for alpha deposition and the absence of reducible S or Se compounds for gamma deposition. Even gamma manganese can be deposited on alpha manganese and vice versa depending upon the absence or presence of reducible sulphur or selenium compounds in the electrolyte.

Introduction

Manganese has been electro-deposited in two allotropic modifications, viz alpha and gamma, from aqueous solutions of its salts. Interestingly, from pure solutions of manganese and ammonium salts, gamma manganese, ordinarily stable between 1095-1134°C, is obtained while with addition of 0.1 gm per litre of sulphur dioxide to the same electrolyte, alpha manganese stable at room temperature is obtained. The electro-deposited gamma manganese is in a metastable state and completely transforms to alpha manganese in about 10 days at a room temperature of 32°C (ref 1).

The effect of sulphur dioxide on the deposition of alpha manganese has been explained by various investigators³ as:

- (i) an anti-oxidant to prevent the precipitation of manganese hydroxide at the pH attained in the catholyte;
- (ii) to suppress the harmful effects of impurities, stabilize the electrolyte and to improve the current efficiency of deposition;
- (iii) a polarizing agent to increase the over-voltage for hydrogen evolution;
- (iv) to remove the disparity between the parameters of substrate metal and the deposit; and
- (v) for the transition of gamma to alpha manganese.

From his studies on micro-structure and hardness, Dean³ concludes that the initial deposit to a thickness of a few thousandths of an inch in an electrolyte containing sulphur dioxide is also in the gamma form but this transforms to fine-grained alpha and further deposition takes place as large-sized crystals of alpha manganese.

According to Schlain⁴, the addition of sulphur dioxide prevents the formation of gamma manganese. The gamma manganese deposits obtained by Schlain on copper cathodes could be stripped off easily in sheets and the back side of the deposit in contact with the cathode had a faint copper colour; on the other hand, the deposits obtained by him on stainless steel cathodes were very poor and porous.

Bell⁵, in her studies on the electroplating of manganese on aluminium, mild steel and copper to a thickness of 0.0015 in., 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.

According to Moiseev^{6,7}, the deposits obtained with sulphur dioxide at current densities of 17-25 amps/sq dm and at pH values of 2.2-3.0 showed clear crystalline structure of alpha manganese while deposits obtained at current densities of 25-30 amps/sq dm and at pH values of 3.5-4.2 showed only a pattern of amorphous body. Moiseev continues to say that the deposits of manganese obtained from electrolysis at a $pH > 4.0$, regardless of other conditions of electrolysis, as a rule, have a structure of amorphous body.

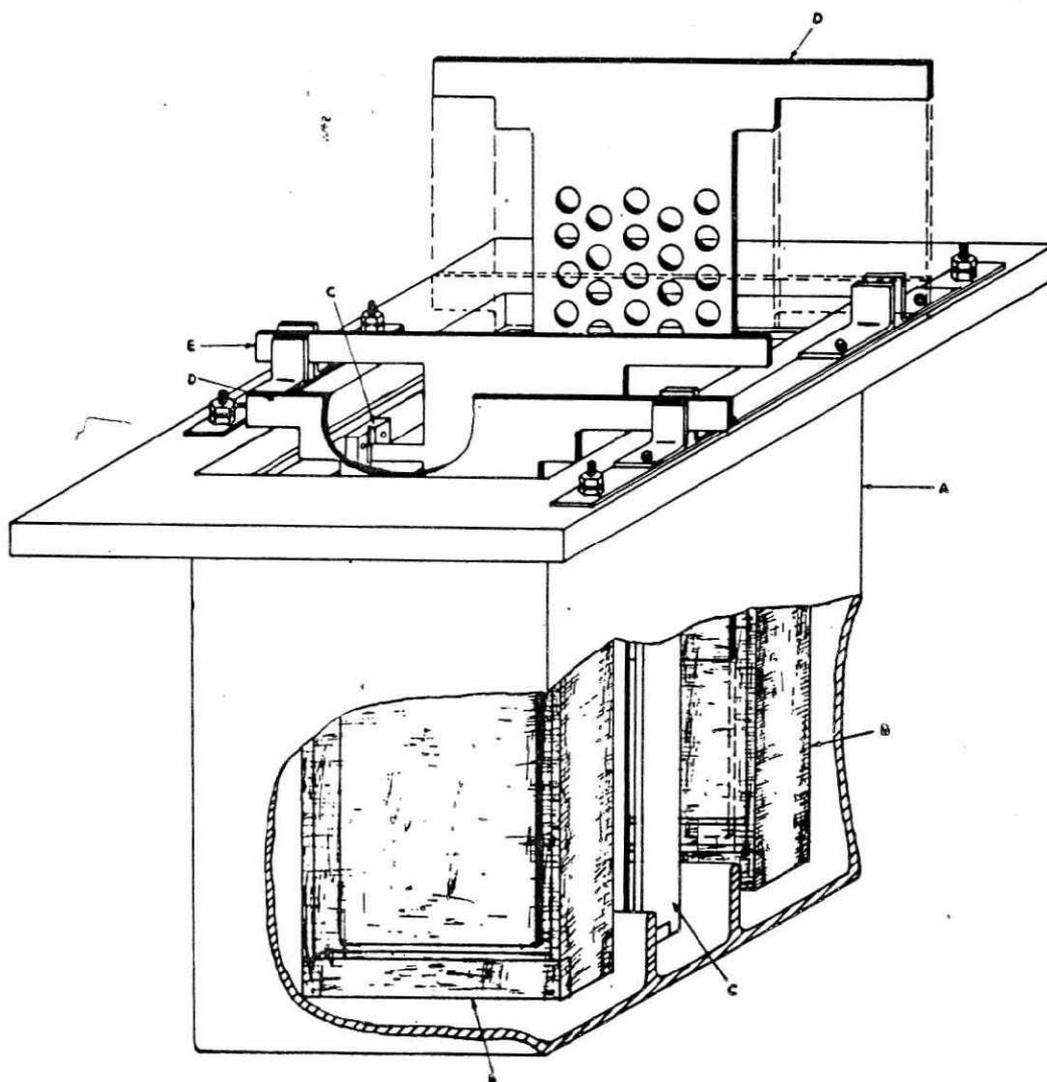
A survey of the literature on the structure of electro-deposits of manganese shows that there is yet no general agreement about the nature and growth of electro-deposits of manganese. It is also found that selenium dioxide as an addition agent in the electrolyte is found to bring about the deposition of manganese in alpha modification⁸ with current efficiencies of the order of 93 per cent compared to the order of 65 per cent obtained with sulphur dioxide.

It is intended in this work to study the growth of electro-deposits of manganese on different substrates, from pure solutions with and without addition agents, while at the same time trying to explain the anomalies observed by earlier workers.

Materials and methods

A sectional view of the electrolytic cell used for the deposition of manganese is given in Fig. 3.I.

Considerable attention was paid for the purity of the electrolyte. For each experiment, fresh electrolyte was used, prepared and purified in the same manner as in other experiments. The manganese sulphate, prepared by dissolving electrolytic manganese of 99.9 per cent purity in CP sulphuric acid, was filtered and mixed with CP ammonium sulphate solution. The pH value of the solution was adjusted to 7.5 by CP ammonium hydroxide, and 0.5 gm of guaranteed reagent ferrous sulphate was added per litre of solution and was air-blown for five hours. At the end of five hours of air-blowing, 0.5 gm of GR activated charcoal per litre of electrolyte was added and was further air-blown for half an hour. Aeration for five hours after addition of ferrous sulphate and further addition of activated charcoal were adopted to remove any dissolved hydrogen sulphide and colloidal sulphur that might come into solution from manganese sulphate prepared by dissolving electrolytic manganese in sulphuric acid. The solution was allowed to settle for about 24 hours before it was filtered through a bed of filter paper pulp and activated charcoal. Unless otherwise mentioned, the concentration was kept at



- A — ELECTROLYTIC CELL
- B — CANVAS DIAPHRAGMS
- C — PERSPEX GUIDE
- D — LEAD SILVER ALLOY ANODE
- E — STAINLESS STEEL CATHODE

FIG. 3.I — ELECTROLYTIC CELL ASSEMBLY

23-24 gm of manganese as manganese sulphate and 135-40 gm of ammonium sulphate per litre, with 10 cc per minute rate of flow of feed electrolyte to the cell.

Stainless steel, copper and aluminium cathodes were polished in a polishing lathe with emery composition and finally finished with pearless polish. For deposition of gamma manganese over alpha and vice versa, the primary deposits were prepared on a stainless steel cathode, and

the stainless steel cathode with the primary deposit was used as the alpha or gamma manganese cathode as the case may be for subsequent deposition.

X-ray examinations — To each cathode, in the middle of a slit, beginning from 1 cm below top solution level, a 0.25 mm thick wire of the corresponding metal as the cathode material was attached. The wires were cold drawn and annealed. They were then mechanically polished with metallographic paper 2/0. A portion was cut from the middle of this wire with the deposited metal and the same was used as the specimen for X-ray examinations. In all cases, within an hour after the experiment was over, the specimen was mounted and put for X-ray examination.

Unicam 60 mm cylindrical camera with S-25 single crystal oscillation goniometer was used for obtaining the X-ray powder patterns. Chromium K radiation without filter from a demountable Raymax crystallographic set with rotating anode was used. The time of exposure was about 3 hours with the tube running at 30 kV and 35 mA. Straumanis film mounting was adopted.

For pin hole back reflection studies of cathodes with deposited manganese, cathodes with deposited manganese from a small cell, which was a complete replica of the big cell, were directly mounted on the specimen holder immediately after the experiments were over. The metropolitan vickers camera with a circular film cassette of 14 cm dia was used. Neither the specimen nor the film was rotated during the exposure period. The specimen to film distance was kept at about 3.5 cm. Iron K radiation without filter from the Raymax crystallographic unit was used. The time of exposure varied from 6 to 7 hours at tube ratings of 30 kV and 35 mA.

Microscopic examination — For micro-examination of alpha manganese either the metal, as deposited on a wire attached to the slit of the cathode, or stripped metal from the cathode, was used. It was mounted, with bakelite powder as the mounting medium, in a hydraulic mounting press at 110°C. The metastable gamma manganese or specimens containing both alpha and gamma were cold mounted with plastic solution and plastic powder. Both were etched for about 40 seconds in 5 per cent Nital. The micro-hardness was measured either with a GKN or IIMT-3 micro-hardness tester.

