CHAPTER I

Crystallographic modifications of manganese and their transformation characteristics

X-ray diffraction data and lattice constants of alpha, beta and electro-deposited gamma manganese have been presented. The transformation characteristics on quenching from high temperatures and the transformation of electro-deposited gamma to alpha manganese at room temperature have been studied and the results are compared with those of early workers. Rapid quenching of gamma and delta manganese from its temperature ranges of stability yielded only beta manganese.

Introduction

Manganese exhibits polymorphism and todate four allotropic modifications of manganese, viz alpha, beta, gamma and delta, have been established. The alpha, beta and gamma modifications were first identified at much about the same time (1925) by Westgren and Phragmen[1], and by Bradley[2], whilst the delta modification was definitely established by Basinski and Christian[3] (1954) even though its existence was postulated by Grube[4] in 1936. Crystal structures, temperature ranges of stability and other physical properties of the different allotropes of manganese are given in Table 1.I.

Both alpha and beta manganese have very complicated structures and the true nature of the states of atoms in these structures is still not completely understood. Alpha manganese has been described as of the body-centered cubic type in which each lattice point is replaced by a cluster of 29 atoms[9]. Westgren and Phragmen[1] initially put forward that there are 56 atoms per unit cell whilst detailed studies of the diffraction photographs by Bradley and Thewlis[9] suggested the number of atoms to be 58 instead of 56. This was confirmed independently by Preston's X-ray studies on single crystals of alpha manganese[10]. The structure contains atoms of four kinds and probably in different states. Fig. 1.1 by Bradley and Thewlis[9] depicts the structure of alpha manganese around the central atom of the cubic lattice.

In this figure it is seen that there are four atoms (A type) arranged tetrahedrally about the central atom, 12 atoms (D_2 type) arranged octahedrally and 12 atoms (D_1 type) arranged polyhedrally having a cubic

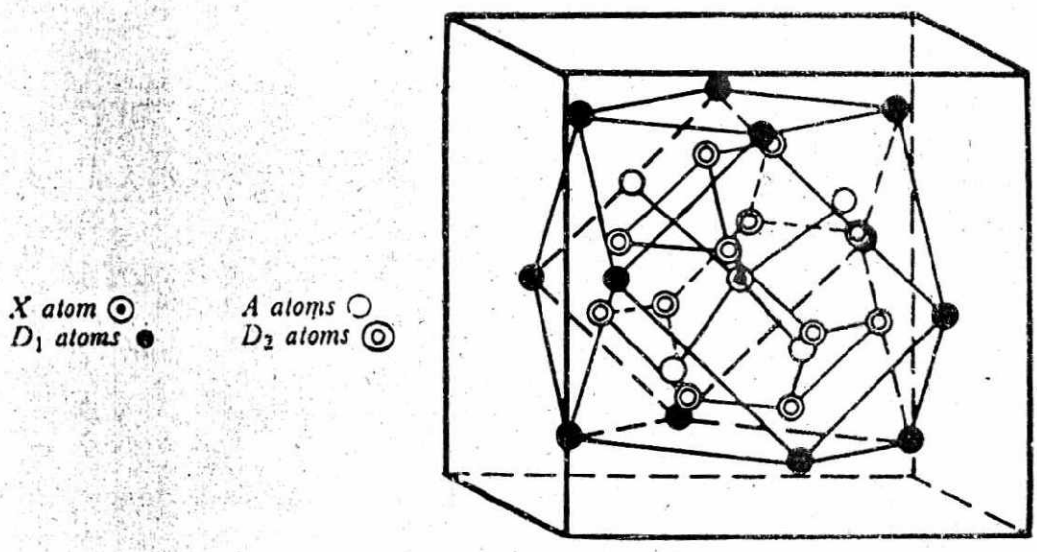


FIG. 1.I — STRUCTURE OF ALPHA MANGANESE
(*After Bradley & Thewlis*[9])

TABLE 1.1 — CRYSTAL STRUCTURES, AND PHYSICAL AND MECHANICAL PROPERTIES OF DIFFERENT ALLOTROPES OF MANGANESE

Phase	Structure[5,7] type	Temperature ranges of stability[3]	Lattice constants[5,31] Lattice parameter		Atoms per unit cell[5]	Interatomic distance kx[5,6]	Specific gravity[7]	Physical characteristics	Hardness[8,31]
			a, kx	Axial ratio c/a					
Alpha	Complex cubic A12	Up to 725°C	8·8959 (25°C)	—	58	2·24-2·97	7·44	Hard brittle	Rockwell C-71 950 VPN
Beta	Complex cubic A13	725-1095°C	6·3018 (25°C)	—	20	2·36-2·68	7·29	do	—
Gamma	Face centred cubic at high temperatures A1	1095-1134°C	3·8546 (1095°C)	—	4	2·7256	—	—	—
	Face centred tetragonal as obtained from electro-deposition at room temperature	—	3·774	0·937	4	—	7·21	Soft ductile	Rockwell C-23 100 VPN
Delta	Body centred cubic A2	1134-1245°C (melting point)	3·0744 (1134°C)	—	2	2·6625	—	—	—

and octahedral faces. A similar arrangement exists around the corner atom. Inter-atomic distances calculated for the structure show the values to be different for the same atom with the same type as well as different neighbours. This variation in inter-atomic distances has led Bradley and Thewlis[9] to suggest that the electrons are not equally shared between different kinds of atoms in alpha manganese and that the structure is similar to that of a compound than a true element. Recent neutron diffraction studies[11,12] of alpha manganese generally confirm the parameters of Bradley and Thewlis and no significant deviation has been detected.

Beta manganese

Westgren and Phragmen[1], who were the first to investigate beta manganese structure, showed that the X-ray powder photograph corresponded to a cubic structure of cube side $6{\cdot}280 \pm 0{\cdot}004$ kX but the presence of three weak lines in the photograph made them suggest that the dimension of the cube side might be twice the above value. Depending upon the size of the unit cell, the number of atoms per unit cell was either 20 or 160. Preston[10] from his single crystal X-ray studies concluded that these three lines do not belong to the structure of beta manganese and confirmed the smaller value for the cell dimension. Wilson[13], on the other hand (reported in the form of an abstract only) differed from Preston and agreed with Westgren and Phragmen's suggestion that the cell dimension is twice the smaller value. Recent neutron diffraction[12] studies have, however, corroborated Preston's conclusions of the smaller value for the cube side.

The 20 atoms in the unit cell of beta manganese are arranged in two sets, one of 12 and the other of 8 atoms[10]. The structure and electron concentration of beta manganese are similar to alloys of copper and silver with elements of higher valency. Considering this, Hume Rothery[14] suggested the possibility of equal numbers of univalent and divalent manganese atoms in beta manganese. Hume Rothery obtained evidence for the existence of univalent manganese atoms in ferromagnetic alloys, such as Cu_2MnIn, so that, according to him, there is justification for assuming their existence in pure metals.

Gamma manganese

Gamma modification of manganese was first detected in electrodeposits of the metal by Westgren and Phragmen[1] and Bradley[2]. They found that the freshly electro-deposited metal had a simple X-ray pattern with a face-centred tetragonal lattice. The identity between

the manganese obtained by electrolysis and the form of manganese stable at high temperatures was first demonstrated by Persson and Ohman[15], and by Sekito[16]. Persson and Ohman showed that the retained manganese-rich, manganese-copper alloys had the same structure. Sekito was successful in partially retaining the gamma structure in a sample of thermite manganese (97·1 per cent purity) and showed by X-rays that it had the same structure and approximately the same lattice constants as electro-deposited gamma manganese.

