CHAPTER VI

Hardness, lattice parameter variation, hydrogen content and its location in electro-deposited metals with particular reference to manganese

The hardness of electro-deposited metals, hydrogen in metals, lattice parameter variation with hydrogen content and the location of hydrogen in electro-deposited metals have been discussed with particular reference to manganese. Unlike other electro-deposited metals, electro-deposited alpha manganese has a hardness value lower than that of its annealed state. The highest broadening observed in X-ray powder patterns of transformed gamma has been attributed to the volume change associated with the transformation of gamma to alpha manganese and the resultant stress. It is discussed that all the hydrogen in electro-deposited alpha manganese cannot be in interstitial position and that a part of the hydrogen goes inside the lattice and the rest are adsorbed upon the crystallite surfaces. The low hardness value of electro-deposited alpha manganese compared to its annealed state and its low density suggest the possibility that a part of the discharged hydrogen ions assuming positions inside lattice or forming complex during the formation of alpha manganese.

Introduction

Electro-deposited metals usually possess hardness values considerably greater than those of fully annealed metals and frequently greater than those obtainable for the same metals by work hardening[1]. In the early days many investigators have connected the increase in hardness of electro-deposits with the absorption of hydrogen but later experimental results have shown that hydrogen appears to have little effect on the hardness of deposited metals although it may seriously affect the ductility of the metals[1,2,3]. To substantiate the same, it was shown that in the electro-deposits of iron, nickel, cobalt and chromium, when the deposits were raised to successively higher temperatures, the hydrogen was almost completely driven out, before the hardness values began to fall down[5]. When electrolytic iron was allowed to stand, the hydrogen content and embrittlement diminished but not the hardness[5].

The extreme hardness of the electro-deposited metals may be due to the combination of several factors some of which are small grain size, preferred orientation, presence of stress in the crystals and the inclusions of dispersed foreign substances distributed throughout the lattice similar to the mechanism of age hardening of alloys[1]. Macnaughton[6] and Hothersall[7] have expressed the view that the hardness of the electro-deposits is connected with their grain size, the finer the grain size, the greater the hardness. Electrolytic iron, deposited at room temperature, exhibits a structure too fine to be resolved by the microscope and is very hard[8]. Arkharov[9] has explained the hardness by a mutual work hardening of the crystallites, the effect of which is determined by the grain size of the deposit. Because the grain size is very fine, the grain boundaries block the slip planes along which deformation of the crystals would occur.

Hydrogen in metals

Hydrogen is reported to occur as an atomic or ionic interstitial solute element, as trapped molecular gas in holes, rifts, voids or lattice imperfections or other spatial defects; or as a chemical compound, usually a hydride[10]. Though considerable work has been done, unfortunately no method has yet been established to determine the mode of occurrence. Nor a standard method has been established at present for the separate determination of the amount of dissolved hydrogen and of the amount of hydrogen present as a chemical compound[11].

Metals are classified mainly into four groups on the basis of their combination with hydrogen[12]. The first group of metals, viz nickel, iron, cobalt, chromium, copper, aluminium, silver, molybdenum and platinum, form with hydrogen true endothermic interstitial solid solutions. The fact that the solubility of hydrogen in these metals increases with increase in temperature and varies linearly with the square root of pressure, has been interpreted as indicative of forming true solid solutions, hydrogen being inside the lattice as an interstitial solute atom or proton[13]. Among this group, nickel takes up maximum hydrogen, about 1·70 cc per 100 gm at 200°C, and 43·1 cc at 1600°C (ref 12).

The second group of metals, viz titanium, vanadium, zirconium, columbium, lanthanum, cerium, tantalum, thorium, and palladium (Groups IVA, VA, rare earths and actinides), form with hydrogen exothermic metal like hydrides (Pseudo-hydrides)[12]. In this group, the amount of gas absorbed by the metal decreases with increase in temperature although the solubility varies with the square root of pressure for certain ranges of values of pressure. The pick up of hydrogen by these metals is very great and is about 10^3-10^4 times that of the earlier group, the maximum being titanium with 407400 cc per 100 gm and lowest being tantalum with 4600 cc, both at 20°C. In this group, the density of the saturated solution is uniformly less than that of the metal. They correspond to hydrides of the composition MH_r where M is the metal, H hydrogen and r is not an integer and varies from 1·75 with titanium to 3·70 with thorium. Because solubility varies with square root of pressure in this group also, it has been interpreted that hydrogen enters the lattice as atoms or protons[12].