Experimental results and discussion

Manganese deposits from pure solutions without addition agents — From the X-ray diffraction patterns of the deposits presented in Fig. 3.II,

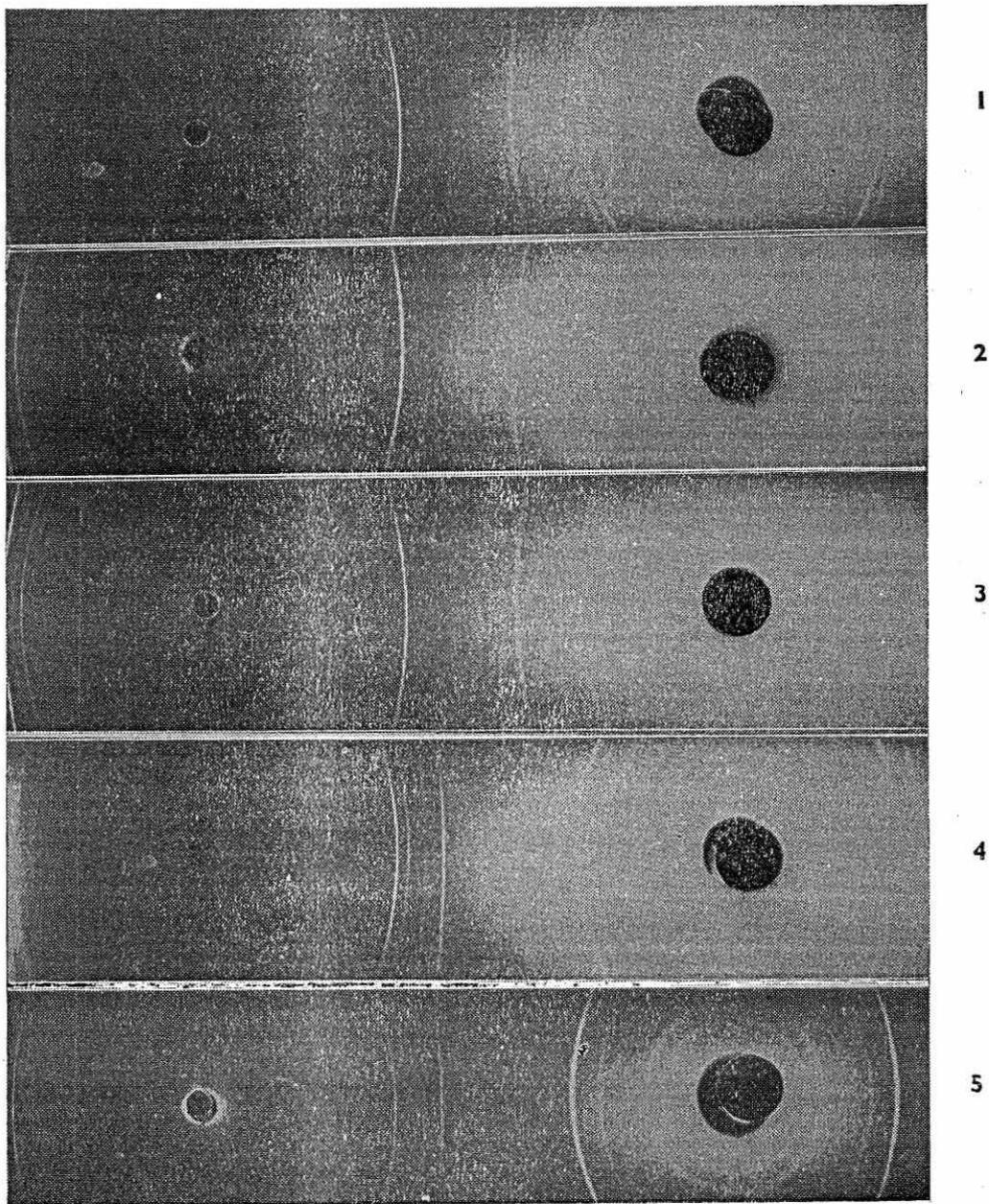


FIG. 3.II — X-RAY DIFFRACTION PATTERNS OF DEPOSITS ON STAINLESS STEEL FROM PURE SOLUTIONS WITH NO ADDITION AGENT

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|-------------------------------|------------------------------|
| 1. Stainless steel substrate | 3. After 2 min of deposition |
| 2. After 30 sec of deposition | 4. After 5 min of deposition |
| 5. Gamma manganese | |

it is seen that, in the absence of any addition agent, deposits on stainless steel after 30 seconds and 2 minutes of deposition give a sharp, though very weak, diffraction line at 2.13 \AA , the intense line of gamma manganese. At 5 minutes of deposition, all the diffraction lines of gamma manganese are visible while the intensity of the

stainless steel substrate lines are found to decrease. This indicates that from pure solutions on stainless steel cathode, gamma manganese starts to build up by about 30 seconds of deposition.

On the other hand, as seen from Fig. 3.III, deposit from the same pure electrolyte on copper cathode gives no diffraction lines of gamma

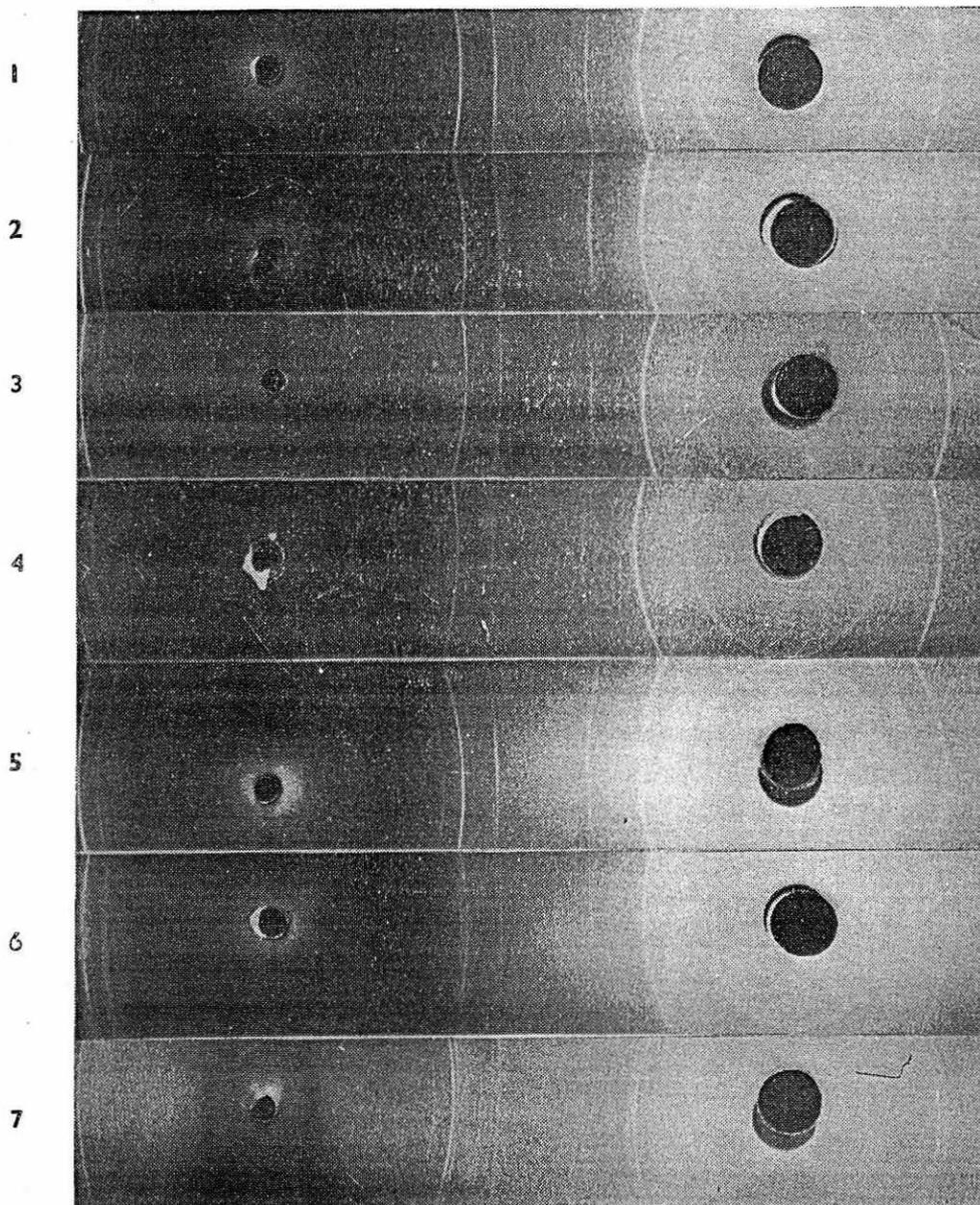


FIG. 3.III — X-RAY DIFFRACTION PATTERNS OF DEPOSITS ON COPPER FROM PURE SOLUTIONS WITH NO ADDITION AGENT

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|-------------------------------|--|
| 1. Copper substrate | 4. After $\frac{1}{2}$ min of deposition |
| 2. After 8 sec of deposition | 5. After 2 min of deposition |
| 3. After 30 sec of deposition | 6. After 3 min of deposition |
| | 7. After 5 min of deposition |

manganese up to one minute of deposition but only the diffraction pattern of copper substrate continues. At 2 and 3 minutes of deposition, besides copper pattern, a very broadened diffused line at low angle of 'd' value 2.08-2.15 Å is noticed. At 5 minutes of deposition all the diffraction lines of gamma manganese are noticed along with copper substrate lines as in the case with stainless steel cathode. This indicates that copper behaves differently from stainless steel in the initial growth of the deposit, although at 5 minutes of deposition both behave similarly.

It is known that manganese forms a series of solid solutions with copper and that with less than 20 per cent manganese, copper forms a solid solution of gamma phase only³. By deposition of manganese on an active substrate of copper, it is quite possible that the first arriving manganese atoms form a solid solution of manganese in copper. Further diffusion between manganese and copper may also occur. Straumanis⁹ and Hoar's¹⁰ observations on zinc diffusion in copper at room temperature give support to this view. Alloy formation and/or diffusion might be the period up to one minute of deposition during which no diffraction pattern other than that of copper is noticed.

Beyond one minute of deposition and up to three minutes of deposition, besides copper substrate pattern, only broad halo at low angle is noticed. At this stage it is worth mentioning that the deposits both on stainless steel and copper in presence of 0.1 gm/l SO₂ up to 10 minutes of deposition show only broad halo at low angle, as will be seen in the next section.

Sharp X-ray diffraction lines will be absent when the crystal size is too small or the broadening of lines may be due to one or more of the following reasons¹¹.

- (i) Some crystals have slightly different unit cell dimensions from others.
- (ii) Crystals are extremely small.
- (iii) The unit cell dimensions vary in different regions of the crystals owing to non-uniformity in composition or to strains.
- (iv) Structural irregularities on a very small scale.
- (v) Thermal movements of the atoms in crystals.
- (vi) When a mixed crystal phase is formed.

Under conditions (i) and (iii) mentioned above, a few of the diffraction lines, if not all, should be present though broadened. If the broadening was due to stress or strain in the deposit, the broadening should have been at the high angle side as is seen in the case of cold worked metals¹². Absence of diffraction lines and broad halos

at the low angle are generally seen in case of amorphous substances like lamp black¹³, chemically deposited nickel¹⁴, etc. At particle sizes much less than 0.01 micron, the back reflection lines disappear entirely and the low angle lines become very wide and more broadened¹⁵. If the particles in a micro-crystalline mass become finer and finer, in the limit all crystalline structure is lost and the solid becomes amorphous¹⁵. According to Bragg¹⁵, even in the amorphous state, the distribution of the atoms cannot be entirely at random. The impossibility of inter-penetration of the atoms and the existence of inter-atomic binding implies that certain arrangements of any given atom with respect to its neighbours are more probable than others¹⁵. The halos of amorphous material, as per Bragg¹⁵, are due to the most probable relative arrangement of nearest neighbours. It is, therefore, according to him, to be expected that the broad halos should correspond to the more intense lines of the crystalline specimens much broadened out because the regions of arrangement can only extend over a few atoms. From Fig. 3.III, it is seen that the broad halos are noticed at 'd' values 2.08 to 2.15 Å (the intense line of alpha manganese is 2.099 Å and that of gamma manganese is 2.121 Å).

Brenner¹⁶ is also of the opinion that of all the causes the small grain size of the electro-deposit may be the resulting factor for the diffuseness of the diffraction bands. Dehlinger and Giesen¹⁸ studied the causes for the diffuseness of the structure of electro-deposited brass. As the line broadening did not disappear after the deposits were annealed at 300°C, they reasoned out that it could not be caused by stresses which would have been removed by the above heat treatment. They ruled out the possibility that the non-uniformity in composition was the cause for the line broadening by annealing the specimen at 400°C for 10 minutes when the broadening totally disappeared. In this short period, diffusion would not have been rapid enough to eliminate the non-uniformity in composition and, therefore, they concluded that the only mechanism capable of producing the change was grain growth. Many other electro-deposited hard brittle alloys such as copper-lead¹⁹, 10 per cent phosphorous-nickel²⁰, phosphorous-cobalt²⁰ give no diffraction pattern other than broad halos at low angles. Similarly, antimony²¹, deposited electrolytically or by evaporation in vacuum, shows the broad halo pattern (characteristics of glass) as does arsenic²² deposited from the vapour phase. Barret²³ and Brenner¹⁶ even say that electro-deposition appears to be the best means of producing amorphous metals or alloys as they cannot be obtained by ordinary metallurgical procedures, such as cold working. However, Bridgeman²⁴ produced amorphous metal by applying very severe shearing forces.