Although the structure of gamma manganese at room temperature as face-centered tetragonal was established beyond all doubts, there was disagreement until recently about its structure within its range of stability. Walters and Wells[18] agreed with Gensamer[19] in suggesting that the gamma phase in manganese rich manganese iron alloys was face-centred cubic at high temperatures and that the same might be true of pure gamma manganese. Worrel[20] found that these quenched alloys have a highly twinned micro-structure, such as are found in face-centred cubic metals. Later, Zener[21] suggested that the high temperature structure of these alloys is face-centred cubic and that the tetragonality is induced by a diffusionless transition during quenching. That the above suggestions were correct and that the transformation from face-centred cubic to tetragonal was a martensitic type was conclusively proved by Basinski and Christian[22] who took X-ray photographs over a range of temperature from −183° to +250°C of manganese copper alloys containing 70-95 per cent manganese. 70 per cent manganese copper alloy changed at −183°C from tetragonal to cubic while 93·5 per cent manganese alloy changed between 160-200°C. The transformation was dependent only upon the temperature and not upon the time at temperature, proving that the change was diffusionless. Zwicker[23] reported similar results for manganese alloys with gallium and germanium. Basinski and Christian[3] confirmed their earlier findings by taking high temperature X-ray photographs of manganese which was rather difficult not only because of the relatively narrow range of temperature over which gamma modification is stable but also by the high volatility of manganese and by its reactivity with refractories at high temperatures.

Gamma manganese, according to Hume Rothery[14], probably involves divalent manganese ions. This, as per Hume Rothery, is indicated by the greater atomic diameter in gamma manganese than in the adjacent elements chromium and iron, and the resultant low valency state.

Delta manganese

Grube[4] postulated the existence of delta-phase beyond gamma phase up to the melting point and Basinski and Christian[3] proved that it

has a body-centred cubic structure from high temperature X-ray photographs.

Transformation temperatures and quenching characteristics

Transformation temperature of these crystallographic modifications have been determined by various authors[7] using thermal analysis, dilatometry, magnetic susceptibility, hydrogen solubility, heat content and density. There is difference in the values of transformation temperatures, especially alpha⇌beta, perhaps due to the sluggishness of the transformation, sensitivity of the methods employed and, to a certain extent, due to the purity of the metal examined. The generally accepted probable values are given in Table 1.I. Beta manganese can be readily obtained in stable condition at room temperature by quenching from above alpha⇌beta transformation temperature[7]. But there is no agreement still as to whether pure gamma manganese with face-centred tetragonal structure at room temperature can be retained on quenching. Sekito[16], as mentioned earlier, suceeded partially in retaining the gamma structure in a sample of thermite manganese (97·1 per cent purity) quenched from 1150°C. Hume Rothery[14] says that the quenched specimens of gamma manganese are face-centred tetragonal, while Sully[7] and Griffiths and O'Neill[8] conclude that it transforms to alpha on quenching from a temperature which lies within its range of stability. On the other hand, recent studies by Booth and co-workers[24] with spectrographically standardized manganese, annealed at 1120°C for 16 hours in an argon atmosphere followed by rapid water quenching, yielded only beta manganese. But there is unanimity among workers[5] that in alloys with copper, nickel, cobalt, iron, zinc, etc, the gamma manganese has a face-centred tetragonal structure on quenching. This structure becomes face-centred cubic in quenched alloys at rather high solute contents.

Attempts to obtain metastable delta structures by quenching manganese alloys have been reported to be unsuccessful as the transformation delta→gamma occurs very rapidly on cooling[3].

Transformation of electro-deposited gamma to alpha manganese

The gamma modification of manganese produced by electro-deposition is in a metastable state and transforms to alpha manganese at room temperature. The effect of temperature on transition rate was studied in detail by Potter and coworkers[17] by electrical resistivity measurements. Potter observed that no appreciable change occurred in nine months at −10°C. Time required at various temperatures for half

completion of gamma→alpha transformation as found by Potter is given in Table 1.II.

TABLE 1.II — TIME FOR HALF COMPLETION OF TRANSFORMATION FROM GAMMA TO ALPHA[17]

Temperature °C	Time	Temperature °C	Time (sec)
20	455 hr	115	240·0
25	238 hr	130	77·0
40	53 hr	140	36·5
58	590 min	150	19·3
80	83 min	160	7·7
100	15 min		

The values of resistivity when plotted against time was found to follow a typical S curve suggesting that the transformation was that of a nucleation and growth process.

It is significant that neither the resistivity curves nor the X-ray measurements made at various stages of transformation showed the presence of beta manganese and it is to be concluded from Potter's work that beta manganese is not formed as an intermediate product during gamma→alpha transition.

It is intended in this work to examine the diffraction data of alpha, beta and electro-deposited gamma manganese in order to identify the various phases obtained during electro-deposition under different conditions. The transformation characteristics on quenching from high temperatures and the transformation of electro-deposited gamma to alpha manganese have also been studied.

Materials and methods

X-ray diffraction data of standard alpha, beta and electro-deposited gamma manganese — Pure manganese metal for the above and for quenching studies, to be described below, was prepared by depositing manganese from extremely pure solutions in the gamma form. No sulphide sulphur could be detected in a 6 gm sample of this specimen. This gamma manganese was heated in a vacuum of 10^{-4} mm of Hg at 500°C for four hours whereby the co-deposited hydrogen was removed and the manganese was completely transformed to alpha. At 160°C gamma manganese completely transforms to alpha in about 16 seconds[17].

The specimens for standard diffraction data of alpha and beta manganese were then prepared by coating a very thin glass fibre with Canada balsam and −250 mesh samples of annealed alpha or quenched beta, while the specimen of gamma manganese was prepared by electro-deposition on a thin stainless steel wire for one hour. The photographs were taken with 57·3 and 114·6 mm cameras in Philips PH/1010/X-ray diffraction unit with FeK_{α} radiation. The time of exposure was 20 hours in case of alpha and beta manganese and 10 hours in case of gamma manganese, at ratings of 12 mA at 24 kV (with the big camera). The distances between the lines were measured on a film comparator to an accuracy of 0·05 mm and the lattice constants were calculated by extrapolation against Nelson and Riley function.

Routine X-ray studies — Routine X-ray examinations of transformation studies of gamma to alpha and of quenched specimens were carried out in a unicam 90 mm camera. Bradley and Jay film mounting was adopted and the distance between the knife edges was calibrated by a standard sample of copper. FeK radiation from a demountable Raymax crystallographic set with rotating anode was used, the time of exposure being 90-100 minutes at tube ratings of 30 kV and 35 mA.

Micro-structure and Micro-hardness — The metastable gamma manganese or specimens containing both alpha and gamma were cold mounted with plastic solution and plastic powder. The mounted specimen was polished with kerosene oil in 3/0 and 4/0 metallographic paper slowly without generation of heat. It was further polished with silvo on a sylvet cloth. Both gamma and alpha manganese were etched for about 40 seconds in 5 per cent Nital.

Micro-hardness of deposited manganese, mounted as above, was measured either with GKN or ПМt-3 micro-hardness tester. Both were fitted with diamond pyramid indentors with a square base and a vertex angle of 136°. Generally 100 gm load was employed in both the testers. The values were checked up in a Vickers hardness tester. Because of the very brittle nature of alpha manganese, tests under Vickers hardness tester generally cracked the specimens.

Quenching experiments — Samples for quenching experiments were prepared from transformed gamma manganese. The powdered, annealed and dehydrogenated sample was vacuum sealed in 5 mm dia Vitreosil silica tubes. A platinum wound vertical furnace was used with a temperature controller, capable of controlling within ±2°C of the required temperature. The quenching was accomplished from the high temperature in a fraction of a second by fusing the thin platinum wire used for holding the specimen inside the furnace. The Pt-Pt-Rh thermocouple was calibrated with a slide wire potentiometer at the melting point of

gold (1063°) and diopside (1392°C). The samples were heated at the particular temperatures for about three hours before quenching.

Results of experiments

X-ray diffraction data and lattice constants of standard alpha, beta and electro-deposited gamma manganese — The X-ray diffraction patterns of alpha, beta and electro-deposited gamma manganese are given in Fig. 1.II. The X-ray powder data of the above allotropes are presented in Tables 1.III, 1.IV and 1.V, while the extrapolation curves of the lattice constants against Nelson and Riley function are given in Figs. 1.III, 1.IV and 1.V.