The other two groups are (1) alkali and alkaline earth metals which form salt like hydrides, with hydrogen as the negative ion and analogous to corresponding halides, and (2) metals of group IVB, VB & VIB which form covalent hydrides, such as H_2S, AsH_3 and SiH_4. These two groups do not concern much in this context.

The solubility of hydrogen in alpha manganese decreases with increasing temperature up to 500°C[14,15], ie manganese behaves up to 500°C as in the exothermic group. Above 500°C, the solubility of hydrogen in manganese increases with rise in temperature and behaves as an endothermic metal. The solubility of hydrogen in manganese is neither as low as in the first group nor as high as in the second group, and is about 21·6 cc per 100 gm at 24°C (ref 15). A comparative idea on the absolute solubility of hydrogen in manganese and nickel can be seen from Fig. 6.I. The solubility of hydrogen varies linearly with pressure in manganese also. Though manganese seems to lie in the border line of the two groups, it has been generally considered as an endothermic metal[12].

Location of hydrogen — With regard to the distribution of hydrogen, when occluded either during electrolytic deposition or cathodic charging or surcharging by gaseous hydrogen, there exist divergent opinions and evidences of several kinds[8,16-49].

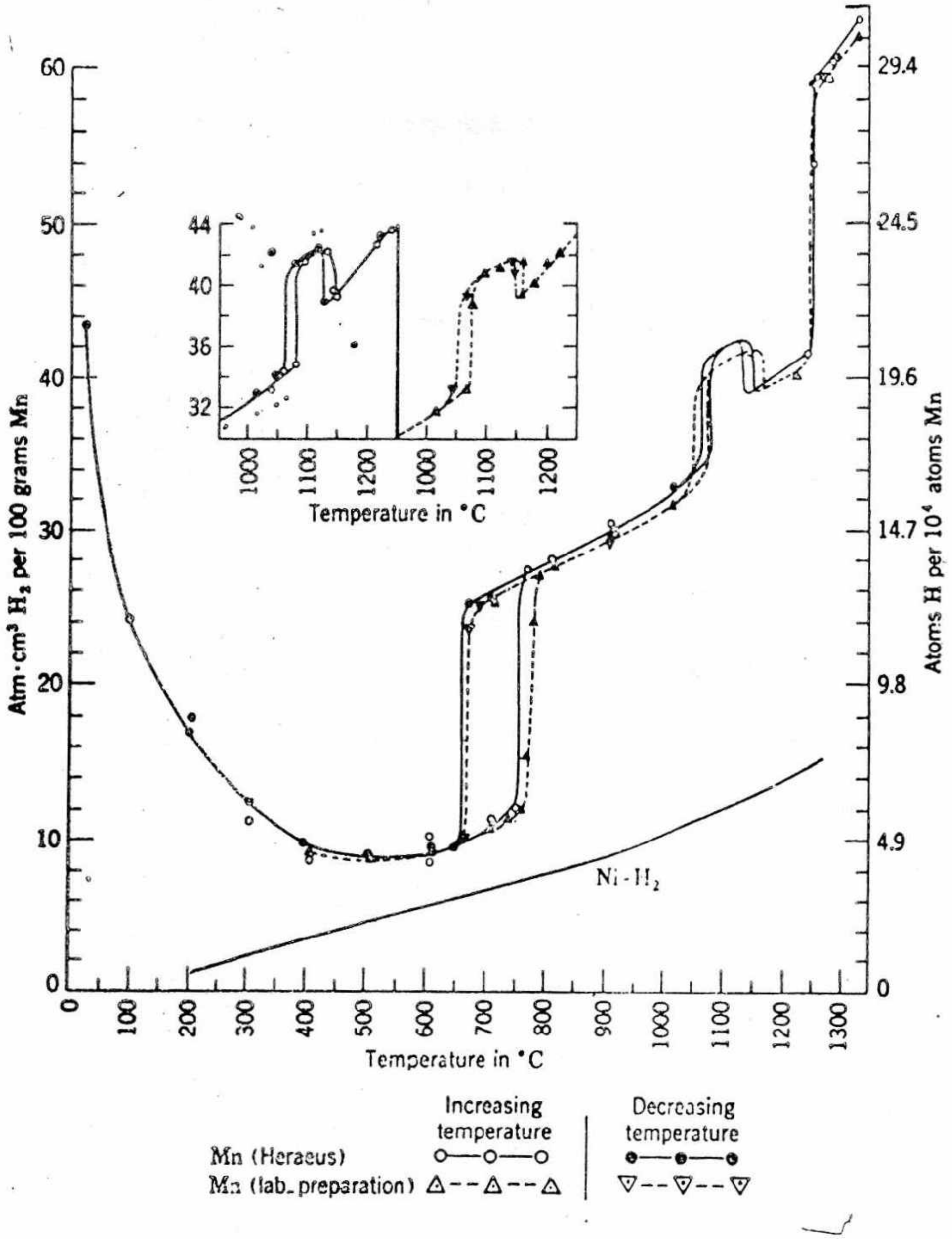

FIG. 6.1 — ABSORPTION OF HYDROGEN BY MANGANESE WITH TEMPERATURE
(*After Sieverts and Moritz*[14])

Displacement of X-ray diffraction lines in the electro-deposits of iron and nickel from solutions containing hydrogen sulphide or arsenic[19,20] and that of chromium from chromic acid bath[22-24] and the appearance of hexagonal close packed modifications in electro-deposited nickel[16] similar to that of sputtered film of nickel in hydrogen[21] and appearance of CPH[17] and FCC[18] modifications in chromium similar to chromium hydrides have all been interpreted as indicative of hydrogen remaining in interstitial positions in the deposited metal. This interpretation has been questioned by other investigators on the grounds that the expansion in the lattice constants of most of these metals were within the usual limits of error of the X-ray methods and that no displacement other than a marked broadening of the diffraction lines[27] occurs in nickel[28], or in iron other than from solutions containing arsenic[27] and the interstitial spaces in BCC chromium are not enough to accommodate 700 cc per 100 gm of hydrogen[22] and that the complete removal of hydrogen by cold bombardment method[30] or at a lower temperature[22,51] do not alter the hardness, lattice parameter or diffuseness of the lines. Most of the workers agree to one ~~point~~[8,31] that the deposited metal produces broadening of diffraction lines rather than any significant expansion of the lattice and the broadening of