With these points in view, it can be concluded that the grain size of the manganese deposit up to 3 minutes of deposition on copper

cathodes from pure solutions should be less than that of 0.01 micron as being below in range of diffraction by X-rays.

At this point, it would be interesting to mention a few experimental observations. Schlain and Prater⁴ in their studies on electro-deposition of gamma manganese were able to obtain good deposits of gamma manganese on copper cathodes. The deposited manganese could easily be stripped off in sheets and according to Schlain, the back of the deposits in contact with the cathode had a faint copper colour. The deposits obtained by Schlain on stainless steel were very poor and porous. On the other hand, the gamma deposits obtained in this investigation, both on copper and on stainless steel, were equally good and adherent to the cathode material. Only with a sharp edge of a knife the deposits could be stripped off from the cathodes in ductile flexible pieces. The deposits obtained on copper did not have any tinge of copper colour on the back side as obtained by Schlain, but, on the contrary, the cathodes of copper and even stainless steel had a thin white coat of manganese on them after stripping off the deposited gamma manganese. The thin white coat of manganese that remained on stainless steel cathode after stripping off the deposited gamma manganese was not so uniform as on the copper cathodes but were rather irregular and discontinuous. Fig. 3.IV shows the discontinuous thin white coat of manganese that remained on a stainless steel cathode after stripping off the deposited gamma manganese. Further, it was observed that on those portions, where the discontinuous thin white coat of manganese was absent, the adherence of gamma manganese on to the stainless steel cathode was also poor.

When the deposited gamma manganese on stainless steel was allowed to transform to alpha at room temperature or at an elevated temperature (125°C), the deposits came off completely leaving the polished surface of the substrate clean and without any undercoat of manganese. It is reasonable to assume that if the deposits obtained from pure solutions in the very initial stages were also gamma manganese (though particle size may be extremely small), during stripping, the whole deposit should have come leaving the polished surface of the electrode as clean as before introduction in the bath and without any white manganese coat. While we strip alpha manganese prepared with sulphur dioxide or selenious acid from polished stainless steel cathodes, the whole deposit generally comes off leaving the polished surface as bright as before introduction in the bath. The fact that a thin white coat of manganese remains on a polished stainless steel cathode after stripping off the deposited gamma manganese and that if the deposited gamma manganese is allowed to transform to alpha, the deposit comes off leaving the cathode as bright as before introduction in the bath, indicates that the very initial deposit during deposition of

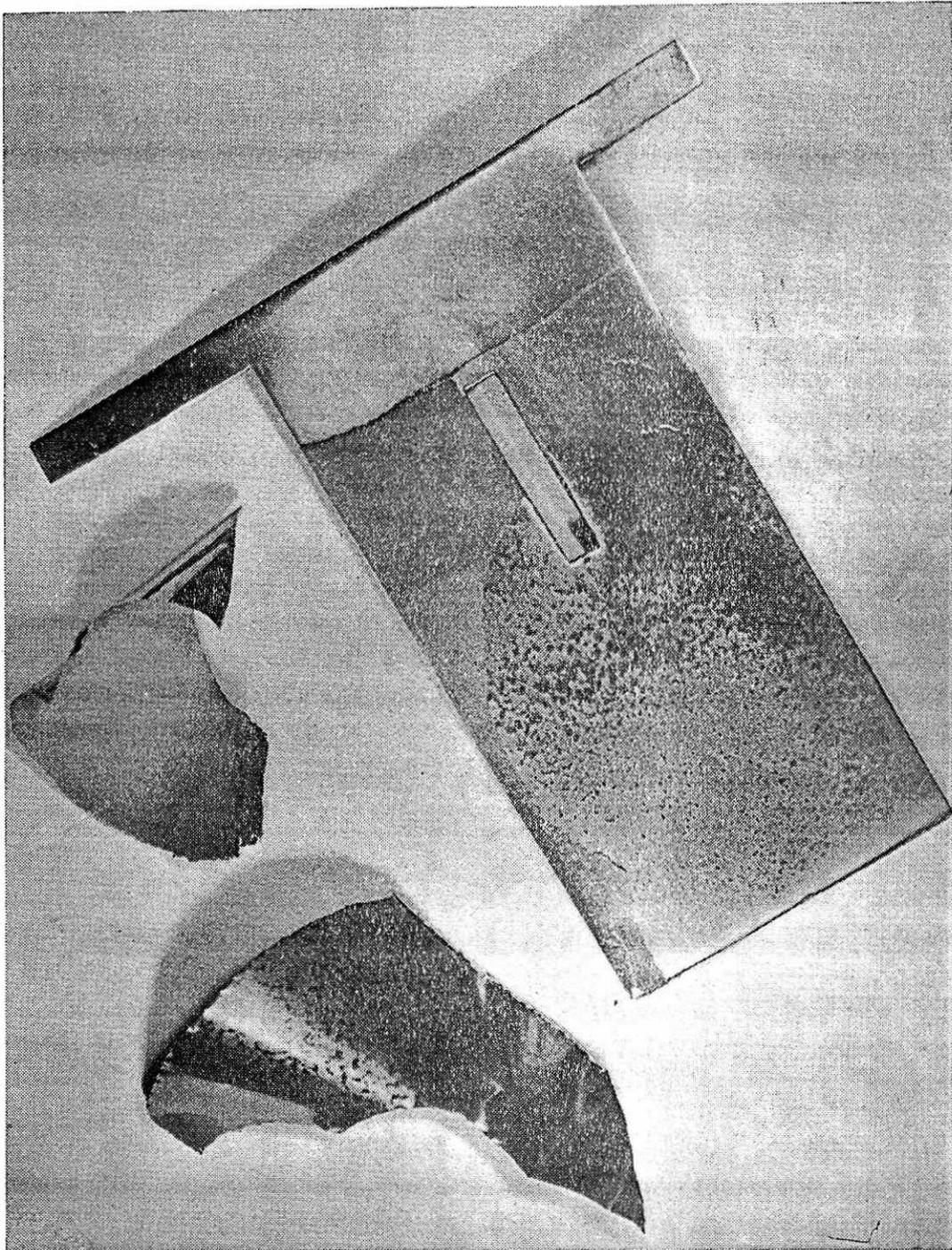


FIG. 3.IV — STAINLESS STEEL CATHODE AFTER STRIPPING OFF DEPOSITED GAMMA MANGANESE SHOWING THE IRREGULAR WHITE UNDERCOAT OF MANGANESE

gamma manganese from pure solutions is in a different phase other than gamma.

The amorphous deposits obtained in presence of sulphur dioxide show a hardness value of 652 VPN indicative of alpha manganese as will be seen later.

When the deposited gamma manganese on the copper cathode was allowed to transform to alpha at ordinary room temperature or at an elevated temperature, the deposit did not peel off from the cathode due to volume change, as in the case of stainless steel cathodes, but was found to be very adherent with the thin white uniform coat of manganese and in turn with the cathode. It was found interesting that, while the gamma deposit from the copper cathode could be stripped off soon after deposition leaving behind a thin white coat of manganese, it was rather difficult to strip off any portion of manganese after its transformation to alpha. This has to be considered along with the fact that the deposited alpha manganese on copper cathodes in presence of sulphur dioxide or selenious acid cannot be stripped off from the cathodes. This indicates that the thin white coat of manganese may be responsible for the strong adherence of deposited manganese on the copper cathode and that it attaches itself strongly with the transformed alpha manganese. Whatever may be the coordination between the copper and manganese atoms in the first few atomic layers, for this strong adherence of thin white coat of manganese on the copper cathode such as to keep the transformed alpha also firmly adherent to it, it can be inferred that this thin white coat, that is left behind after stripping off gamma manganese, is in a different phase other than gamma.

These experimental evidences about adherence of gamma deposits are in conformity with Dean's³ observation that the plates on copper show no tendency to peel when the manganese transforms from gamma to alpha but heavier plates on steel and particularly magnesium peel on standing due to volume change on transformation.

Examination of the back reflection X-ray patterns of copper substrate alone and of the copper cathode along with the thin white coat of manganese that remained after stripping off gamma manganese immediately after deposition shows that both give only copper lines excepting that the β line of 0.9012 \AA is faintly visible in the pure copper pattern while it is absent in the pattern obtained with the copper cathodes covered with the thin coat of manganese. The fact that the undercoat of manganese does not give any back reflection pattern has to be considered with the earlier finding that the deposits on copper at 2 minutes and 3 minutes of deposition give only broad halos at 'd' value $2.08\text{-}2.15 \text{ \AA}$ and no back reflection lines and that at 5 minutes of deposition all the lines of gamma manganese are noticed. It can hence be safely inferred that the white coat of manganese that remained back on the copper cathode must be the deposit up to 3 minutes of deposition. This coat is amorphous or rather the particle size is extremely small. The same is true with that on the stainless steel cathode except that the amorphous deposit forms only for the first few seconds of deposition.

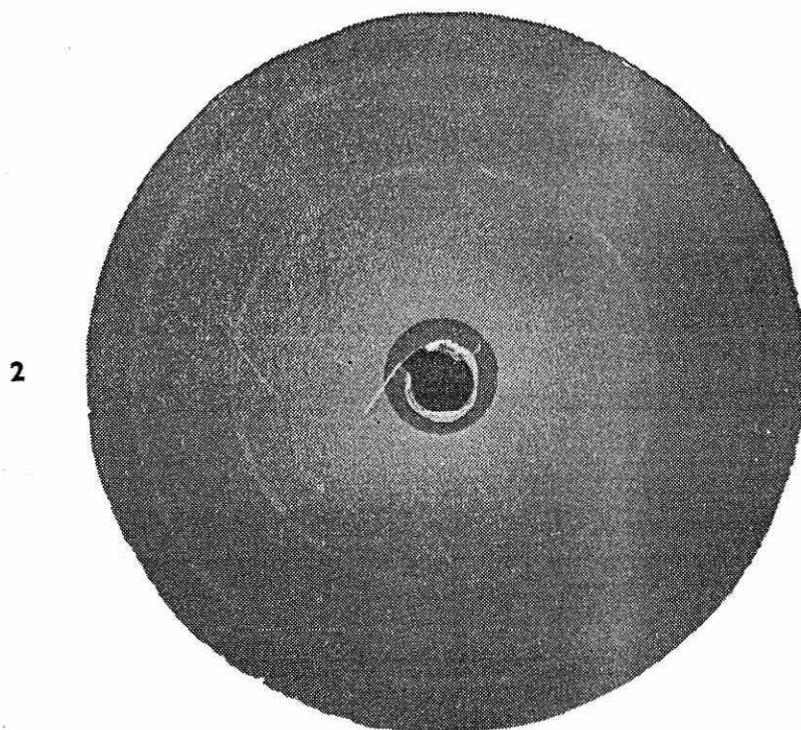
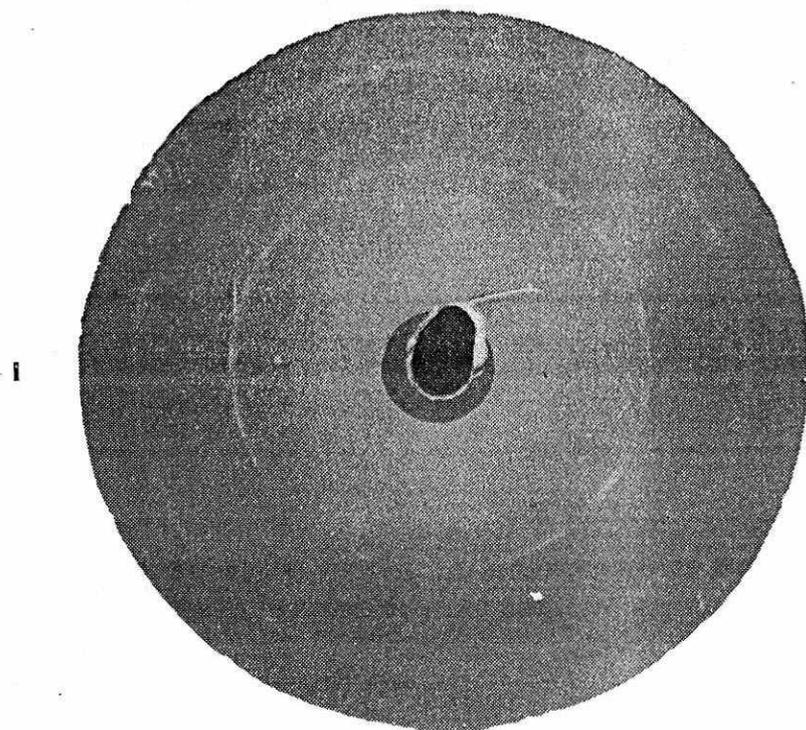


FIG. 3.V — BACK REFLECTION X-RAY PATTERNS OF (1) COPPER SUBSTRATE; AND (2) COPPER SUBSTRATE AFTER STRIPPING OFF GAMMA MANGANESE DEPOSITED ON THE SAME

This dissimilarity in time between copper and stainless steel cathodes for the initial formation of amorphous deposit can be clearly observed from a look at the cell immediately after the cathode is introduced with the current flowing. In case of deposition of gamma manganese from pure solutions on stainless steel cathodes, it is always seen that as soon as the cathode is introduced with the current flowing, manganese begins to deposit with extremely low hydrogen evolution for the first 8-10 seconds, which evidently is the thin irregular white coat of manganese that remains on the cathode after stripping off the deposited gamma manganese, and that immediately after this initial period, large bubbles of hydrogen can be seen sticking to the cathode followed by large evolution of hydrogen. Presumably the amorphous coat catalyses hydrogen evolution considerably. Hammerquist²⁵ has made a similar observation. In about 3 minutes of deposition, the large-scale evolution of hydrogen considerably subsides down, and uniform evolution of small bubbles of hydrogen can be seen indicating the high hydrogen over-voltage of gamma manganese.