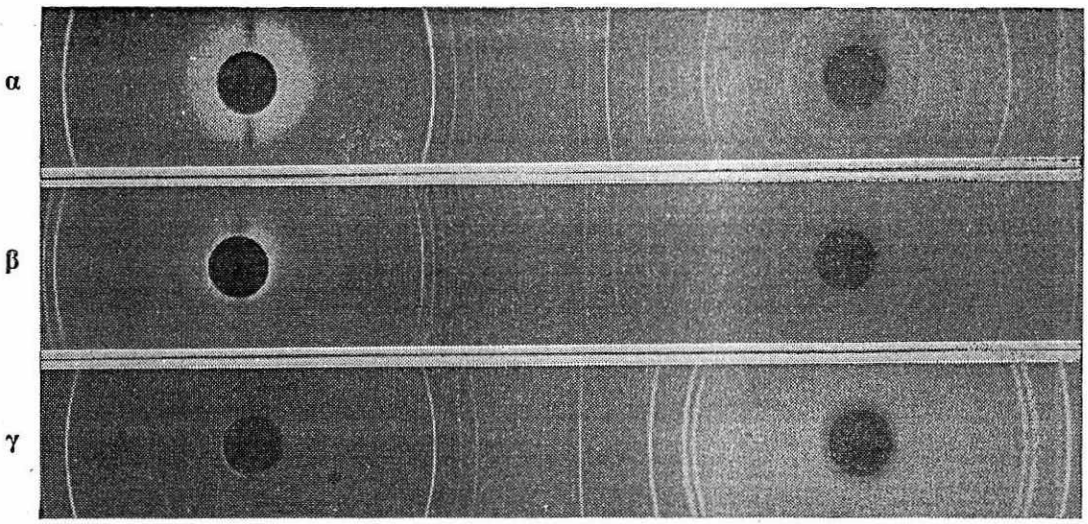


FIG. 1.II — X-RAY DIFFRACTION PATTERNS OF ALPHA, BETA AND ELECTRO-DEPOSITED GAMMA MANGANESE

Quenching studies of manganese from high temperatures — Results of studies of the structure of rapidly quenched specimens of manganese from temperatures at 825°, 1110° and 1180°C are given in Table 1.VI.

Time for transformation of electro-deposited gamma manganese to alpha manganese — The calculated 'd' values from X-ray photographs of electro-deposited gamma manganese during its transformation at an average temperature of 32°C to alpha manganese with passage of time have been shown in Table 1.VII.

Time for half completion of transformation from gamma to alpha manganese, as determined from the above, has been plotted along with Potter's[17] values in Fig. 1.VI.

Change in hardness of electro-deposited gamma manganese during its transformation with passage of time at 25°C has been plotted in Fig. 1.VII.

TABLE 1.III — X-RAY POWDER DATA AND LATTICE CONSTANTS OF ALPHA MANGANESE

Manganese 99·99%: Electro-deposited gamma manganese, hydrogen removed and transformed to alpha manganese by annealing in vacuum at 500°C

Radiation: FeK_α

$\lambda K\alpha_1 = 1{\cdot}93597$ Å, $\lambda K\alpha_2 = 1{\cdot}93991$ Å, $\lambda K_\alpha = 1{\cdot}93728$ Å

Temperature: 25°C

θ	Intensity (visual)	dÅ	(h k l)	Lattice parameter a, Å	Extrapolated value of 'a' from Fig. 1.III
15°29.22′	VW	3·628	2 1 1	*	
17°56.28′	VW	3·145	2 2 0		
22°11.28′	W	2·565	2 2 2		
24°3.78′	W	2·376	3 2 1		
25°51.78′	MS	2·221	4 0 0		
27°29.28′	VS	2·099	3 3 0		
			4 1 1		
30°41.34′	S	1·898	3 3 2		
32°12.84′	MS	1·817	4 2 2		
33°42.84′	S	1·745	4 3 1		
			5 1 0		
36°36.90′	W	1·624	5 2 1		
38°3.90′	VVW	1·571	4 4 0		
39°20.40′	VW	1·528	4 3 3		
			5 3 0		
40°44.40′	VW	1·484	4 4 2		
			6 0 0		
42°8.40′	VW	1·444	5 3 2		
			6 1 1		
46°11.46′	W	1·342	6 2 2		
47°32.46′	VW	1·313	6 3 1		
48°53.34′	MS	1·286	4 4 4		
50°17.48′	MS	1·259	5 4 3		
			5 5 0		
			7 1 0		
53°2.51′	S	1·212	5 5 2	8·9078	
			6 3 3		
			7 2 1		
54°28.02′	S	1·190	6 4 2	8·9077	
55°55.03′	MS	1·170	7 3 0	8·9070	
58°52.05′	MS	1·132	6 5 1	8·9104	
			7 3 2		
$\alpha_1$61°56.57′	W	1·097	7 4 1	8·9110	
$\alpha_2$62°8.56′		1·097	8 1 1	8·9130	
$\alpha_1$63°37.08′	W	1·081	8 2 0	8·9102	
$\alpha_2$63°50.58′		1·081		8·9108	

(*Continued on page* 13)

TABLE 1. III — X-RAY POWDER DATA AND LATTICE CONSTANTS OF ALPHA MANGANESE — *Continued*

θ	Intensity (visual)	dÅ	(h k l)	Lattice parameter a, Å	Extrapolated value of 'a' from Fig. 1.III
65°25.57′	VW	1·065	6 5 3	8·9115	
$\alpha_1$67°10.08′	MS	1·048	6 6 0	8·9113	
$\alpha_2$67°26.58′		1·048	8 2 2	8·9115	
$\alpha_1$69°7.12′	W	1·036	7 4 3	8·9124	
$\alpha_2$69°23.62′		1·037	7 5 0	8·9140	
			8 3 1		
71°19.14′	VW	1·023	6 6 2		
$\alpha_1$75°34.15′	MS	1·009	7 5 2	8·9132	
$\alpha_2$73°59.66′		1·009		8·9119	
$\alpha_1$79°34.20′	MS	0·984	9 1 0	8·9126	
$\alpha_2$80°14.68′		0·984		8·9119	8·9127

*Lattice parameter values for $\theta < 53°$ are not taken into account for extrapolation and hence are not included in the Table.

Remarks — The values of lattice constants of alpha and other modifications of manganese, as found in the course of this investigation, have been compared with the published values in literature in Table I.VIII.

VVW = very very weak, VW = very weak, W = weak, MS = medium strong, S = strong and VS = very strong.

TABLE 1.IV — X-RAY POWDER DATA AND LATTICE CONSTANTS OF BETA MANGANESE

Manganese 99·99% : Electro-deposited gamma manganese, hydrogen removed, sealed in evacuated silica tube, kept at 825°C for 1½ hr and quenched in water.

Radiation: FeK_α

$\lambda K\alpha_1 = 1{\cdot}93597$ Å, $\lambda K\alpha_2 = 1{\cdot}93991$ Å, $\lambda K_\alpha = 1{\cdot}93728$ Å

Temperature: 25°C

θ	Intensity (visual)	dÅ	(h k l)	Lattice parameter a, Å	Extrapolated value of 'a' from Fig. 1.IV
12°33.01′	W	4·458	1 1 0	*	
20°5.33′	W	2·820	2 1 0		
22°11.27′	W	2·565	2 1 1		
25°51.03′	W	2·222	2 2 0		
27°24.78′	VS	2·104	3 0 0		
			2 2 1		
29°3.79′	S	1·994	3 1 0		

(*Continued on page* 14)

