

Reactions in the production of high-carbon ferromanganese from Mamatwan ore

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SYNOPSIS

The influence of Iscor coke and Delmas coal on the reduction of Mamatwan manganese ore to ferromanganese was examined by use of a variation of the 'stationary charge in controlled environment' (SCICE) technique.

The charges of Mamatwan ore and the appropriate reducing agent were heated to temperatures between 1300 and 1600°C and either allowed to cool immediately the required temperature had been reached or held at that particular temperature for periods of up to 4 hours. The heating rate was 350°C per hour, the particle size of the ore was between 2,83 and 12,7 mm, and the particle size of the reducing agent was between 2,83 and 6,35 mm.

After being allowed to cool in air, the reacted charges were examined by optical microscopy, X-ray-diffraction analysis, scanning electron microscopy, and electron-microprobe analysis. No significant difference was found between the changes observed during the reduction of Mamatwan manganese ore by Iscor coke and by Delmas coal. A hypothesis is advanced to explain the mechanism of formation of the Fe-Mn-C alloy.

SAMEVATTING

Die invloed van die reduseermiddels Yskor-kooks en Delmas-steenkool op die reduksie van Mamatwan-mangaanerts tot ferromangaan is ondersoek met gebruik van 'n variasie van die tegniek wat van 'n stilstaande lading in 'n beheerde omgewing gebruik maak (SCICE-tegniek).

Die ladings van Mamatwan-erts en die toepaslike reduseermiddel is verhit tot temperature van tussen 1300 en 1600°C en sodra die verlangde temperatuur bereik is, afgekoel of vir tydperke van tot 4 uur op daardie bepaalde temperatuur gehou. Die verhittingstempo was 350°C per uur, die partikelgrootte van die erts tussen 2,83 en 12,7 mm en die partikelgrootte van die reduseermiddel tussen 2,83 en 6,35 mm.

Die gereduseerde ladings is, nadat hulle toegelaat is om in lug af te koel, deur optiese mikroskopie, X-straaldiffraksieontleding, aftaselektronmikroskopie en elektronmikrosondeontleding ondersoek. Daar is geen beduidende verskil tussen die veranderinge tydens die reduksie van Mamatwan-mangaan-erts met Yskor-kooks en met Delmas-steenkool waargeneem nie. Daar word 'n hipotese aan die hand gedoen om die meganisme van die vorming van die Fe-Mn-C-legering te verklaar.

Introduction

This investigation involved a study of the nature of the reactions taking place in a submerged-arc furnace during the production of high-carbon ferromanganese, with particular emphasis on the influence of reducing agents on these reactions.

The effects of temperature and retention time at a particular temperature were examined for charges of Mamatwan manganese ore and either Delmas coal or Iscor metallurgical coke. The experimental method was a variation of the 'stationary charge in controlled environment' (SCICE) technique¹. The technique is an attempt to simulate in the laboratory the conditions in the stack of a blast furnace. The theory and uses of the technique have been given by Klemantaski¹ and other investigators^{2, 3}.

A variation of the SCICE technique was used by Urquhart⁴ in a study of the production of high-carbon ferrochromium in a submerged-arc furnace. Urquhart heated the charges at a controlled rate of 400°C per hour to a predetermined temperature, which was maintained for a measured interval before the charge was allowed to cool.

From the work of Grimsley⁵ and Pentz⁶, it was evident that further investigations would have to be carried out into the processes that take place in the hotter regions of ferromanganese furnaces when Mamatwan ore is treated with various reducing agents. Since the rate of descent of the charge and the temperature profiles in ferromanganese furnaces are not well

known, it was decided to use a technique similar to that used by Urquhart⁴. The mass of the experimental charge was 4 kg, and its composition was similar to that of industrial charges.

The aim of this investigation was to obtain results that, on their own or in combination with the results of other investigations, would lead to a better understanding of the processes that take place in submerged-arc furnaces.

Materials, and the Preparation of SCICE Charges

The materials used in this investigation were Mamatwan manganese ore, Iscor metallurgical coke, and Delmas coal. These materials were supplied by Metalloys (Pty) Ltd, Meyerton. Tables I and II give details of the proximate and ash analyses of Iscor coke and Delmas coal, and of the composition of the Mamatwan man-

TABLE I
PROXIMATE AND ASH ANALYSES OF THE REDUCING AGENTS

Constituent	Delmas coal Mass %	Iscor coke Mass %
Fixed carbon	49,91	79,99
Volatile matter	28,33	2,75
Ash	15,65	15,98
Moisture	6,11	1,28
Sulphur	1,20	0,72
Phosphorus	0,16	0,20
Ash analysis:		
MgO	2,79	1,19
Al ₂ O ₃	26,38	30,05
SiO ₂	43,38	50,58
CaO	7,87	4,37
Mn ₂ O ₃	0,95	0,40
Fe ₂ O ₃	7,74	7,37
S	2,48	0,35