the lines have been mainly interpreted[32-35] as due to (a) small grain or crystallite size, and (b) plastic deformation. Wood[28,31] interpreted the broadening of the diffraction lines as due to the division of the lattice into minute " crystallites " ranging in the order of magnitude from 10^{-5} cm for softer deposits to 10^{-6} cm for the hardest and concluded that the hydrogen is not contained in full within these crystallites but is adsorbed upon their surfaces.

On the other hand, some investigators have regarded these systems as hydrides, which are unstable at normal conditions. Among the endothermic group too electrolytically charged or electro-deposited metals like nickel, chromium, etc, containing hydrogen, have been called as hydrides. Simons and Ham[46] have recorded their belief that the solution and diffusion of gases through metals could be considered purely as a chemical phenomena. It was claimed that the specific nature of the solubility of gases in metals indicates that the gases are present mainly as compounds with the metal. Since the rate of diffusion of a gas through a metal is inversely proportional to the thickness of the metal, it was felt that the adsorbed film of gas, usually postulated in diffusion processes, could not be related to the empirical results. For this and other reasons, diffusion was treated as a case of chemical equilibrium between the metal and the gas. It is interesting to note similarly that nitrogen is soluble only in those metals which are capable of forming nitrides[13].

The hydrogen atoms are not reported to replace the metal atoms in the lattice but may combine to form complexes with the metal atoms known as ' pseudo-atoms '. These complexes may either take their places in the metal lattice without altering its symmetry or may perhaps form new lattices[8]. Except Barrer, most authors regard the interstitial hydrogen dissolved in a metal to be substantially ionized[8].

According to Vagramyan[2], the absorbed hydrogen in electro-deposit, in part, combines into molecules and leaves the surface and in part enters the crystal lattice of the metal, ' assuming positions originally occupied by metal atoms or positions between them and forming solid solutions '. As mentioned earlier, the solubility of hydrogen in metal in the course of electro-deposition, as per Vagramyan, may also result from the direct inclusion of a hydrogen ion into the lattice in the form of a proton as distinct from the inclusion of adsorbed atoms. In acid solutions it is the hydrogen ion which is reduced while, in alkaline solutions, it is the water molecule.

$$H^+ + M \text{ (Metal)} + e^- = MH$$
$$H_2O + e^- = OH^- + H_{ads}$$

The probability of hydrogen entering the deposit according to Vagramyan, is therefore greater in acid solutions than in alkaline solutions because of the possibility of the proton inclusion.