TABLE 1.IV — X-RAY POWDER DATA AND LATTICE CONSTANTS OF 'BETA MANGANESE — *Continued*

θ	Intensity (visual)	dÅ	(h k l)	Lattice parameter a, Å	Extrapolated value of 'a' from Fig. 1.IV
30°36.79′	MS	1·902	3 1 1		
33°36.79′	VVW	1·750	3 2 0		
35°3.79′	W	1·686	3 2 1		
37°48.80′	VVW	1·580	4 0 0		
39°12.80′	W	1·532	4 1 0		
			3 2 2		
40°37.75′	VVW	1·487	3 3 0		
			4 1 1		
42°0.80′	VW	1·447	3 3 1		
43°14.45′	VVW	1·412	4 2 0		
46°12.80′	VVW	1·342	3 3 2		
48°57.41′	VVW	1·285	4 2 2		
50°8.31′	VVW	1·262	4 3 0	6·3094	
			5 0 0		
51°30.81′	MS	1·238	4 3 1	6·3098	
			5 1 0		
52°54.81′	W	1·214	3 3 3	6·3096	
			5 1 1		
55°44.32′	MS	1·172	4 3 2	6·3114	
			5 2 0		
57°11.32′	W	1·152	5 2 1	6·3121	
63°29.33′	W	1·082	4 3 3	6·3117	
			5 3 0		
$\alpha_1$65°6.83′	W	1·067	5 3 1	6·3127	
$\alpha_2$65°20.33′		1·067		6·3143	
$\alpha_1$66°56.33′	W	1·052	4 4 2	6·3123	
$\alpha_2$67°12.83′		1·052	6 0 0	6·3124	
$\alpha_1$68°50.33′	VW	1·038	6 1 0	6·3136	
$\alpha_2$69°9.83′		1·038		6·3128	
$\alpha_1$70°56.33′	VW	1·024	5 3 2	6·3132	
$\alpha_2$71°15.83′		1·024	6 1 1	6·3137	
75°57.84′	W	0·998	6 2 0	6·3147	
$\alpha_1$79°0.09′	MS	0·986	4 4 3	6·3143	
$\alpha_2$79°35.35′		0·986	5 4 0	6·3147	6·31475
			6 2 1		

*Lattice parameter values for $\theta < 50°$ are not taken into account for extrapolation and hence are not included in the Table.

VVW = very very weak, VW = very weak, W = weak, MS = medium strong, S = strong, and VS = very strong.

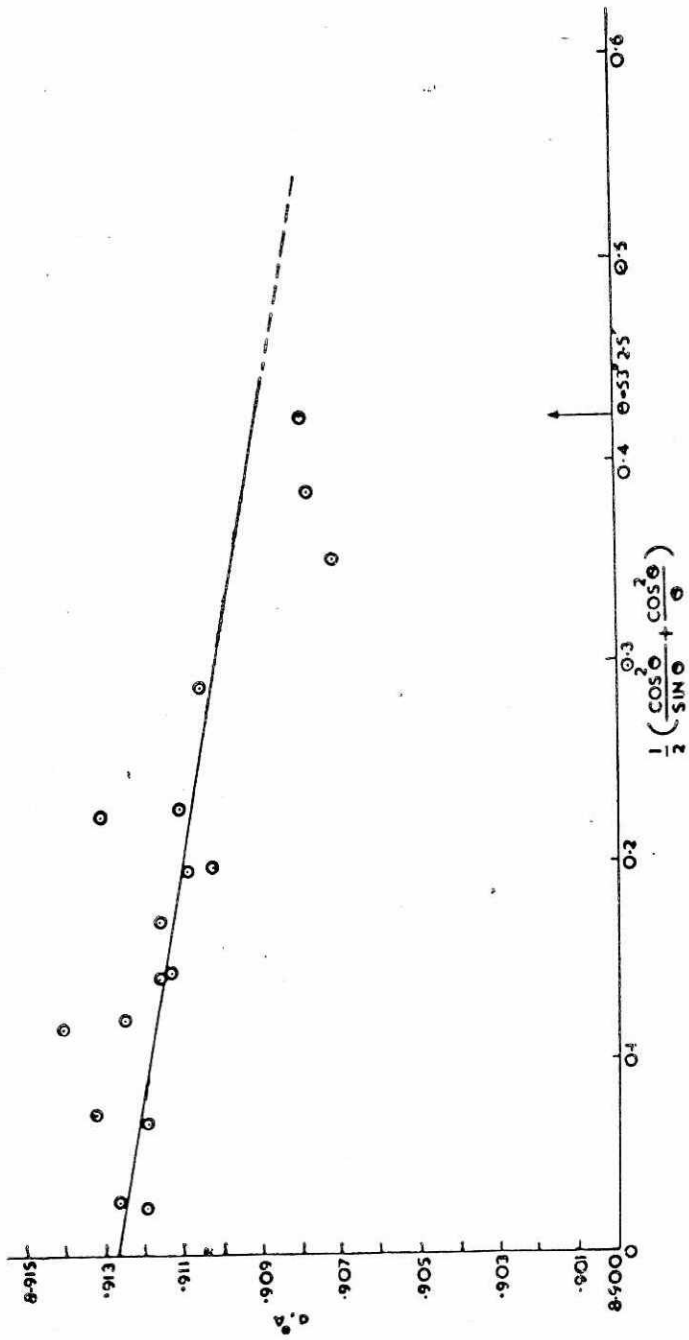


FIG. 1.III — EXTRAPOLATION OF 'a' OF ALPHA MANGANESE VS NELSON AND RILEY FUNCTION

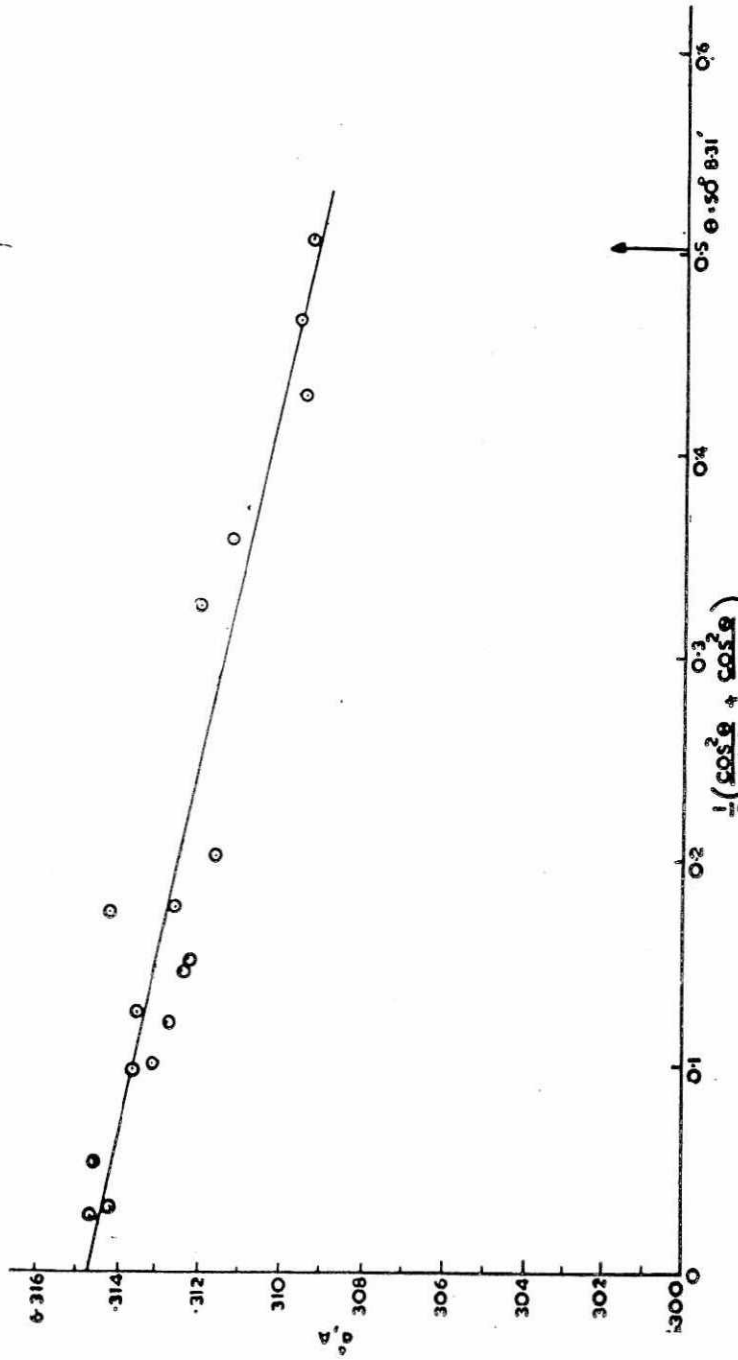


FIG. 1.IV — EXTRAPOLATION OF 'a' OF BETA MANGANESE VS NELSON AND RILEY FUNCTION

TABLE 1.V — X-RAY POWDER DATA AND LATTICE CONSTANTS OF ELECTRO-DEPOSITED GAMMA MANGANESE

Manganese 99·99%: Electro-deposited gamma manganese containing about 40 cc of hydrogen per 100 gm
Radiation: FeKα λKα=1·93728 Å
Temperature: 25°C