In case of alpha deposition also on stainless steel cathodes, both in presence of sulphur and selenium in the electrolyte, manganese deposits for the first 8-10 seconds with extremely low hydrogen evolution followed by large-scale evolution of hydrogen. While in presence of selenium this large-scale evolution is arrested in another few seconds, in presence of sulphur it takes about 1-2 minutes for the large-scale evolution to subside considerably.

On the other hand, in cases of both gamma and alpha deposition on copper cathodes, no such large-scale evolution of hydrogen is seen after 8-10 seconds but continues to be small and uniform from the moment the cathode is introduced with the current flowing. It is well known²⁶ that, when a metal that is being deposited is able to form a solution in the cathode, or better, when it forms a compound with the cathode material which dissolves in the latter, the partial molar free energy of the deposited substance is diminished and deposition can occur at a potential that is less cathodic than the reversible value for the pure metal. Possibly this explains the easier initiation of manganese deposits on copper cathodes than on stainless steel.

To summarize, it is seen that deposition of manganese from pure solutions of manganese and ammonium sulphate on stainless steel cathode results in a non-uniform amorphous deposit for the first 8-10 seconds over which gamma begins to build up by about 30 seconds deposition. Deposits on copper up to one minute of deposition do not show any lines other than copper pattern after which up to 3 minutes of deposition besides substrate lines broad halos at low angle indicating amorphous nature of the deposit is noticed. At 5 minutes of deposition both stainless steel and copper give all the lines of gamma manganese.

And there are reasons to infer from the following points that the amorphous deposit does not belong to the gamma form but on the other hand to the alpha form.

- (i) When gamma manganese is stripped from the stainless steel cathode, this amorphous deposit is left behind. If it belonged to gamma structure, but only particle size being extremely small, it should have come along with gamma deposit.
- (ii) When the gamma transforms to alpha either at room temperature or at an elevated temperature, the whole deposit comes off leaving the polished surface as clean as before introduction in the bath. The amorphous deposit has attached itself strongly to the transformed alpha.
- (iii) With introduction of 0.1 gm of sulphur dioxide per litre to the same electrolyte, the deposit continues to be amorphous up to 10 minutes of deposition as will be seen in the next section. But when deposits of one or few hours of deposition are stripped, the whole deposit comes off leaving the polished surface of stainless steel clean. The amorphous deposit is not left behind but is coherent with the crystalline alpha deposit.
- (iv) On copper cathodes, after stripping off gamma manganese, the amorphous deposit is left behind on the cathode. When the deposited gamma transforms to alpha on the cathode, it is almost impossible to strip off the transformed alpha along with the amorphous coat of manganese.
- (v) Deposits on copper cathodes with 0.1 gm/l of SO_2 in the electrolyte are also amorphous up to 10 minutes of deposition. But deposits obtained on copper with SO_2 are impossible to be stripped off.
- (vi) The amorphous deposits obtained in presence of sulphur dioxide show a hardness of 652 VPN indicative of alpha manganese.

Manganese deposits from solutions with an addition agent of 0.15 gm of SO_2 per litre of electrolyte — X-ray patterns of deposits obtained from the same electrolyte but with an addition agent of 0.15 gm of SO_2 per litre on stainless steel and copper cathodes show only broad diffused halos at the low angle up to ten minutes of deposition as can be seen from Figs. 3.VI and 3.VII.

With increasing time of deposition from 2 to 10 minutes it is also noticed that substrate metal lines decrease in intensity or begin to disappear indicating that substrate is being covered with deposited manganese. This is more so with copper because of the easier initiation of deposition for reasons already mentioned. At 15 minutes of deposition, deposits both on copper and stainless steel have given clear diffraction

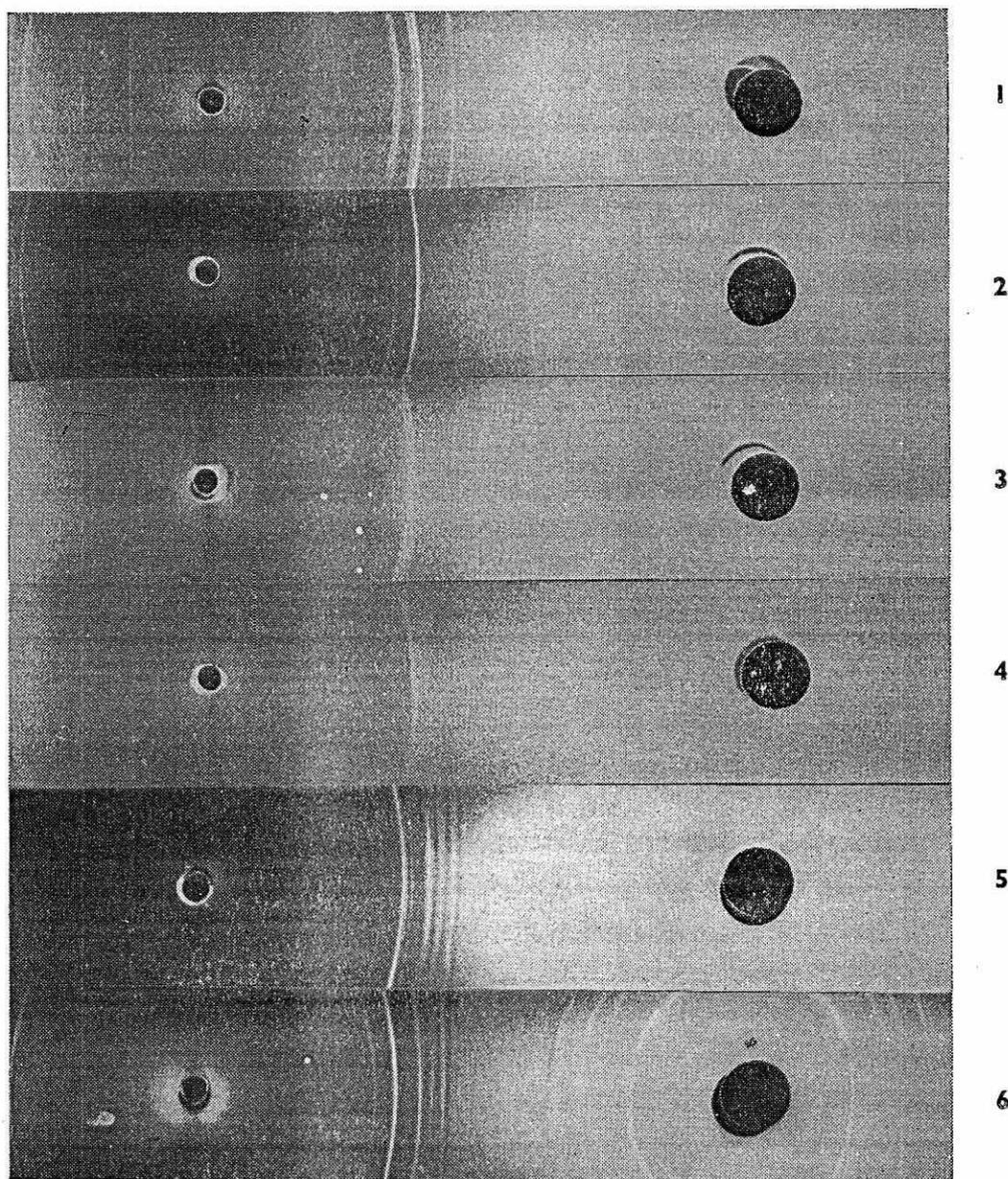


FIG. 3.VI — X-RAY POWDER PATTERNS OF DEPOSITS ON STAINLESS STEEL FROM SOLUTIONS CONTAINING 0.15 GM OF SO_2 PER LITRE

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|------------------------------|-------------------------------|
| 1. Stainless steel substrate | 4. After 10 min of deposition |
| 2. After 2 min of deposition | 5. After 15 min of deposition |
| 3. After 5 min of deposition | 6. Alpha manganese |

lines of alpha manganese. The broad halos occur in the case of stainless steel at 'd' value of 2.10 \AA and in case of copper at 2.11 (from 2.08 - 2.14) \AA while the strong intense line of alpha manganese is 2.099 \AA and that of gamma manganese is 2.121 \AA . The back reflection X-ray picture of deposit (surface facing solution side) obtained in presence of sulphur dioxide to a thickness of $0.002''$ is given in Fig. 3.VIII.

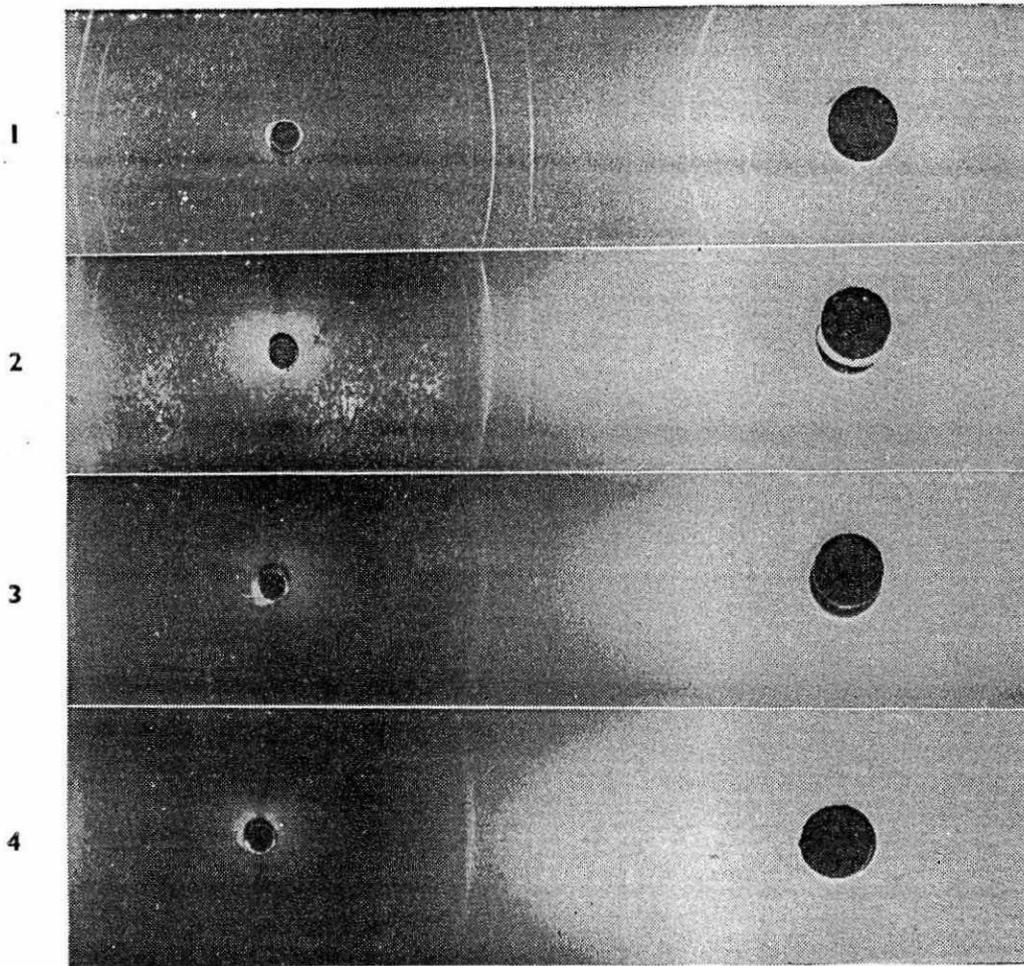


FIG. 3.VII — X-RAY POWDER PATTERNS OF DEPOSITS ON COPPER FROM SOLUTION CONTAINING 0.15 GM OF SO_2 PER LITRE

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|------------------------------|-------------------------------|
| 1. Copper substrate | 3. After 5 min of deposition |
| 2. After 2 min of deposition | 4. After 10 min of deposition |

From the absence of back reflection lines and broad halos at low angle, as mentioned earlier, it can be inferred that the deposit obtained in presence of SO_2 up to 10 minutes of deposition consists of extremely small grains or rather is in an amorphous condition. These amorphous state deposits of 10 minutes give only broad halos at low angle even after ageing at room temperature for 3 months.