Diffusion — The adsorbed hydrogen atoms can diffuse through (a) the interstices of the lattice structure, (b) grain boundaries, and (c) structural imperfections within grains. There are divergent viewpoints in these also[47]. Edward's experiments[48] showing that ' no difference could be detected between the rate at which hydrogen diffuses through a single crystal of iron and through the same material after it had been recrystallized into a mass of small crystals ' has been viewed, as in general, diffusion occurs through the crystal lattice and not along grain boundaries. Andrew's and others' observations[37,38], that cold work decreases the rate of hydrogen diffusion and increases the saturation of hydrogen, show that cold work has an effect on the diffusion of hydrogen. Fast[41] thinks that the surface effect and not the diffusion itself is frequently the deciding factor in the diffusion velocity. However, when there is solubility of hydrogen in the metal, it can be concluded that hydrogen can diffuse through the metal whether it is through grain boundaries or through lattice.

Hydrogen in electro-deposited manganese — Manganese, which has a normal solubility of 21·6 cc per 100 gm at 24°C ($MnH_{0\cdot001}$), ie one atom of hydrogen for 10^3 atoms of manganese, takes up 250-580 cc ($MnH_{0\cdot012}$-$MnH_{0\cdot028}$), ie one atom of hydrogen for 80-35 atoms of manganese. Manganese super-saturated by cathodic hydrogen has been reported[4] to give a hydride having a formula $MnH_{0\cdot020}$, about 400 cc per 100 gm of metal. Electro-deposited alpha manganese has a density of 7·42-7·43, while that of degassed manganese is 7·48 (ref 50).

Both Potter[51] and Moissev[52] agree that the hydrogen in electrolytic manganese produces an expansion of the lattice and most of the hydrogen can be removed by heating the specimen at 300°C in a vacuum of 10^{-3} mm of mercury. Both give the value of the normal parameter at 8·894 Å. But the expansion data as given by Potter and Moiseev do not agree; while Potter says that substantially all hydrogen can be removed at 300°C without significantly altering the parameter, Moiseev says that the normal value of 8·894 is obtained by heating it at 300°C.

Moiseev's data indicate that the normal parameter value of 8·894 Å is reached by heating the deposited manganese at 300°C when, according to him, the deposit still contains 150 and 277 cc of hydrogen per 100 gm. This does not seem to be consistent with the statement that hydrogen produces an expansion of the lattice (vide data in Table 6.I). According to Potter[51], degassing the metal at 300°C has virtually no effect on its lattices probably because the mobility of the atoms at this temperature is too low to permit any appreciable readjustment of the lattice in the time required for removing the gas. As per Potter the X-ray pattern of 300°C degassed electrolytic manganese cannot be distinguished from the untreated metal, showing that the metal was essentially the same even though the gas has been removed.

According to Potter[51], the broadening of lines in the X-ray patterns was highest at 95 cc per 100 gm of metal, and decreased with increasing gas content up to the observed maximum gas content of 615 cc per 100 gm of metal. Potter explains this behaviour that as the hydrogen is increased, the metal is getting saturated with gas and there should be an integral number of atoms of gas in each unit cell of manganese, when the line width approaches the value of vacuum distilled or annealed manganese. As per Potter, the value would be normal at some value of gas content near 615 cc. If each unit cell of alpha manganese absorbs two atoms of hydrogen, then it would require 695 cc of hydrogen per 100 gm of manganese to saturate the metal and only about 90 per cent of the unit cells in the sample containing 615 cc of hydrogen per 100 gm of metal would be saturated. The remaining 10 per cent of the unit cells would be distorted various amounts and cause the diffraction lines to be wider. Potter concludes that the unit cells of electrolytic alpha manganese take two rather than one atom of hydrogen because, if the latter was true, the unit cells could be uniform with about 350 cc of gas per 100 gm of metal and the observed diffraction patterns show no evidence to support the latter.

Experimental results and discussion

The hardness of electro-deposited and annealed electrolytic manganese are given in Tables 3.I-3.III of Chapter III. Like in many other properties, manganese behaves differently with its neighbours, viz Cr, Fe and Ni, in this also. While the electro-deposited Cr, Fe or Ni shows high hardness values compared to their annealed states, electro-deposited manganese does not behave so, and shows a low hardness value compared to its annealed state.