θ	Intensity (visual)	dÅ	(h k l)	Parameter, Å		Extrapolated value of 'a' & 'c' from Fig. 1.V
				a	c	
27°10.56′	VS	2·121	1 1 1			
31°0.30′	MS	1·880	2 0 0	3·7604	—	
33°22.92′	S	1·761	0 0 2	—	3·52115	
46°34.20′	W	1·334	2 2 0	3·7725	—	
48°43.32′	S	1·289	2 0 2	3·7848	3·54105	
58°42.98′	S	1·133	3 1 1	3·7811		
63°57.72′	S	1·078	1 1 3	—	3·54105	
65°24.00′	S	1·065	2 2 2	3·7848	3·54105	
						a = 3·7865
						c = 3·5445
						$\frac{c}{a}$ = 0·9361

W = weak, MS = medium strong, S = strong, and VS = very strong.

TABLE 1.VI — STRUCTURE OF QUENCHED SPECIMENS OF MANGANESE FROM TEMPERATURES AT 825°, 1115° AND 1180°C

Temperature from which quenched	Structure of manganese obtained
825°C	Beta
The above quenched specimen after ageing for a period of 4½ years	do
1115°C	do
1180°C	do

The micro-photographs of the gamma manganese deposit during the period of transformation have been shown in Fig. 1.VIII(1-6). Every time the specimen was mildly polished and etched. No significant changes were observed up to about 48 hours of deposition.

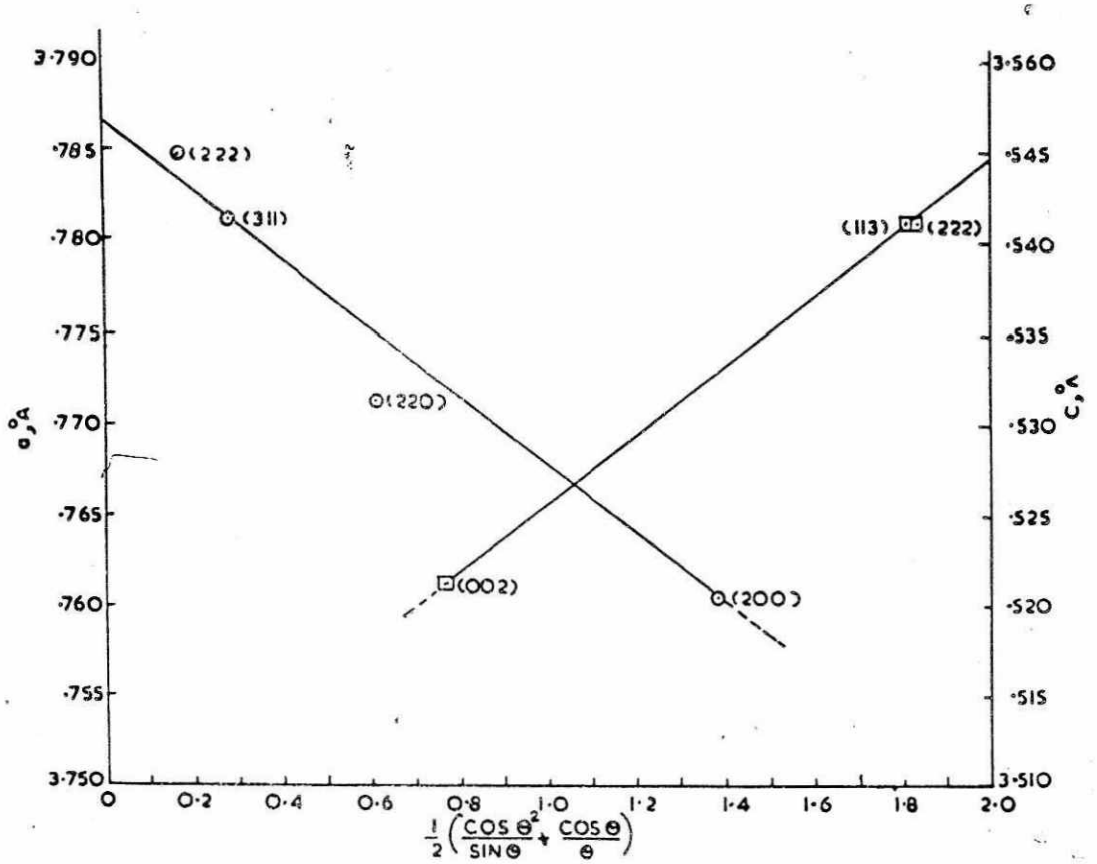


FIG. 1.V — EXTRAPOLATION OF 'a' AND 'c' OF ELECTRO-DEPOSITED GAMMA MANGANESE VS NELSON AND RILEY FUNCTION

Discussion

X-ray powder data and lattice constants of alpha, beta and electro-deposited gamma manganese — The lattice constants of the above allotropes of manganese, as determined in the course of this investigation, are given in Table 1.VIII along with the latest published values in literature.

It is seen that the lattice constants of the above allotropes of manganese, as found in the course of this investigation, agree within very reasonable limits with the values obtained by earlier investigators. These values have been taken as the standard for the identification of various phases of electro-deposited manganese in this investigation.

Quenching characteristics — Beta manganese is readily obtained by quenching pure manganese from temperatures within its range of stability. As seen from Table 1.VI, the quenched specimen retains its structure even after a lapse of $4\frac{1}{2}$ years.

In this investigation attempts to obtain quenched gamma manganese from its temperature range of stability resulted only in getting beta manganese. Perhaps the transformation gamma→beta occurs very

TABLE 1.VII — CALCULATED 'd' VALUES FROM X-RAY PHOTOGRAPHS ON STUDIES OF TRANSFORMATION OF GAMMA TO ALPHA MANGANESE; GAMMA MANGANESE DEPOSITED ON STAINLESS STEEL WIRE FOR ONE HOUR

X-ray exam: Iron K radiation — 9 cm camera Temperature: 32°C

Pure gamma		As deposited		After 72 hr of deposition		After 120 hr of deposition		After 240 hr of deposition		After 336 hr of deposition		Pure alpha	
Intensity	'd' value	Intensity	'd' value	Intensity	'd' value	Intensity	'd' value	Intensity	'd' value	Intensity	'd' value	Intensity	'd' value
												VW	3·143
												VW	2·575
				VW	2·207	W	2·210					VW	2·382
				S	2·082	S	2·071			W	2·193	MS	2·223
VS	2·121	VS	2·115*	S	2·102*	S	2·113	VS	2·067				
										VS	2·081*	VS	2·089
				W	1·805	S	1·809	MS	1·879	MS	1·888	S	1·892
MS	1·880	MS	1·871	S	1·871	S	1·886	MS	1·800	MS	1·811	S	1·813
								MS	1·729	MS	1·736	S	1·739
S	1·761	S	1·758*	S	1·755*	S	1·748					W	1·620
												W	1·560
												W	1·525
												W	1·478
												W	1·443
								W	1·329	W	1·337	W	1·333
MS	1·334	MS	1·336	S	1·329	W	1·333						
S	1·289	MS	1·290	S	1·286	S	1·288						
								W	1·280	W	1·282	W	1·283
				W	1·257	W	1·260	W	1·252	W	1·257	W	1·259
				W	1·210	S	1·210	MS	1·207	MS	1·211	MS	1·211
				W	1·181							MS	1·190
												MS	1·167
												W	1·133
S	1·133	MS	1·137	S	1·129	S	1·129						
S	1·078	MS	1·076	S	1·077	S	1·080			W	1·049		1·044
S	1·065	MS	1·064	S	1·064	S	1·068						

Remarks — It is noticed that alpha manganese lines appear 72 hours after deposited and both gamma and alpha manganese lines are observed in almost equal intensity at 120 hours.