It is of particular interest to mention that no indication of gamma manganese was noticed from the X-ray photographs of specimens taken after 2, 5 and 10 minutes of deposition, though from this electrolyte, in the absence of sulphur dioxide, gamma lines were distinguishingly clear after 5 minutes of deposition as seen earlier.

Dean³ has mentioned that manganese is initially deposited up to a few thousandths of an inch thick in gamma modification and in presence of reducible sulphur compounds in the electrolyte this gamma

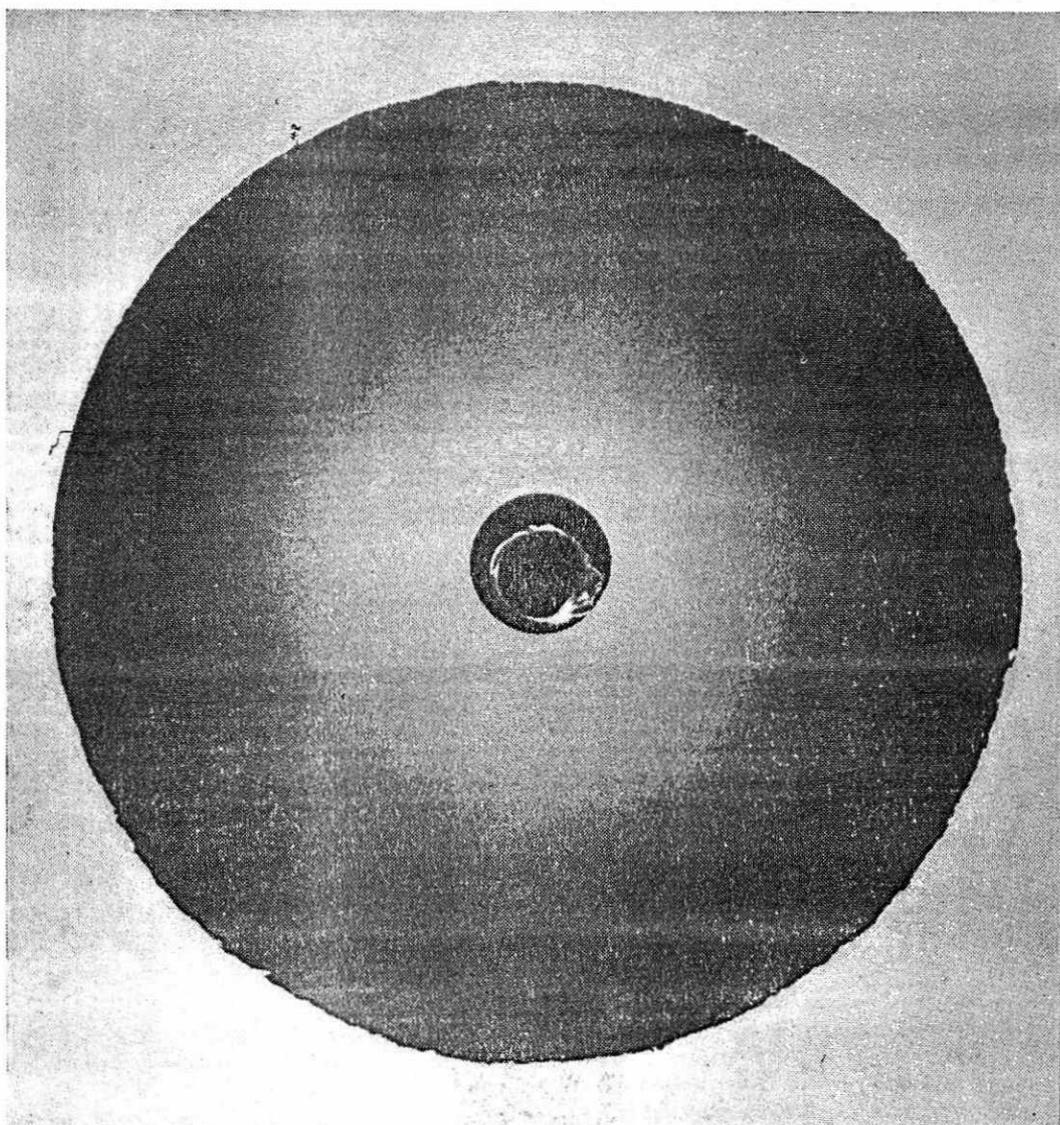


FIG. 3.VIII — BACK REFLECTION X-RAY PATTERN OF DEPOSIT (SURFACE FACING SOLUTION SIDE) OBTAINED IN PRESENCE OF SULPHUR DIOXIDE

is transformed to fine-grained alpha and further deposition takes place as macroscopic crystals of alpha manganese. The question then arises why in presence of sulphur dioxide the deposits at 5 minutes of deposition, when the thickness of the deposit is much below 0.001", do not give any diffraction lines of gamma manganese while, in absence of sulphur dioxide, from the same electrolyte at 5 minutes of deposition clear diffraction lines of gamma manganese are noticed. The electro-deposited gamma manganese takes about 10 days at 32°C for complete transformation to alpha¹. Dean³ has based his inference on the micro-structure of deposited manganese and the hardness and tarnish resisting brightness of the deposit towards the cathode side.

According to Dean, the thin layer of finer crystalline metal towards the cathode side in the micro-photographs represents gamma manganese that has transformed to alpha. Its hardness, as per Dean, is 700-900 Brinell and is approximately that of quartz.

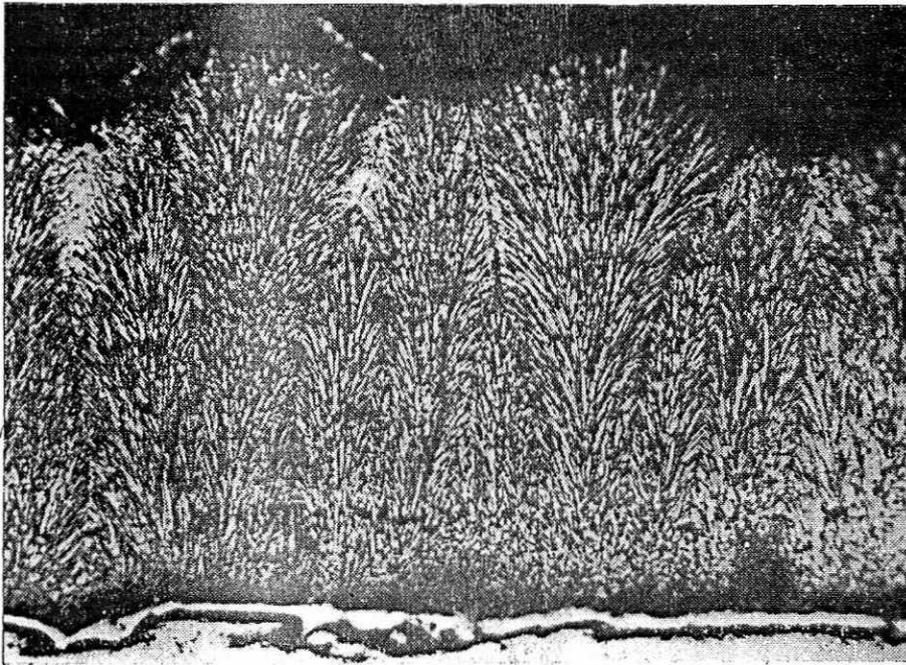
Micro-structure — The micro-photographs of deposited alpha manganese and gamma manganese on stainless steel and copper cathodes are given in Fig. 3.IX (1-6).

Electro-deposited alpha manganese, in presence of reducible sulphur or selenium compounds, show a clear columnar structure while in deposited gamma manganese twins are generally observed as is usually found in face-centred cubic metals.

The side towards the cathode of electro-deposited alpha manganese in presence of sulphur dioxide immediately after deposition, or after a period of 4 years of ageing at room temperature, does not give any back reflection X-ray pattern even after 7 hours exposure with iron radiation. The same specimen only after heating at 500°C for two hours in a vacuum of 10^{-4} mm of Hg gave faint but sharp lines of alpha manganese. When the surface of the deposit towards the cathode does not give any back reflection pattern, ie its grain size being so small as not being resolved by X-rays, it cannot be expected to be resolved or revealed by microscopes. Apparently the thin crystalline deposit towards the cathode side mentioned by Dean seems to be this amorphous deposit.

Hardness — The hardness of electro-deposited alpha manganese in presence of sulphur dioxide with increase in thickness from cathode side has been given in Table 3.I. Hardness values of a number of specimens of electro-deposited alpha and hydrogen removed alpha and transformed gamma at surfaces facing solution and cathode sides and at cross section are given in Table 3.II and the average values are given in Table 3.III.