TABLE 6.I — HYDROGEN CONTENT AND LATTICE PARAMETER OF ELECTRO-DEPOSITED MANGANESE

Potter and Huber[51]				Moiseev and Popova[52]			
Nature of manganese	Hydrogen content cc/100 gm	Parameter Å	After heating at 300° Å	Nature of manganese	Hydrogen liberated cc/100 gm	Hydrogen remaining cc/100 gm	Parameter after heating Å
Vacuum distilled manganese	—	8·8948	—	Electrolytic Mn produced at high CD and heated at 125°C	350	220	8·967
Transformed gamma to alpha	95 ± 13	8·898	—	at 300°C	420	150	8·894
Regular electrolytic Mn	250 ± 25	8·904	8·902	Electrolytic Mn produced at high CD in presence of glycerol heated at 125°C	350	420	8·978
Electrolytic Mn with high hydrogen content	615 ± 50	8·910	—	at 300°C	500	277	8·894

TABLE 6.II — HARDNESS VALUES IN DPN OF MANGANESE

Nature of manganese	As found in the course of this work, vide Tables 3.I-3.III of Chapter III	Dean[50]	Bell[55]	O'Neill[54]	Sanzharovski[59]	Hadfield[53]
Electrolytic alpha manganese	690	1170 (Rockwell c-71)	550-725	—	1000	—
Electrolytic gamma manganese	110	240 (Rockwell c-23)	—	100 (By extrapolation from quenched alloys)	—	—
Annealed electro-deposited alpha	1000	—	—	950	—	—
Vacuum distilled alpha	—	—	—	1042	—	650 (550 Br)

Hardness of manganese, as found by various investigators, differ widely. Those values are given in Table 6.II in diamond pyramid hardness numbers (kg/sq mm) along with values as determined in the course of this investigation. The only value of hardness of pure manganese, found in literatures[53], other than that of electro-deposited, is that of vacuum distilled manganese prepared by Marie Gayler and Rosenhain. Hadfield[53] mentions the hardness of the pure metal to be 550 Brinell while later studies by O'Neill[54] of Marie Gayler's specimen (impurities less than 0·01 per cent) has shown the value to be 1042 VPN. O'Neill[54] further says that the micro-structure of Gayler's specimen was not homogeneous and it may have contained some beta phase.

However, the value of 690 DPN for electro-deposited alpha manganese, as found in the course of this work, agrees with that of Bell's[55] figures 550-725 DPN. Heating this manganese in vacuum at 500°C expels most of the hydrogen when the hardness values are found to be 1000 DPN in agreement with the value of 950 DPN as given by O'Neill The electro-deposited manganese does contain slight occlusions of manganese hydroxide and heating the same to 500°C even in vacuum may result in the formation of manganese oxide. It is not known whether the high hardness of annealed electro-deposited manganese is because of fine dispersion of manganese oxide and/or sulphide.

It is felt that the value of annealed alpha manganese should be in the range of 950-1000 DPN for the reason that annealed transformed gamma manganese, which contains no sulphur, also gives hardness values of about 1000 DPN. If 950-1000 DPN is taken as the standard hardness value of pure manganese, then electro-deposited alpha manganese shows a low value. One thing can definitely be concluded that the hardness of electro-deposited manganese is not higher than that of annealed manganese contrary to what has been found in the case of Cr, Fe, Ni and many other electro-deposited metals.

Lattice parameter variation, hydrogen content and its location — In Fig. 6.II, the X-ray patterns of the following deposits have been given:

1. Electro-deposited transformed gamma→alpha manganese-ground to —250 mesh and then annealed at 500°C.
2. Same specimen-annealed and then ground to —250 mesh.
3. Transformed gamma on stainless steel cathode (42 cc of hydrogen per 100 gm) — ground to —250 mesh.
4. Transformed gamma on copper cathode (70 cc of hydrogen per 100 gm) — ground to —250 mesh.
5. Alpha manganese after standing at room temperature for one year (224 cc of hydrogen per 100 gm) — ground to —250 mesh.
6. Alpha manganese with selenium (343 cc of hydrogen per 100 gm) — ground to —250 mesh.