*Lines of K_β radiation corresponding to the same interplanar spacing were present in the diffraction pattern as no filter was used.

VW = very weak, W = weak, MS = medium strong, S = strong, and VS = very strong.

TABLE 1.VIII — LATTICE CONSTANTS OF ALPHA, BETA AND ELECTRO-DEPOSITED GAMMA MANGANESE

(All values are given in Angstrom units)

PHASE	AS FOUND IN THE COURSE OF THIS INVESTIGATION VIDE TABLES 1.III, 1.IV AND 1.V, AND FIGS. 1.III, 1.IV AND 1.V	VALUES GIVEN BY PEARSON[5]	VALUES GIVEN BY BOOTH[24]	VALUES GIVEN BY TAYLOR[25]	VALUES GIVEN BY DEAN[26]	VALUES GIVEN BY PERSSON[27] AND ELLSWORTH & BLAKE[28]	VALUES GIVEN BY SCHLAIN & PRATER[29]
Alpha	8·9127	8·9139	8·914	8·912	8·9127		
Beta	6·3147	6·3146	6·312	6·32	6·3177		
Thermal gamma*					a 3·782	a 3·782	
					$\frac{c}{a}$ 0·937	$\frac{c}{a}$ 0·934	
Electro-deposited gamma manganese	a 3·7863						a 3·762
	c 3·5450						
	$\frac{c}{a}$ 0·9361						$\frac{c}{a}$ 0·938

*The values of face-centred tetragonal gamma manganese (thermal) given by Dean, Persson, and Ellsworth & Blake are by extrapolation of the lattice spacings of the gamma copper manganese alloys to zero copper content.