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TABLE II—
THE CHEMICAL COMPOSITION OF MAMATWAN ORE

Constituent	Mass %
MgO	3,10
Al ₂ O ₃	< 0,10
SiO ₂	4,27
CaO	12,96
Mn ₂ O ₃	55,90*
Fe ₂ O ₃	5,99
Cr ₂ O ₃	0,36
P ₂ O ₅	0,17
K ₂ O	0,21
CO ₂	14,91
H ₂ O	0,54

*This is the total manganese content of the ore expressed as Mn₂O₃.

gane ore, as determined by the National Institute for Metallurgy

The materials were crushed and screened, and the size ranges retained for the SCICE experiments were 2,83 to 12,7 mm for the ore and 2,83 to 6,35 mm for the reducing agents.

The SCICE charges were made up of ore and reducing agent in stoichiometric proportions. (Stoichiometric

carbon is defined as the amount of carbon required to reduce all the oxides of manganese and iron in the ore to the respective metals.) Fluxing materials were not added because it was desirable for the system to be as simple as possible and because Mamatwan ore is largely self-fluxing.

The ore and the reducing agent were mixed on a plastic sheet and transferred to a tray in which they formed a bed about 30 mm deep. From the tray, the mixture was transferred in small batches to the crucible to minimize segregation.

Apparatus and Procedure

The SCICE experiments that were carried out are listed in Table III. The charge was contained in a graphite crucible of 150 mm internal diameter and 515 mm depth, which acted as a susceptor when heated in a 40 kW 3 kHz induction furnace. The crucible assembly is shown in Fig. 1. The crucible was divided horizontally into a re-usable top and bottom. The central graphite electrode shown in Fig. 1 was used for resistance measurements, which are reported elsewhere⁷.

Two Pt-6%Rh/Pt-30%Rh thermocouples were used to measure the temperature, one positioned in the centre of the charge and the other 15 mm from the crucible