From Table 3.I and 3.II it is seen that the hardness values do not significantly vary with thickness of the deposit in the case of manganese and the hardness values obtained on the cross-section are almost identical with the values obtained on nodular growths. The hardness values on the surface of the deposit, facing the cathode side, are sometimes found to be higher than the values obtained on cross-section or on nodular growths. These high values on the surface facing cathode are found to be identical with the value of annealed manganese. The high hardness values of electro-deposited metals have been attributed to the small grain size of the electro-deposits²⁷⁻³¹. The high hardness values of the manganese surface facing cathode can be attributed to the fine grain size of the surface, as seen from the absence of any back reflection pattern even after ageing for four years at room temperature. Regarding tarnish resisting brightness of this surface, it is well known that the same plating



1. Alpha manganese in presence of selenium on copper cathode $\times 270$

2. Same as above $\times 450$

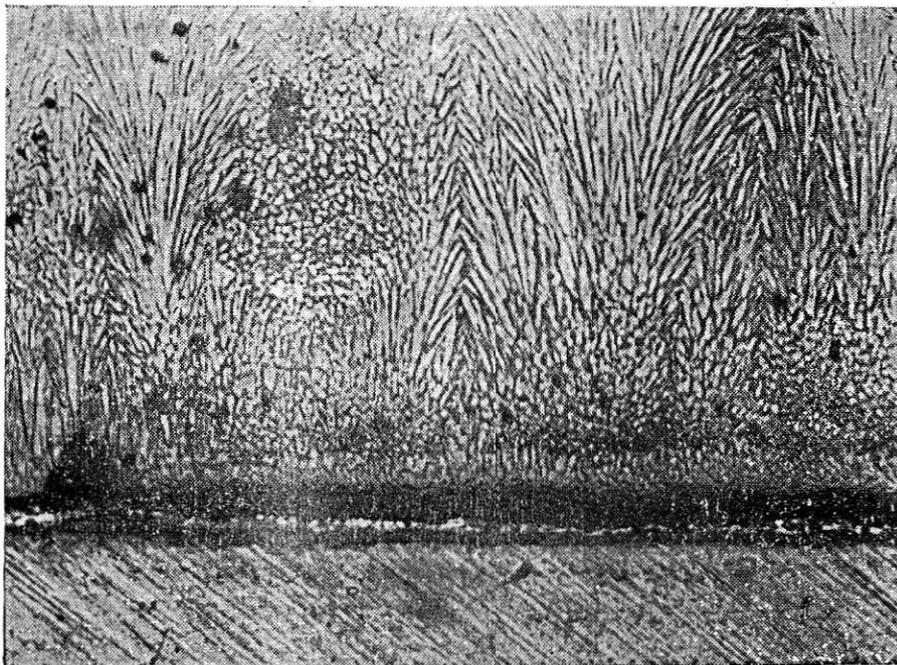
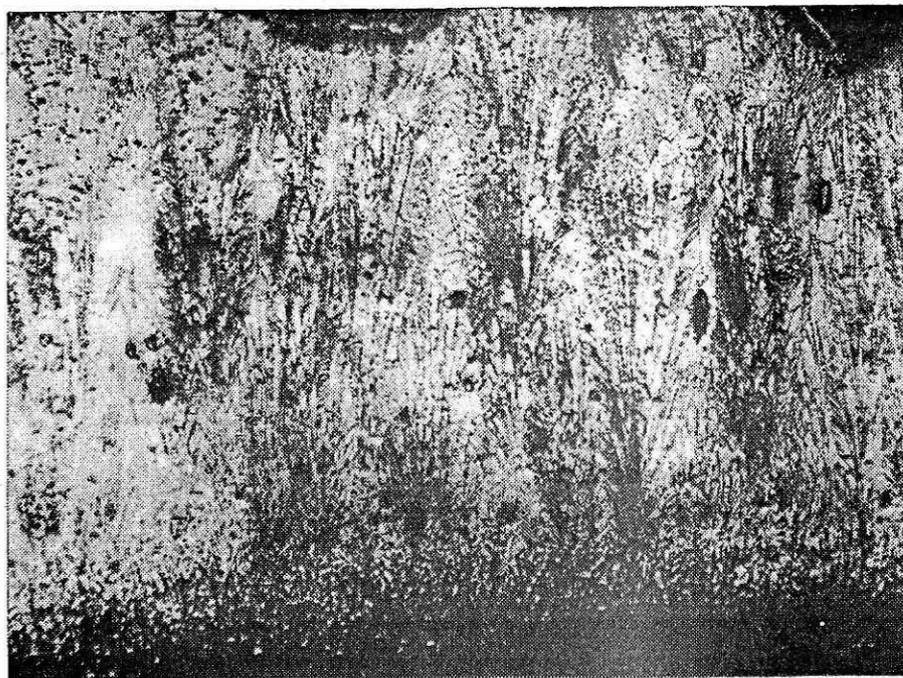


FIG. 3.IX — MICRO-PHOTOGRAPHS OF ALPHA AND GAMMA MANGANESE



3. Pilot plant sample of alpha manganese in presence of sulphur dioxide $\times 55$

4. Gamma manganese on stainless steel cathode $\times 270$

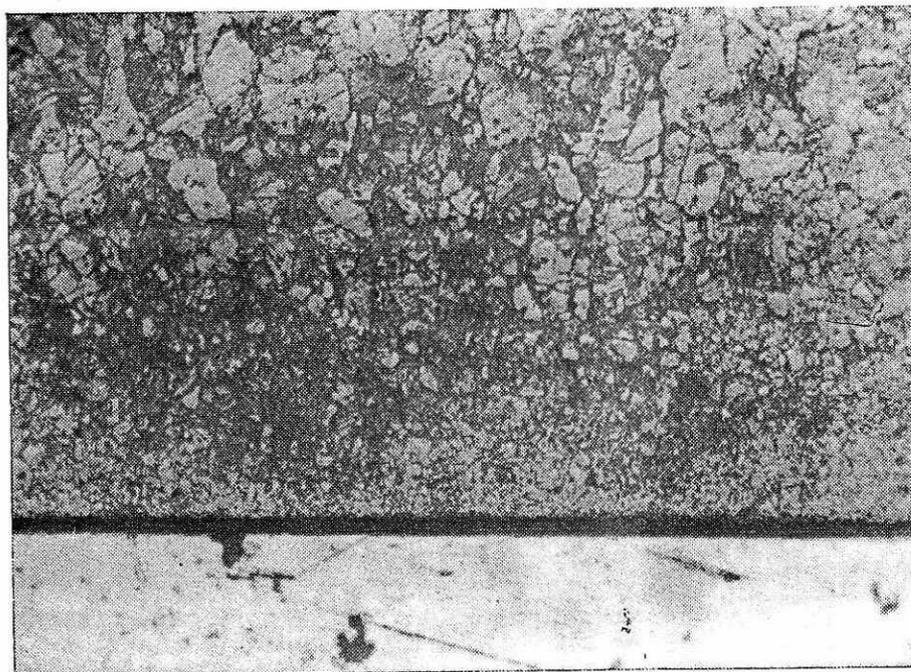
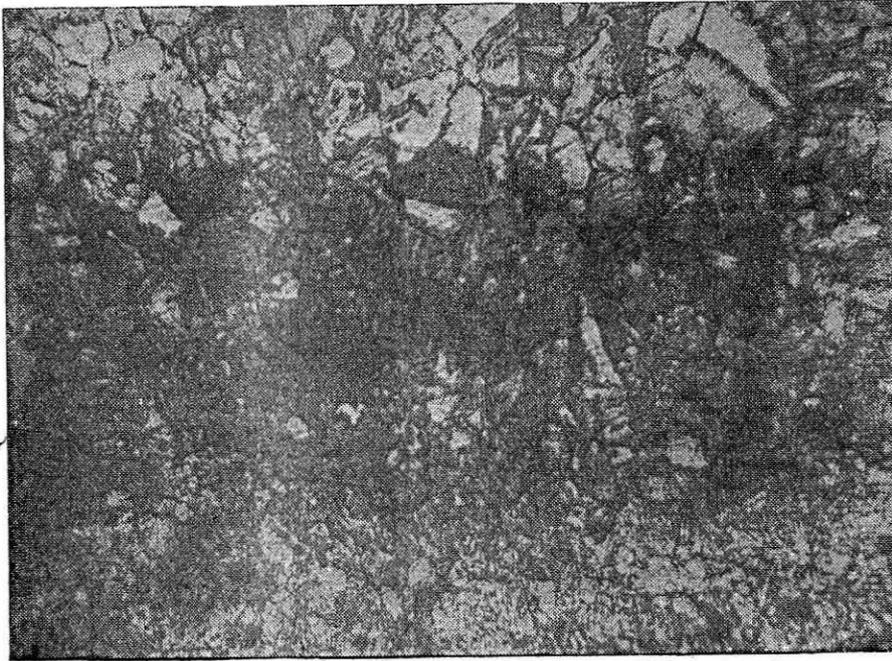


FIG. 3.IX (continued) — MICRO-PHOTOGRAPHS OF ALPHA AND GAMMA MANGANESE



5. Same as Fig. 3.XI (4) on page 67 $\times 360$

6. Gamma manganese on copper cathode $\times 270$

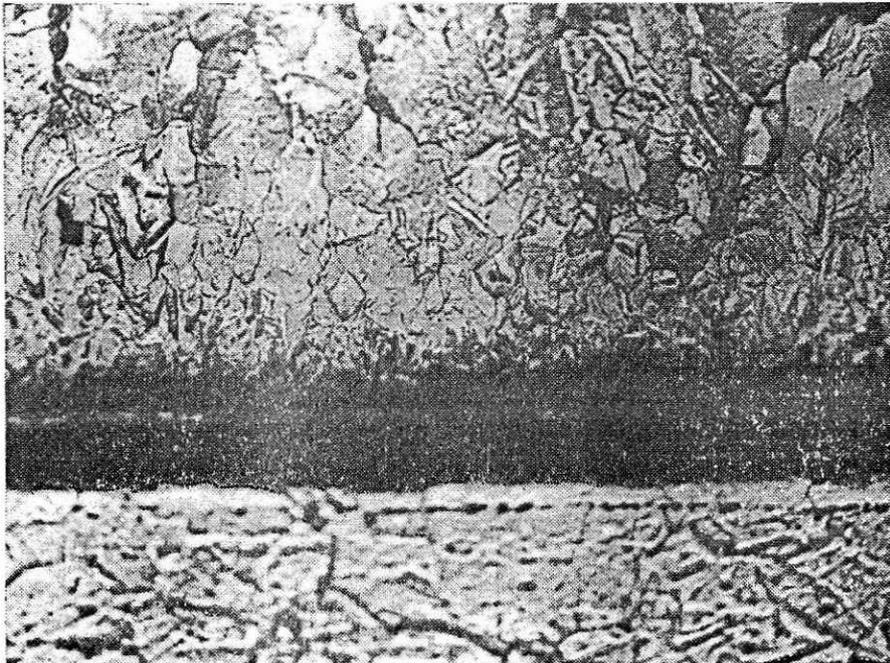


FIG. 3.IX (continued) — MICRO-PHOTOGRAPHS OF ALPHA AND GAMMA MANGANESE

TABLE 3.I—HARDNESS VALUES OF ELECTRO-DEPOSITED ALPHA MANGANESE WITH INCREASE IN THICKNESS FROM CATHODE SIDE TO SOLUTION SIDE

Specimen: Pilot plant alpha manganese; 67 hr run
 GKN Micro-hardness tester
 Load: 100 gm

DPN	DPN
649 Cathode side	698 Cathode side
657	620
592	690
554	690
681	690
673	803
707	665
	665
782	743
847	554
698	634
762	690
743	548 Solution side
743	
657	
715 Solution side	

Remarks— It is seen that no significant variation is found in hardness values with increase in thickness from cathode side to solution side.

conditions, which produce the hardest chromium plate, also produce the brightest plate³². Similarly, in the case of nickel, according to Clark³¹, the only deposits showing the broadening of diffraction rings indicating grain sizes at or below the lower optimum range of diffraction were the bright plates deposited from a nickel cobalt-bath and from a watts-bath plus a sulphonate addition agent. The surfaces facing the cathode material of most of the electro-deposits including gamma manganese are unusually bright. This may be due to the grain size and the orientation of the initial deposit.

With reducible sulphur compounds in the electrolyte, sulphur is adsorbed on the growing borders of the crystals, and initial high concentration of manganese ions in the vicinity of the cathode with selective adsorption of sulphur on the growing border can possibly account for the small crystal size of the initial deposit. Absence of diffraction rings other than broadening of low angle line, tarnish resisting brightness and higher hardness altogether can be attributed to the very small crystal size of the initial deposit.

TABLE 3.II — HARDNESS VALUES IN DPN OF A NUMBER OF SAMPLES OF ELECTRO-DEPOSITED ALPHA AND GAMMA MANGANESE, TRANSFORMED GAMMA MANGANESE AND HYDROGEN REMOVED ALPHA AND HYDROGEN REMOVED, TRANSFORMED GAMMA MANGANESE

	SURFACE FACING SOLUTION			CROSS SECTION			SURFACE FACING CATHODE		
	Mini-mum value	Maxi-mum	Total aver-age	Mini-mum value	Maxi-mum	Total aver-age	Mini-mum value	Maxi-mum	Total aver-age
Electro-deposited alpha	585	813	690	548	847	690	553	975	793
Electro-gamma manganese	65	137	110	86	125	110	92	125	110
Transformed gamma → alpha at room temperature	—	—	—	707	1003	790	707	1048	820
Hydrogen removed alpha	975	1110	1037	915	1076	1005	915	1076	980
Hydrogen removed alpha (transformed gamma)	944	1008	952	—	—	—	944	1110	1030

TABLE 3.III — AVERAGE PROBABLE HARDNESS VALUES IN DPN

SPECIMEN	HARDNESS IN DPN
Electro-deposited alpha manganese	690
Electro-deposited gamma manganese	110
Annealed alpha manganese	1000
Quenched beta manganese	946-1003

Coming back to Dean's conclusions that the fine layer of very crystalline manganese in the micro-structure and the hardness values of the surface indicate that manganese was initially deposited as gamma which has subsequently transformed to alpha, it can be seen from the above discussion that both these characteristics can equally be explained by the extremely fine-grained character of the initial deposit unresolvable by X-rays. According to Schalin⁴, the addition of sulphur dioxide to the electrolyte prevents the formation of gamma manganese and that at the end of 24 hours of deposition of alpha manganese on gamma manganese cathodes, the starting sheets were still flexible enough to be handled without special care.