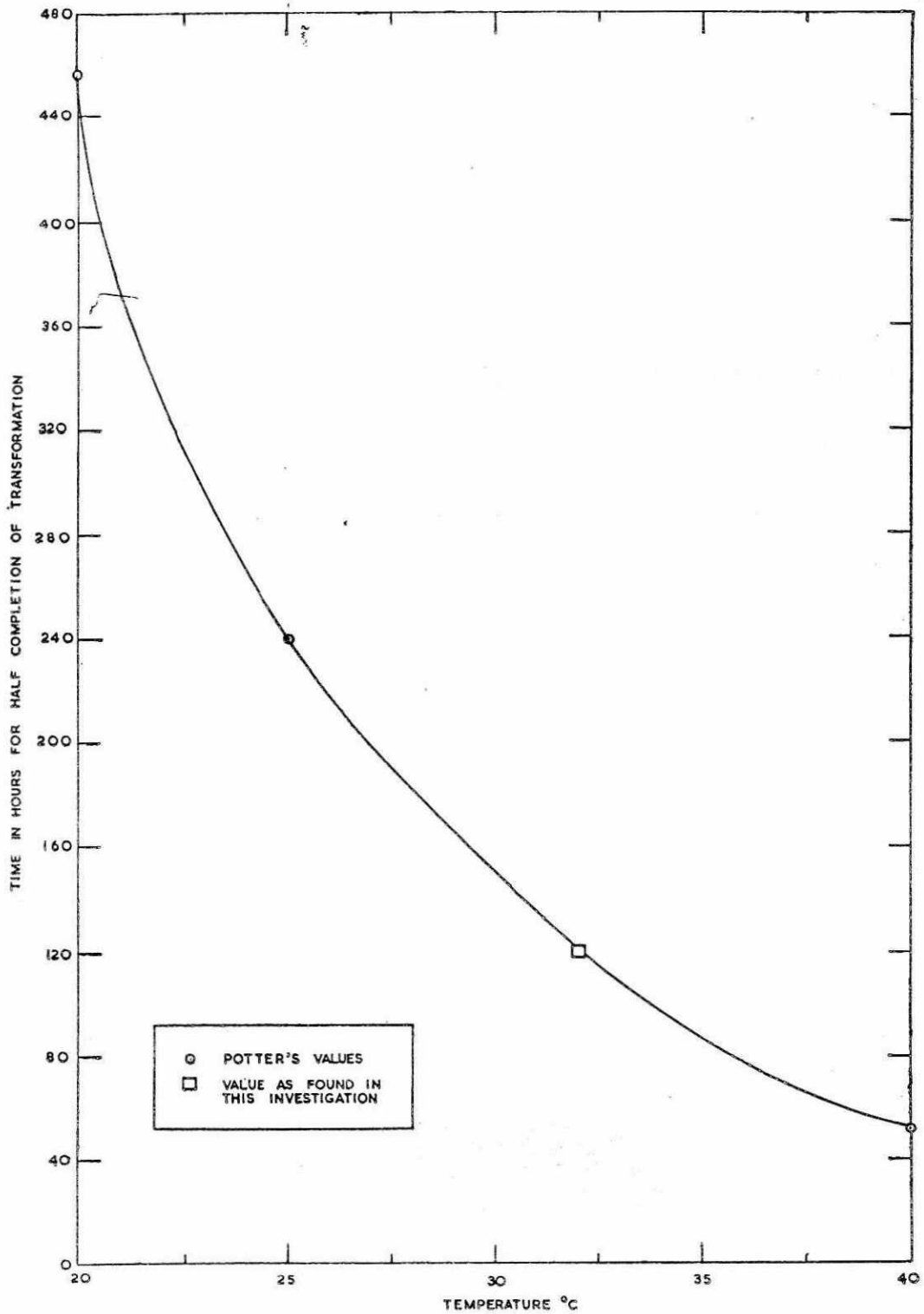


FIG. 1.VI — TIME FOR TRANSFORMATION OF GAMMA TO ALPHA MANGANESE VS TEMPERATURE

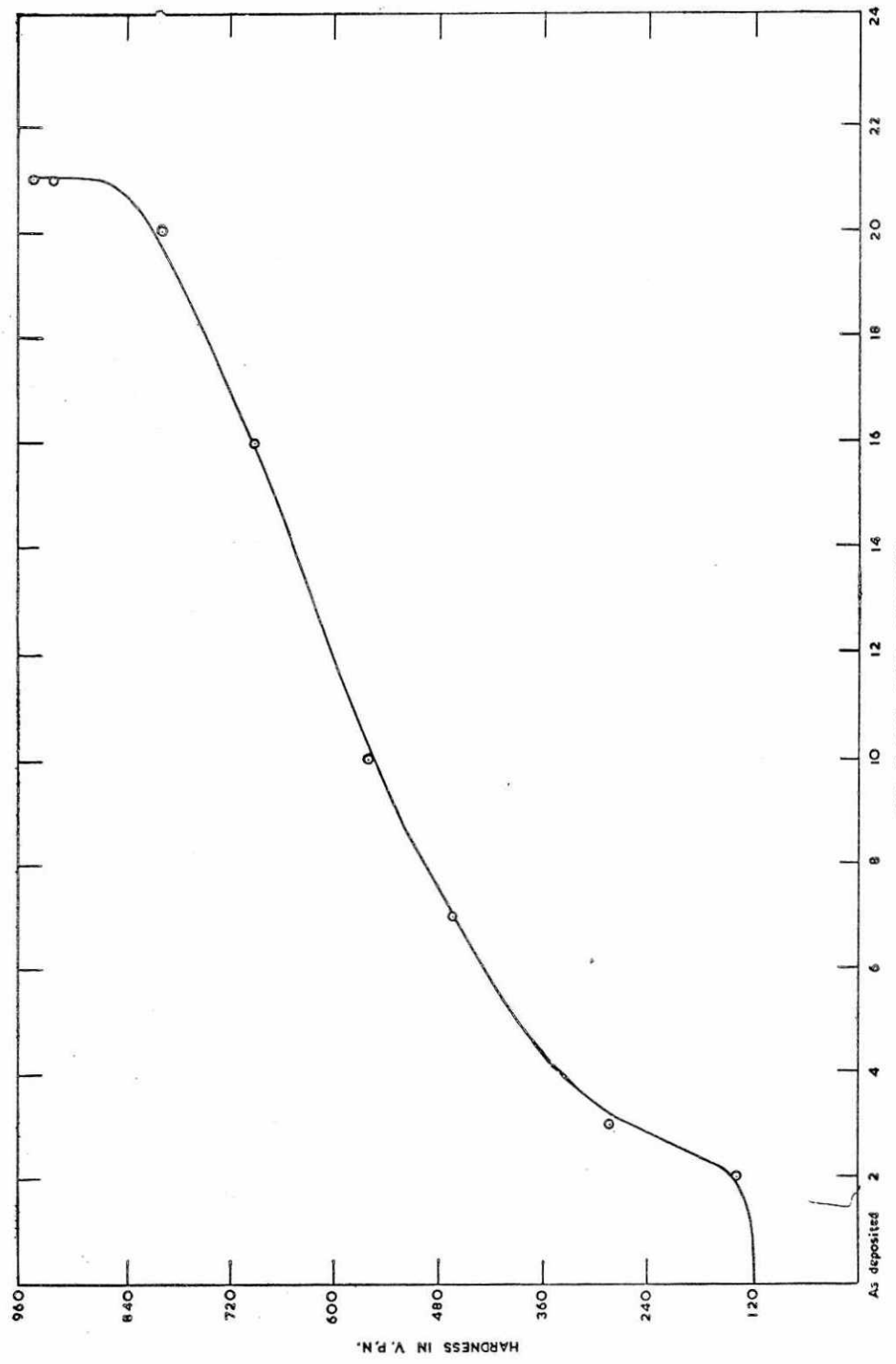
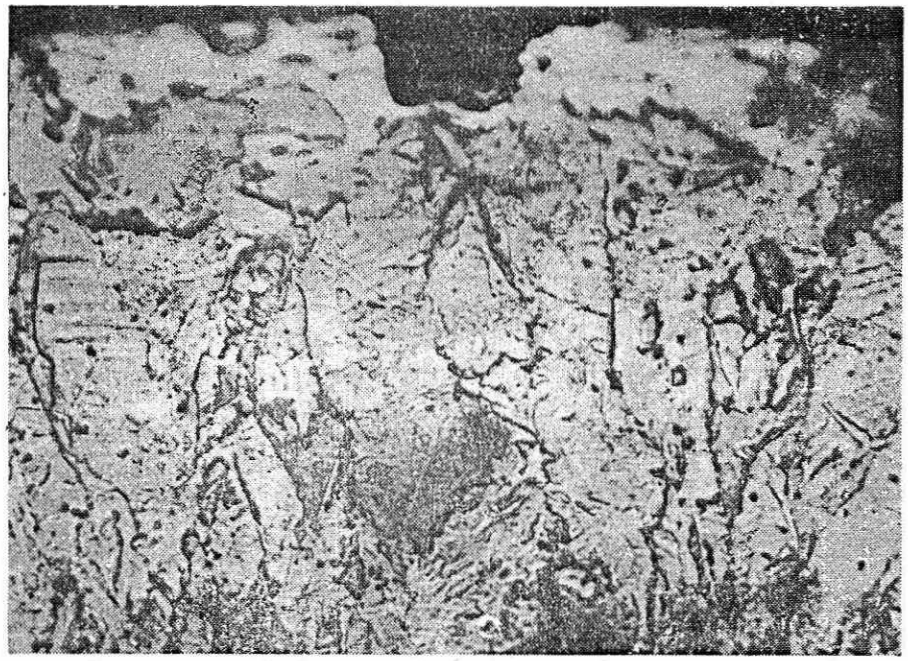


FIG. 1.VII — CHANGE IN HARDNESS WITH TIME OF ELECTRO-DEPOSITED GAMMA MANGANESE DURING TRANSFORMATION TO ALPHA MANGANESE AT 25°C



1. As deposited ×450

2. After 72 hr of deposition ×270

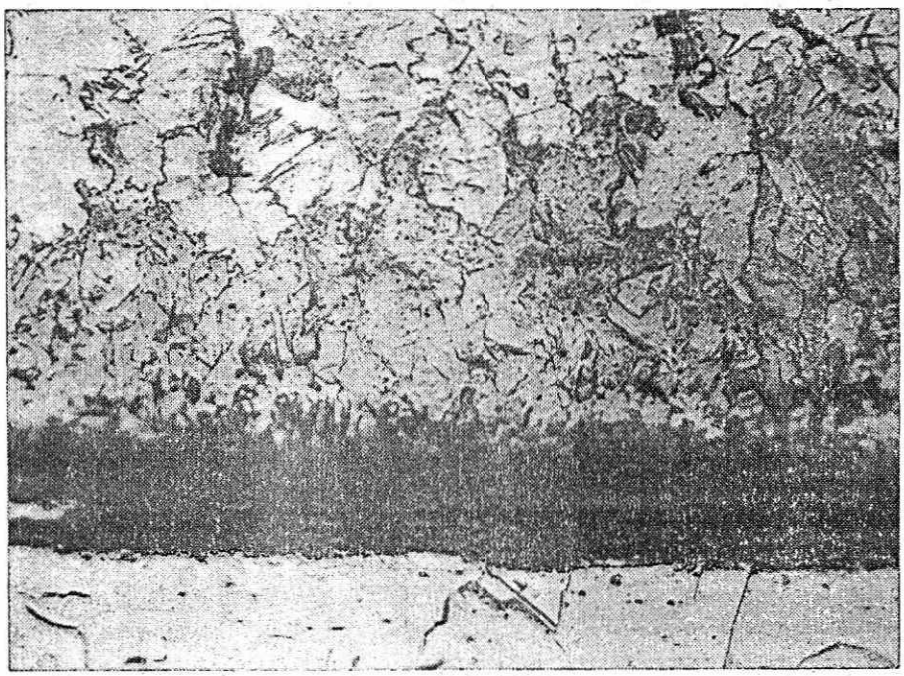


FIG. 1.VIII — MICRO-PHOTOGRAPHS OF DEPOSITED GAMMA MANGANESE DURING THE PERIOD OF TRANSFORMATION FROM GAMMA TO ALPHA MANGANESE

3. After 96 hr of deposition ×450

4. After 120 hr ×270

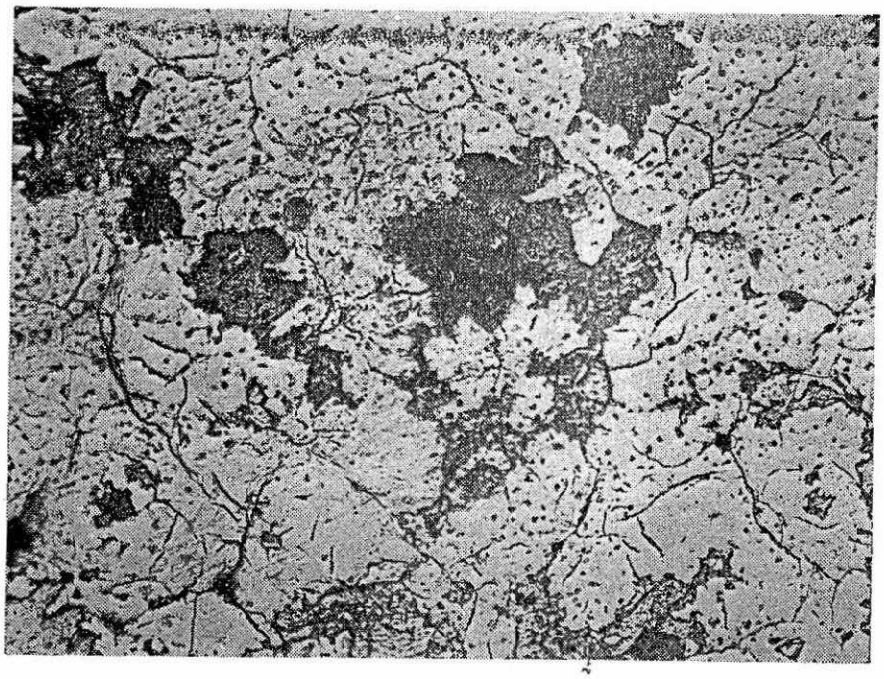
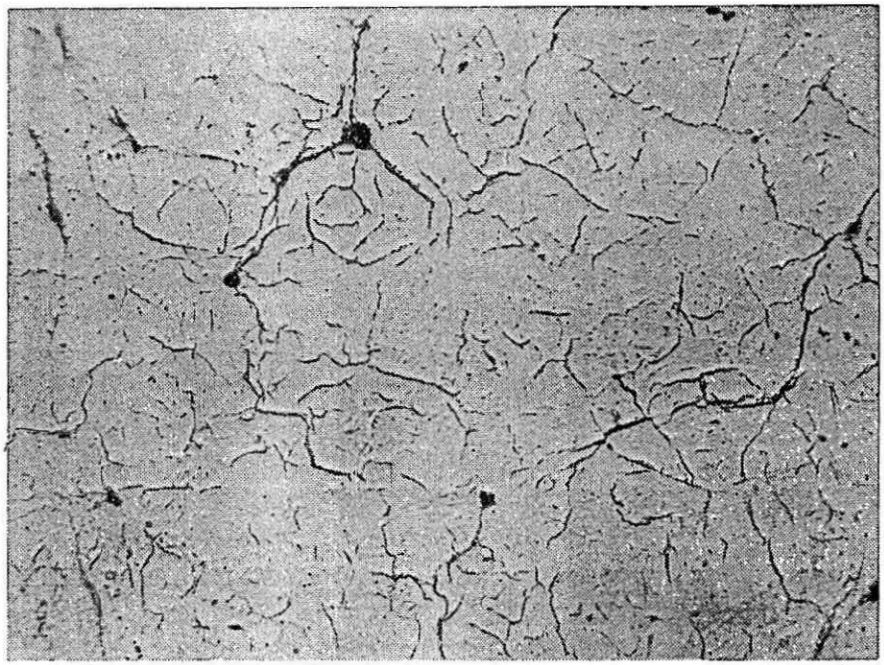