The deposits containing 550 cc/100 gm and above of hydrogen obtained in this investigation were amorphous. The patterns in Fig. 6.II confirm Potter's findings that the broadening of the lines was highest with transformed gamma manganese. Gamma manganese contains much less hydrogen compared to alpha manganese as seen earlier. Potter explains the highest broadening in the X-ray pattern of transformed gamma manganese because of an uneven distribution of hydrogen ~~in~~ the unit cell of alpha manganese so formed. Taking the value of Potter of 95 cc per 100 gm (instead of the value of 42-70 cc per 100 gm as found in this investigation), on the same basis of calculation as per Potter, it comes to 27 atoms of hydrogen per 100 unit cells of alpha manganese, corresponding to $MnH_{0.005}$. And, if each unit cell takes up two rather than one atom of hydrogen, as per Potter, should this variation be attributed to the highest line broadening. On the other hand, it is felt that the highest broadening observed with transformed gamma manganese should be attributed to the volume change associated with the transformation of gamma to alpha and the resultant stress. Phase changes in metals and alloys show effect of such transformational stresses[57]. In the case of transformation in electro-deposited chromium, which is also accompanied by a large volume change, such broadening of lines are observed. nSavely[18] suggests that "micro-fissures" are formed during the volume change and the hydrogen, which has a very low solubility in chromium lattice, is occluded in the fissures. These fissures, according to him, are apparently the cause of line broadening in the diffraction patterns.

Potter's conclusions are based on the assumption that the whole of hydrogen in electrolytic manganese is in a solid solution. If the existence of hydrogen inside the metal is limited to a single mode, the conclusions can be justified. On the other hand, as mentioned earlier, there are divergent opinions regarding the location of hydrogen inside the deposited metal.

Before proceeding to discuss the possible location of hydrogen in manganese, it would be interesting to recall some of the experimental observations:

1. Electro-deposited gamma manganese on 2 hours of deposition absorbs 40-72 cc/100 gm of hydrogen, almost the same amount soluble in gamma manganese within its temperature range of stability.
2. On longer periods of deposition, higher contents of hydrogen are observed making the metal less ductile but structure remaining the same (vide Table 6.III).
3. The electro-deposited alpha manganese left at room temperature is sometimes found to be less brittle with passage of time.
4. The liberation of hydrogen from electro-deposited alpha manganese is almost completely accomplished at 300°C (vide Table 6.IV).
5. Heating to 500°C in a vacuum of 10^{-3} mm of Hg for one hour reduces the hydrogen content to less than the amount soluble at 500°C.
6. On heating to 500°C, the hardness of electro-deposited alpha manganese is increased (vide Tables 3.I and 3.II of Chapter III).
7. On heating to 500°C though the hardness values are increased, the ductility of the metal also increases. Jacobs[56] also supports this contention and says that it was more difficult to break the manganese after the hydrogen has been removed.
8. Manganese obtained with higher hydrogen contents above 550 cc per 100 gm are amorphous.
9. The initial amorphous deposit (surface facing solution side), obtained in presence of sulphur dioxide in the electrolyte, on