Bell's⁵ and Moiseev's^{6,7} works also do not support Dean's contention. In her studies on plating of manganese on aluminium, mild steel and copper to a thickness of 0.0005-0.0015", Bell 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 there were no sulphur compounds present in the electrolyte. 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. Presumably, the high current density Bell had employed and the sulphur present in the electrolytic manganese, which was used directly in the anolyte for making up the manganese content, is responsible for the absence of gamma modification in her deposits.

According to Moiseev also, " the deposits of manganese obtained from electrolysis with $pH > 4.0$, regardless of other conditions of electrolysis, as a rule, have a structure of amorphous body "

Substrate influence in deposition of gamma and alpha — In Table 3.IV structure of electro-deposits obtained on copper, stainless steel and aluminium cathodes from pure solutions and on addition of 0.1 gm of sulphur dioxide or selenious acid per litre, under otherwise exactly similar conditions, from 15 minutes to about 7 hours of deposition has been given.

The results clearly indicate that deposits on stainless steel, aluminium and copper from extremely pure solutions of manganese and ammonium sulphate result in gamma modification of manganese while, the addition of 0.05 gm/l of selenium as selenious acid or 0.05 gm/l of sulphur as sulphur dioxide results in alpha modification of manganese on any of these cathodes. In all cases, within 15 minutes of deposition only the lines of alpha or gamma manganese alone were noticed, depending upon the presence or absence of selenious acid or sulphurous acid in the electrolyte. With all other conditions of deposition like current density, pH , temperature, flow of electrolyte and even current efficiency remaining the same, on the same and similarly prepared substrates, gamma and alpha manganese can be prepared. Addition of 0.1 gm/l sulphur dioxide or selenious acid results in the deposition of alpha manganese while in the absence of sulphur or selenium compounds gamma manganese is deposited.

To conclude on the substrate influence, it may be stated that copper has some influence in the first few layers of the deposit, up to about one minute of deposition, possibly forming a solid solution with manganese. Beyond that it is found that the substrate has no directing influence on the structure of the deposit. The presence of reducible sulphur or selenium compounds alone in the electrolyte determine the ultimate structure.

TABLE 3.IV — SUBSTRATE INFLUENCE

Composition of electrolyte: 65-70 gm of manganese sulphate per litre of electrolyte
 135-40 gm of ammonium sulphate per litre of electrolyte
 Initial pH of cell solution and feed electrolyte: 7.3
 Current density: 4.2 amps/sq dm; Temperature of electrolysis: 28-30°C

EXPERI- MENT NO.	CATHODE MATERIAL	ADDITION AGENT GM/LITRE OF ELECTROLYTE	TIME OF DEPOSITION	AVERAGE VOLTAGE	CURRENT EFFICIENCY	STRUCTURE (X-RAY)	REFERENCE TO X-RAY OR MICRO-STRUCTURES
1	Copper	Nil	15 min	—	—	Gamma	—
2	do	Nil	2 hr	5.11	67.35	do	—
3	do	Nil	5 hr	4.95	—	do	Vide Fig. 3.IX (6)
4	do	0.15 gm of SO ₂	15 min	—	—	Alpha	—
5	do	do	2 hr	—	—	do	—
6	do	0.1 gm of H ₂ SeO ₃	15 min	5.7	93.24	do	—
7	do	do	2 hr	4.8	85.39	do	Vide Fig. 3.IX (1 and 2)
8	Stainless Steel	Nil	15 min	6.1	—	Gamma	—
9	do	Nil	3 hr	5.24	73.72	do	Vide Fig. 3.IX (4 and 5)
10	do	Nil	7 hr	5.1	55.62	do	—
11	do	0.1 gm of SO ₂	15 min	6.3	—	Alpha	Vide Fig. 3.VI (5)
12	do	do	7 hr	5.5	63.75	do	—
13	do	0.1 gm of H ₂ SeO ₃	15 min	—	—	do	—
14	do	do	2 hr	—	—	do	—
15	Aluminium	Nil	15 min	5.7	—	Gamma	—
16	do	Nil	1 hr	5.3	—	do	—
17	do	0.1 gm of H ₂ SeO ₃	1 hr	—	86.62	Alpha	—

Remarks — This table indicates that, with all other conditions of deposition remaining the same, alpha and gamma manganese can be electro-deposited on cathodes of copper, stainless steel or aluminium, depending upon the presence or absence of SO₂ or selenious acid in the electrolyte.

It is interesting to mention that the deposit on stainless steel with selenious acid as an addition agent, even after one minute of deposition, gives clear diffraction lines of alpha manganese, while in its absence gamma manganese is only obtained as seen earlier.

Deposition of alpha over gamma manganese and vice versa — Having seen that the presence of reducible sulphur or selenium compounds alone in the electrolyte determine the ultimate structure, it would now be interesting to examine the structure of the deposit obtained on alpha and gamma manganese cathodes in the presence and absence of these compounds.

The results of the experiments on deposition of gamma over alpha and vice versa have been summarized in Table 3.V. It is seen that gamma manganese over alpha manganese and alpha manganese over gamma manganese can be deposited depending upon the absence or presence of reducible sulphur or selenium compounds in the electrolyte. Whether the alpha manganese cathode is prepared by transformation of deposited gamma manganese at room temperature by passage of time, or by deposition in presence of sulphur or selenium in the electrolyte, the deposits obtained on these cathodes from pure solutions in absence of any of these addition agents are of gamma modification. Similarly, alpha manganese is obtained on gamma manganese cathodes in presence of sulphur or selenium compounds in the electrolyte.

It is interesting to mention some of the observations made during deposition of gamma over alpha and vice versa.

1. Gamma manganese deposited on alpha manganese cathodes could be stripped off separately as seen from Fig. 3.X.

On stripping off the gamma manganese from the alpha manganese, the alpha manganese cathode looked more bright and lustrous than before introduction in the bath.

2. Alpha manganese with sulphur or selenium deposited over gamma manganese could not be stripped separately. On stripping from the basis metal, both deposits came together in pieces showing that there was considerable adherence between the two deposits.
3. Gamma manganese deposited over gamma is coherent similarly as alpha manganese deposited over alpha manganese.
4. On etching the cold mounted specimens of gamma deposit over alpha for micro-examination, the continuity between gamma and alpha is blurred as seen from Fig. 3.XI (1 and 2).
5. On etching the specimen of alpha over gamma, the continuity between alpha and gamma is observed as seen from Fig. 3.XI (3 and 4).

6. On back reflection X-ray examination of alpha deposit with selenium on 10 minutes of deposition over gamma deposit shows diffraction lines of alpha and gamma.
7. On back reflection X-ray examination of the deposit from pure solutions, at 10 minutes of deposition over alpha, shows diffraction lines of alpha manganese only.

On powder pattern, along with alpha manganese diffraction lines, broadened diffused line at 'd' value 2.10 \AA is observed.

8. The current efficiency of deposition of gamma manganese over alpha manganese is much less than that of gamma over gamma or on stainless steel cathodes.
9. Immediately on introduction of gamma manganese cathode for deposition from pure solutions, the hydrogen evolution was seen exactly similar as towards the end in the deposition of gamma manganese used as the cathodes.
10. On introduction of gamma manganese cathode for deposition from solutions containing sulphur dioxide, for the first five seconds the hydrogen evolution was almost similar as towards the end in the case of gamma deposit, but soon changed over to few but larger bubbles of hydrogen, as is usually seen in presence of sulphur dioxide in alpha deposition, than the small bubbles of hydrogen seen in gamma deposition.

These experimental results and observations indicate that while the deposition of alpha manganese and gamma manganese over gamma manganese is initiated smoothly, the deposition of gamma manganese over alpha manganese is preceded by an amorphous deposit. Absence of back reflection lines of gamma on 10 minutes of deposition, the broadened diffused line in the powder pattern, the lower current efficiency of deposition of gamma over alpha, the easier stripping of gamma over alpha, the blurred characteristics in the continuity in the microphotographs and the bright lustrous character of the alpha cathode substrate after stripping of gamma manganese definitely indicate the amorphous structure preceding the gamma deposition.

The deposition of this amorphous nature of deposit in the initial period and its low hydrogen over-voltage, as mentioned earlier, make the initiation of gamma deposition over alpha rather difficult and the efficiency of deposition falls down. But after 10-15 minutes of deposition when gamma manganese begins to build up, the hydrogen evolution near the cathode gets normalized and the efficiency of deposition increases.

The difficulties in the initiation of gamma manganese on transformed gamma \rightarrow alpha manganese substrates than on a stainless steel cathode