FIG. 1.VIII (*continued*) — MICRO-PHOTOGRAPHS OF DEPOSITED GAMMA MANGANESE DURING THE PERIOD OF TRANSFORMATION FROM GAMMA TO ALPHA MANGANESE



5. After 240 hr ×270

6. Completely transformed alpha manganese ×450

FIG. 1.VIII (*continued*) — MICRO-PHOTOGRAPHS OF DEPOSITED GAMMA MANGANESE DURING THE PERIOD OF TRANSFORMATION FROM GAMMA TO ALPHA MANGANESE

rapidly on cooling. This confirms Booth's recent findings[24] that rapid water quenching of a spectrographically standardized manganese after annealing at 1120°C for 16 hours in an argon atmosphere yielded only beta manganese. Previous investigators[7,8,14] have reported that on quenching gamma manganese either alpha or meta-stable face-centred tetragonal gamma manganese is obtained. Perhaps the purity of the manganese used by previous workers may be the cause for divergent results, Sekito[16] using manganese of 97 per cent purity.

Quenching pure manganese from a temperature of 1180°C, at which delta manganese should be stable, yielded also beta manganese in this investigation. Attempts to obtain meta-stable delta structures by quenching manganese alloys had been reported to be unsuccessful[3].

Transformation of electro-deposited gamma manganese to alpha — It is seen from Table 1.VII that alpha manganese lines appear 72 hours after removal from the electrolytic bath and both gamma and alpha manganese lines are observed in almost equal intensity after 120 hours. No gamma manganese lines are visible after 240 hours and full pattern of alpha manganese is obtained. The time for half completion of transformation to alpha manganese, as found in this investigation, agrees very well with Potter's[17] data as seen from Fig. 1.VI.

As pointed out by Potter[17], no indication of beta manganese was noticed in any of the X-ray patterns during transformation from gamma to alpha, though quenched specimens of gamma manganese from temperatures within its range of stability retains the beta structure. Though beta manganese should form as an intermediate product during transformation of gamma to alpha under normal conditions, this transformation of electro-deposited gamma manganese takes place at a temperature below the alpha→beta transformation temperature which, according to Christian[30], explains the absence of beta manganese as an intermediate product.

Conclusion

The X-ray diffraction data as found in this investigation agrees, within very reasonable limits, with the values published in literature. Rapid quenching of gamma manganese from its temperature range of stability yielded only beta manganese. Electro-deposited gamma manganese takes about ten days for complete transformation to alpha at a temperature of 32°C.

REFERENCES

1. WESTGREN, A. & PHRAGMEN, G., *Z.f. Physik*, **33** (1925), 777.
2. BRADLEY, A. J., *Phil. Mag.*, **50** (1925), 1018.
3. BASINSKI, Z. S. & CHRISTIAN, J. W., *Proc. Roy. Soc.*, **A223** (1954), 554.
4. GRUBE, G., BAYER, K. & BUMM, H., *Z., Elektrochem*, **42** (1936), 805.
5. PEARSON, W. B., *A Handbook of lattice spacings and structures of metals and alloys* (Pergamon Press, London), 1958, 126, 735.
6. KASPER, J. S., *Theory of alloy phases* (American Society for Metals, Cleveland, Ohio), 1956, 266-9.
7. SULLY, A. H., *Manganese* (Butterworths Scientific Publications, London), 1955, 125, 152.
8. GRIFFITHS, V. & O'NEILL, H., *J. Inst. of Metals*, **85** (1956-57), 105.
9. BRADLEY, A. J. & THEWLIS, J., *Proc. Roy. Soc.*, **A115** (1927), 456.
10. PRESTON, G. D., *Phil. Mag.*, **5** (1928), 1198, 1207.
11. SHULL, C. G. & WILKINSON, M. K., *Rev. of Mod. Phys.*, **25** (1953), 100.
12. KASPER, J. S. & ROBERTS, B. W., *Phys. Rev.*, **101** (1956), 537.
13. WILSON, T. A., *Phys. Rev.*, **47** (1935), 332.
14. HUME ROTHERY, W. & RAYNOR, G. V., *The structure of metals and alloys* (Institute of Metals, London), 1962, 47, 85, 95.
15. PERSSON, E. & OHMAN, E., *Nature*, **124** (1929), 333.
16. SEKITO, S., *Z. Krist.*, **72** (1929), 406.
17. POTTER, E. V., LUKENS, H. C. & HUBER, R. W., *Trans. Am. Inst. Min. Met. Engrs*, **185** (1949), 399.
18. WALTERS, F. M. & WELLS, C., *Trans. Amer. Soc. Steel Treat*, **19** (1932), 590; **21** (1933), 1021; *Trans. Amer. Soc. Metals*, **23** (1935), 727.
19. GENSAMER, M., *Manganese* by A. H. Sully (Butterworths Scientific Publications, London), 1955, 139.
20. WORREL, F. T., *Phys. Rev.*, **72** (1947), 533.
21. ZENER, C. M., *Elasticity & anelasticity of metals* (The University of Chicago Press, Chicago), 1948.
22. BASINSKI, Z. S. & CHRISTIAN, J. W., *J. Inst. Met.*, **80** (1951-52), 659.
23. ZWICKER, U., *Z. Metallk.*, **42** (1951), 246.
24. BOOTH, G. L., HOARE, F. E. & MURPHY, B. T., *Proc. Phys. Soc.*, **68** (1955), 830.
25. TAYLOR, A. & BRENDA J. KAGLE, *Crystallographic data on metal and alloy structures* (Dover Publications, New York), 1963, 258.
26. DEAN, R. S., *Metals handbook, Am. Soc. for Metals, Ohio*, Eighth edition, Vol I (1961), 1915.
27. PERSSON, E., *Z. Phys. chem.*, **9** (1930), 25.
28. ELLSWORTH, L. D. & BLAKE, F. C., *J. appl. Phys.*, **15** (1944), 507.
29. SCHLAIN, D. & PRATER, J. D., *Trans. Elec. Chem. Soc.*, **94** (1948), 58.
30. CHRISTIAN, J. W., *J. Inst. of Metals*, **78** (1950-51), 195.
31. DEAN, R. S., *Electrolytic manganese and its alloys* (Ronald Press Company, New York), 1952.