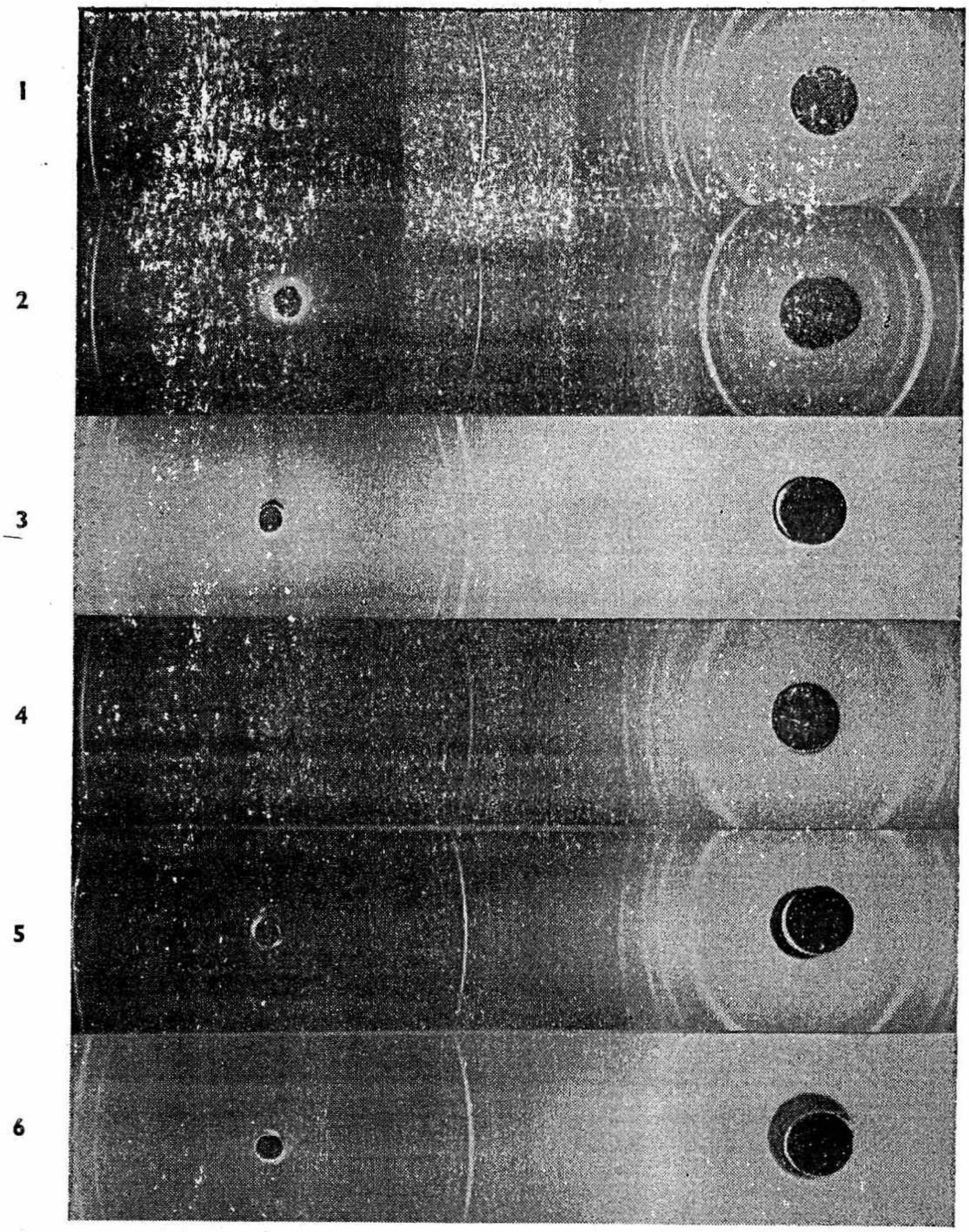

FIG. 6. II — X-RAY DIFFRACTION PATTERNS OF DEPOSITED MANGANESE WITH VARYING HYDROGEN CONTENT

1. Electro-deposited transformed gamma manganese annealed at 500°C after grinding
2. Same specimen — annealed and ground afterwards
3. Transformed gamma (42 cc/100 gm)
4. Transformed gamma (70 cc/100 gm)
5. Alpha manganese from baths containing SO_2 — after standing at room temperature for one year (224 cc/100 gm)
6. Alpha manganese from baths containing selenious acid (343 cc/100 gm)

TABLE 6.III — TIME OF DEPOSITION AND HYDROGEN CONTENT OF GAMMA MANGANESE

Conditions of deposition:

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

Initial *p*H of feed electrolyte and cell solution: 7·3
Flow of electrolyte: 10 cc/min
Current density: 4·6 amps/sq dm
Temperature of electrolysis: 28-30°C

TIME OF DEPOSITION hr	CATHODE MATERIAL	CURRENT EFFICIENCY %	HYDROGEN CONTENT cc/100 gm
2	Copper	67·35	70
2	Stainless steel	73·72	42
3	do	81·32	32·78
5	do	60·00	79·35
5	do	58·55	116·6
7	do	55·62	123·4

TABLE 6.IV — EVOLUTION OF HYDROGEN FROM ELECTRO-DEPOSITED ALPHA MANGANESE (Pilot Plant Sample) DURING HEATING TO VARIOUS TEMPERATURES

TEMPERATURE °C	EVOLVED HYDROGEN IN 15 MINUTES cc/100 gm
75	11·58
100	15·45
200	106·9
300	154·5
400	16·73
500	2·57

ageing at room temperature for 4½ years gives a pattern of crystalline alpha manganese.

10. On heating the amorphous deposit obtained at high current densities to 125°C, when part of the hydrogen is liberated, pattern of alpha manganese is obtained.

11. Deposits in presence of sulphur dioxide at low *p*H values show crystalline structure initially, compared to the amorphous patterns obtained at alkaline *p*H values.