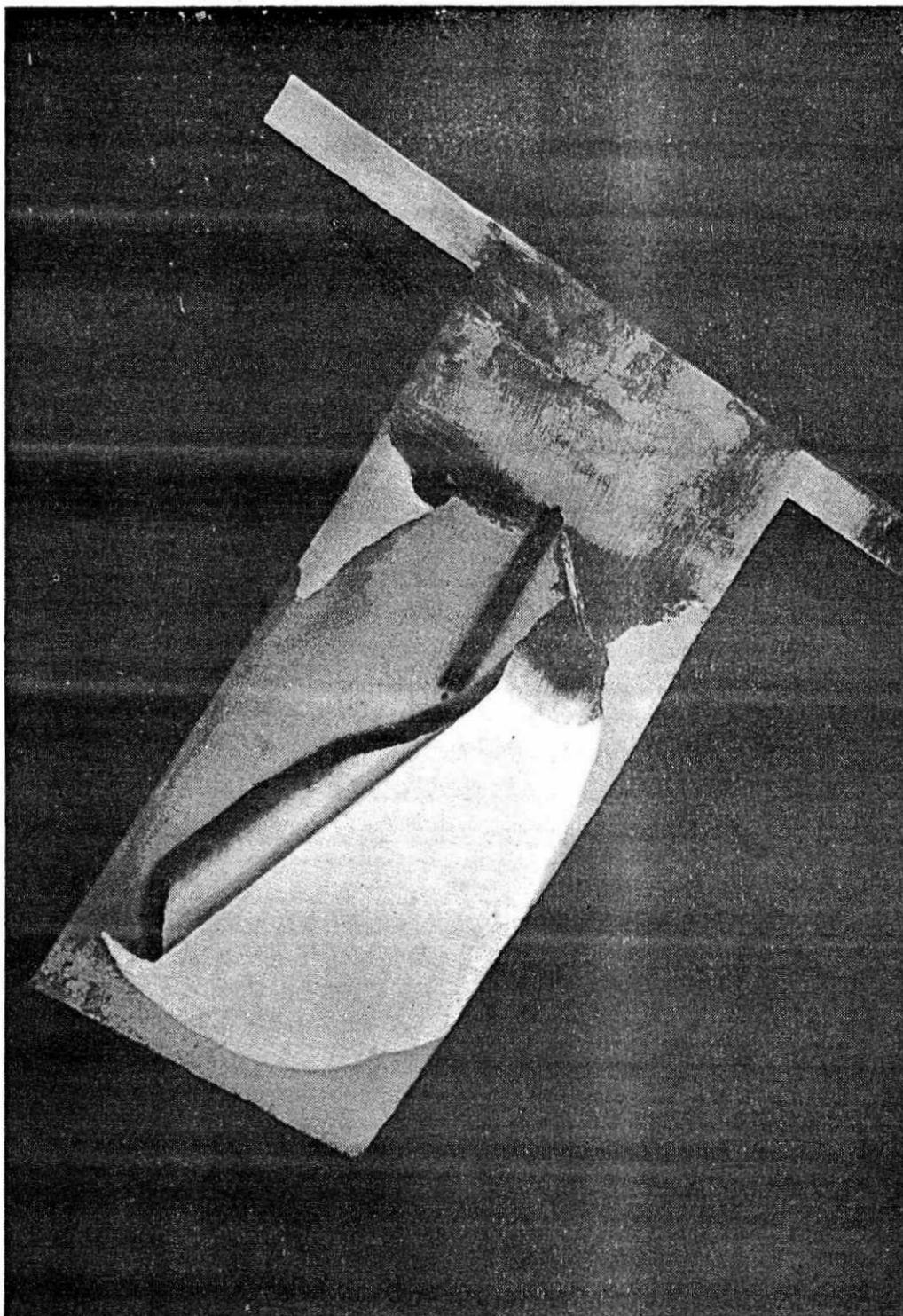
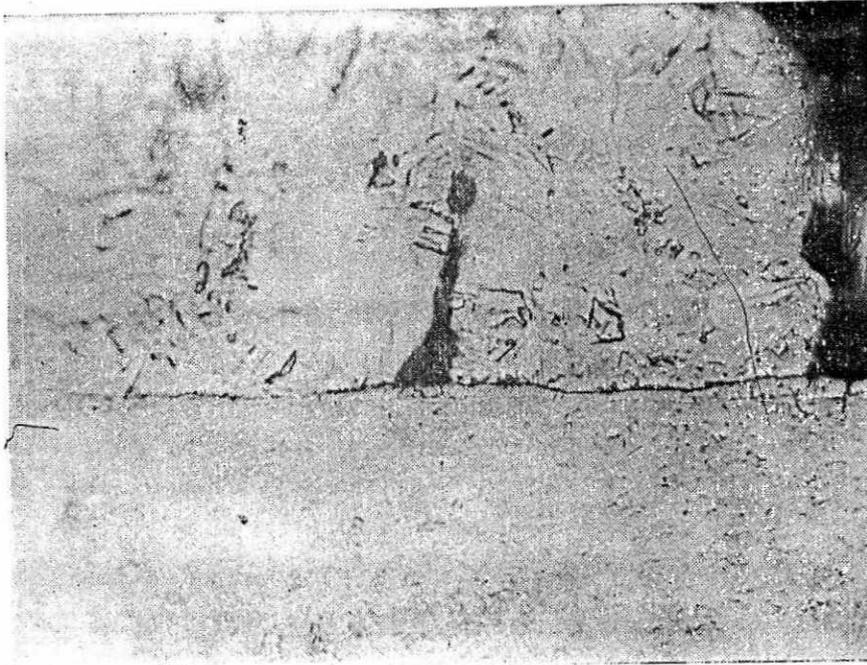


FIG. 3.X — STRIPPING OFF GAMMA MANGANESE DEPOSITED OVER TRANSFORMED ALPHA MANGANESE ON A STAINLESS STEEL CATHODE



1. Gamma manganese over alpha manganese $\times 450$

2. Same as above to show the blurred discontinuity $\times 450$

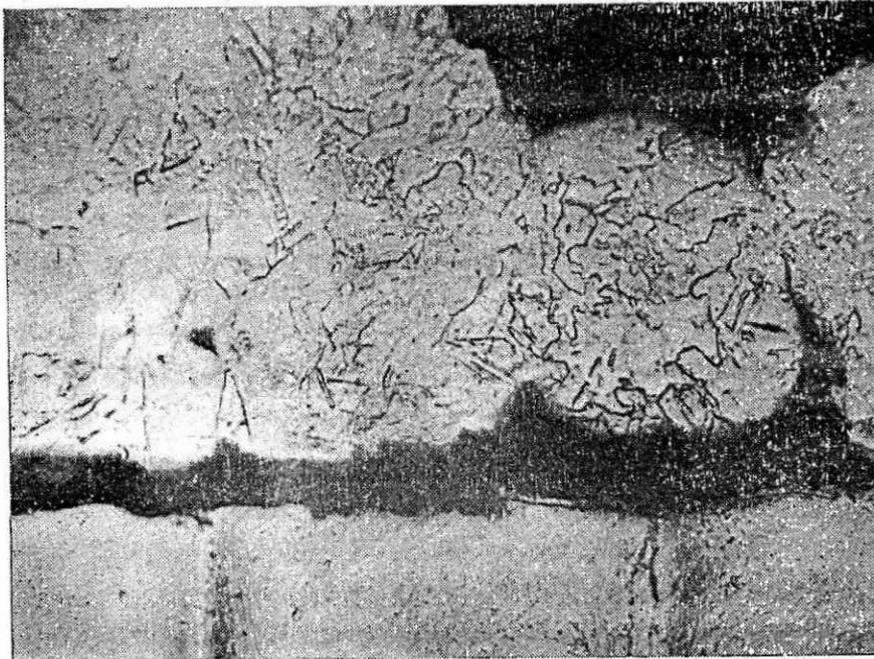
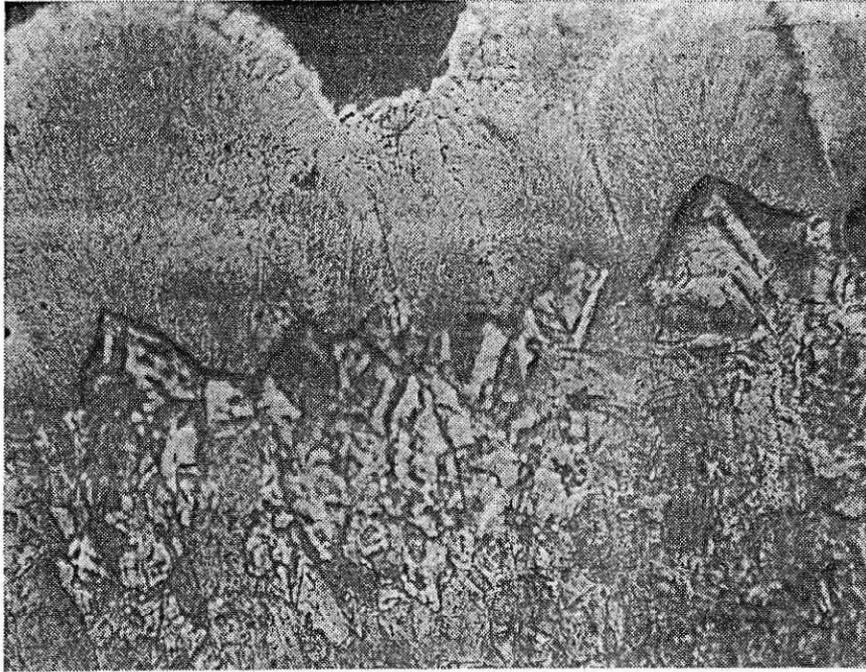


FIG. 3.XI — MICRO-PHOTOGRAPHS OF GAMMA MANGANESE DEPOSITED OVER ALPHA MANGANESE AND VICE VERSA



3. Alpha manganese over gamma $\times 450$

4. Same as above $\times 450$

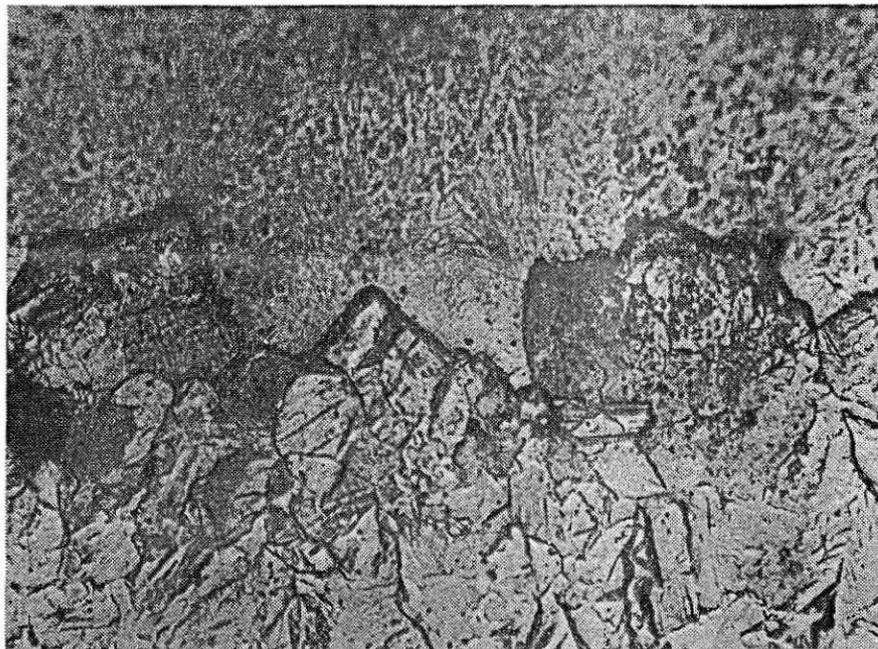


FIG. 3.XI (continued) — MICRO-PHOTOGRAPHS OF GAMMA MANGANESE DEPOSITED OVER ALPHA MANGANESE AND VICE VERSA

may presumably be due to the low hydrogen over-voltage of pure alpha manganese, as is seen from the large hydrogen evolution during the initial period of deposition. The current efficiency on one hour of deposition of gamma manganese on transformed alpha manganese cathode was also definitely less than that on stainless steel or copper indicating the difficulties for initiation of deposition on transformed alpha manganese cathodes.

Dean³ has remarked that "under conditions, where even the small amount of sulphur for gamma \rightarrow alpha transition during plating is objectionable, the possibility of plating on gamma manganese cathodes, which have been transformed to alpha on the surface by mechanical work, is interesting. On such cathodes manganese is plated directly as alpha without the formation of an initial layer of gamma". This could not be substantiated in this work. If it were possible to plate alpha manganese from pure solutions of manganese and ammonium sulphate on gamma manganese that has been transformed to alpha, it would be really very interesting for, then, it means that pure alpha manganese can be electro-deposited without the presence of sulphur or selenium, but depending on the substrate. In this investigation, deposition from pure solutions in absence of sulphur or selenium on gamma manganese cathode, that has been transformed to alpha, resulted only in gamma deposition, though initially for the first ten minutes of deposition, the deposit did not give any crystalline X-ray pattern.

According to Gamali², also "gamma manganese is deposited from pure solutions with a total current efficiency of 10 per cent on deposits of alpha manganese obtained from solutions containing SO_2 or H_2SeO_3 , while the current efficiency of alpha manganese during its deposition from solutions containing SO_2 or H_2SeO_3 on gamma manganese obtained from pure solution is 65 and 90 per cent, respectively". Gamali explains the difficulty in the initiation of deposition of gamma manganese and the low current efficiency of gamma deposition over alpha manganese on the disparity of the parameters of the crystalline lattices of the metal base and gamma manganese. If it were based only on the disparity of the parameters, why is it that alpha manganese is not obtained from pure solutions on alpha manganese cathodes, but only gamma manganese is obtained.

Conclusions

It is found that a flash layer of amorphous manganese is deposited from pure solutions, fitting in or resembling that of alpha manganese, over which gamma manganese begins to build up in absence of reducible sulphur or selenium compounds. In presence of sulphur dioxide, the

amorphous nature continues to build up to an increasing thickness over which crystalline pattern of alpha manganese is obtained. With selenious acid, crystalline alpha manganese is obtained within one minute of deposition.

No evidence for initial deposition of gamma manganese which subsequently transforms to alpha was found from X-ray studies of deposits obtained in presence of sulphur dioxide, though in its absence gamma manganese lines were distinguishingly clear.

Gamma manganese can be deposited on alpha manganese and vice versa depending upon the absence or presence of reducible sulphur or selenium compounds in the electrolyte. Substrate has a directing influence only in the first few atomic layers of the deposit and beyond that presence of reducible sulphur or selenium compounds in the electrolyte alone determines the ultimate structure of the deposit.

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