12. Deposits obtained at low pH values are more adherent and less brittle and have low internal stress.
13. Unlike other electro-deposited metals like Fe, Ni and Cr, electro-deposited manganese does not show a high hardness value.
14. The density of electro-deposited manganese is lower than that of annealed manganese.

Considering that hydrogen takes up only interstitial positions in transition metals, because of its small size, it is well known that face centred cubic and close packed hexagonal structures are generally preferred by the metalloid elements[57]. For a given atomic diameter they possess interstitial spaces having larger linear dimensions than body centred cubic and other common lattices. For example, the linear dimensions are nearly 10 per cent larger in these lattices than in the corresponding BCC lattices[57]. In the case of manganese also, the same fact holds good as is seen in the decrease of hydrogen solubility at the gamma (FCC) $\rightarrow$ delta (BCC) transformation. Similarly Mn_4N and Mn_2N are face centred cubic and close packed hexagonal structures respectively[57].

In the light of the above facts, it should be regarded that face centred gamma manganese could take up more hydrogen if surcharged than the complex body centred cubic alpha manganese. For 695 cc of hydrogen per 100 gm of metal, if each unit cell of alpha manganese takes up 2 atoms of hydrogen, one unit cell of simple gamma manganese has to take up only about 1×10^{-1} atom. From this it can be safely concluded that on addition of sulphur or selenium, alpha manganese is obtained not because that the gamma manganese is not able to take up in solid solution the resulting hydrogen content on addition of S or Se. The reason has to be traced to some other effects.

The early appearance of crystalline structure in deposits obtained in presence of sulphur dioxide in acid medium compared to deposits obtained in alkaline medium, has to be traced either to direct proton inclusion or electro-chemical change in the reduction of sulphur dioxide in acid medium. The earlier appearance of crystalline structure with sulphur dioxide in acid medium, the low hardness and low density of electro-deposited alpha manganese and the increase in hardness together with ductility on heating suggest the possibility that a part of the discharged hydrogen ions assuming positions inside lattice or forming complex during the formation of alpha manganese.

On the other hand, the observations on the evolution of hydrogen from the deposited manganese point out that desorption of hydrogen takes place in electro-deposited manganese at room temperature or at slightly elevated temperature and that the bond between hydrogen and manganese is not very stable. If, on the other hand, desorption takes place because of super saturation of hydrogen, desorption should continue to the limit of its normal solubility. These observations do not favour the view that all the hydrogen in electro-deposited manganese is completely in interstitial solid solution. One is inclined to think that a part of the hydrogen goes inside the lattice, as mentioned in the earlier paragraph, and the rest are located outside the lattice in voids. In any case, it seems unlikely that all the co-deposited or adsorbed hydrogen enters the lattice.

However, as is apparent from the above discussion, very little is yet known about hydrogen in metals with certainty. As pointed out by Cupp[58], much more study is needed before a reasonable theory can be developed to cover the entire gas metal field. With regard to electro-deposited metals, a comparison can be made only if it is possible to carry out each deposition under exactly the same conditions and this cannot be done in all cases. It is necessary to study systematically the hydrogen content, lattice parameter variation, resistivity, density, and hardness of electro-deposited metals with as much exact conditions as possible to throw more light on the location of hydrogen inside the metal.

Conclusions

The hardness of annealed alpha manganese is found to be in the range of 950-1000 DPN while that of electro-deposited alpha manganese is found to be 690 DPN. Thus, electro-deposited alpha manganese shows a lower value compared to its annealed state, unlike other electro-deposited metals. Transformed gamma manganese shows the highest broadening of diffraction lines which has been attributed to the volume change associated with the transformation and the resultant stress. It is discussed that a part of the hydrogen in electro-deposited alpha manganese goes inside the lattice and the rest are adsorbed on the crystalline surface. The appearance of alpha manganese in presence of sulphur dioxide or at high current densities when the hydrogen content is high, along with other experimental evidences like low hardness, low density, early crystalline structure of the deposit in presence of sulphur dioxide at low *p*H values, suggests the possibility that a part of the discharged hydrogen ions assuming positions inside the lattice or forming complex during the formation of alpha manganese. It is likely that the amorphous nature obtained at high current densities when the hydrogen content is over 550 cc per 100 gm is due to the division of the lattice into minute crystallites and the adsorption of a high amount of hydrogen on the surfaces of the crystallites.

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