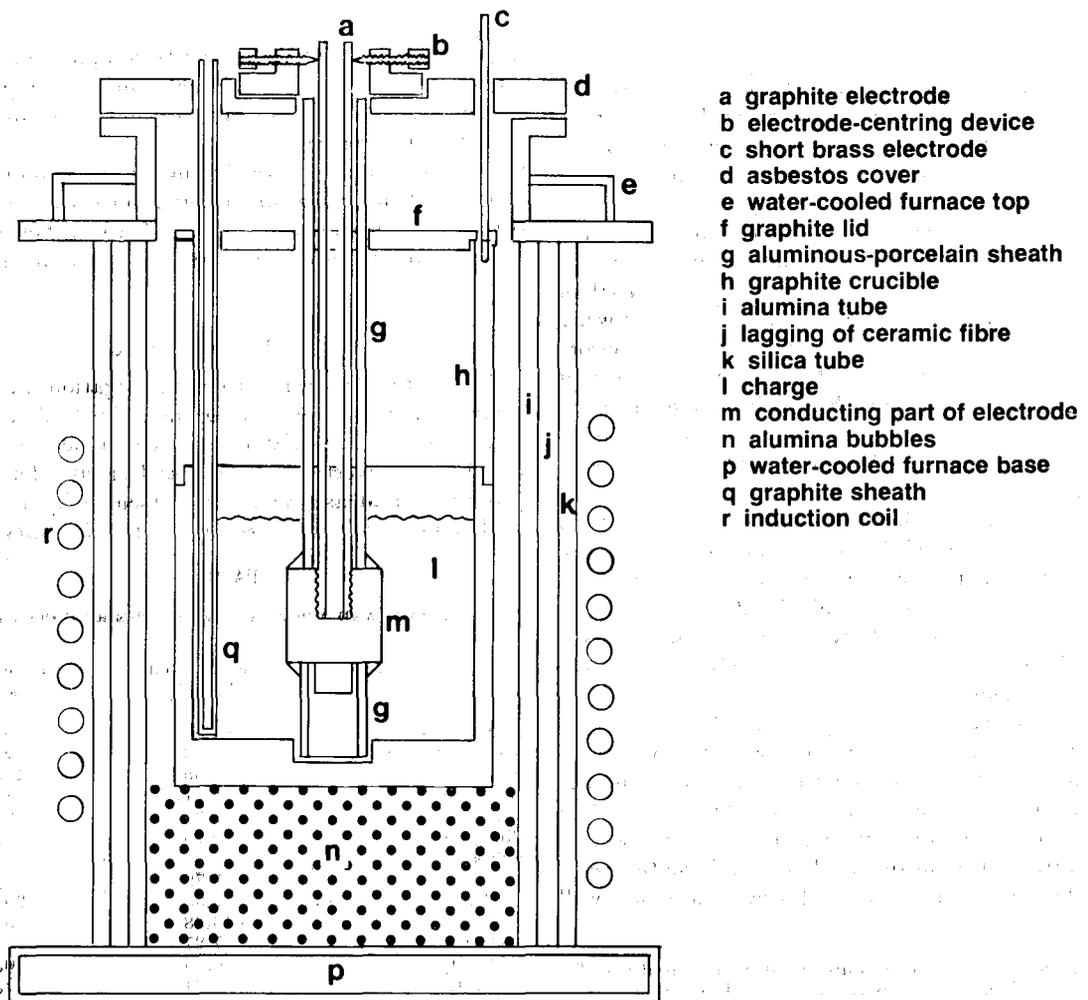


Fig. 1—Schematic section of the SCICE apparatus

TABLE III

DETAILS OF THE SCICE EXPERIMENTS
 Heating rate 350°C/h
 Particle size: Ore 2,83 to 12,7 mm
 Reducing agent 2,83 to 6,35 mm

Temperature °C	Retention time at temperature h			
	0	1	2	—
<i>Iscor coke</i>				
1300	0	1	2	—
1400	0	1	2	4
1500	0	—	—	—
1600	0	1	2	—
<i>Delmas coal</i>				
1400	0	—	2	4
1600	0	1	2	—

— No experiment conducted under these conditions

wall. The central thermocouple was lowered into the electrode, and the outer one into a graphite sheath of 10 mm inside diameter and 14 mm outside diameter. The outer thermocouple was used for temperature control, and all the temperatures quoted in this article refer to measurements made by this thermocouple unless otherwise stated. All the temperature measurements were made with the thermocouple junctions 60 mm above the bottom of the crucible.

During the heating of charges of ore with coke or coal, there was a temperature difference of about 140°C between the inner and outer thermocouples for temperatures of up to about 1000°C. Above 1000°C, the temperature difference decreased to 100°C for charges of ore and coke, and to 80°C for charges of ore and coal.

During cooling, there was no significant temperature difference between the edge and the centre of the charges.

The temperature was controlled manually according to the temperature of the charge measured next to the crucible wall. The power input was adjusted to maintain a heating rate of 350°C per hour.



Fig. 2—Charge of ore and coal heated to 1600°C and held for 1 hour. (Note partially reacted particles of ore in the slag layer)

Examination and Sampling of Reacted SCICE Charges

The reacted charges were examined visually, either by being removed from the crucible or by sectioning of the crucible and its contents with a diamond disc. The charges were photographed, weighed, and sampled for further analysis, the sampling procedure varying according to the extent of the reaction that had taken place. Samples were prepared for chemical analysis (so that the percentage metallization could be determined), for X-ray-diffraction analysis, and for microscopic examination. The authors' attempts to determine the percentage metallization were unsuccessful⁸.

In general, a Philips X-ray unit with a copper tube was used for the X-ray-diffraction analysis.

Results

The Mineralogy of the Ore

The mineralogy of Mamatwan ore has been studied by several investigators^{8,9-11}. The mineralogy of the batch of ore used in the present investigation was studied by the examination of polished sections and by X-ray-diffraction analysis, and the results obtained were in good agreement with those reported by previous investigators.

The ore studied had a fine grain size with interlocking manganese and gangue minerals. Local concentrations of gangue minerals occurred as veins and oolites. The major phases in the ore were found to be braunite ($3\text{Mn}_2\text{O}_3$, MnSiO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and calcite (CaCO_3). Smaller amounts of hausmannite (Mn_3O_4), hematite (Fe_2O_3), and cryptomelane ($\text{KMn}_8\text{O}_{16}$) were also present.

Examination of the Reacted SCICE Charges

A detailed account of the findings has been given elsewhere⁸. Here, mention needs to be made only of the following.

Charges of ore with coke or coal reacted under the same conditions had a similar appearance. The reduction of the ore resulted in the formation of beads of alloy and a film of slag on the surface of the ore particles. The colour of the ore changed to green when heated to 1300°C or above. The duration of the retention time at temperatures below 1500°C had little effect on the amounts of alloy and slag formed, but the retention time at 1600°C had a marked effect on the extent of reduction as shown in Figs. 2 and 3.

Microscopic Examination of the Reacted SCICE Charges

The structures of the samples taken from the two

types of charge that had been subjected to the same experimental conditions were similar.

The early stages of reduction of the ore caused the formation of rounded grains of impure manganous oxide in a matrix of slag, together with the random nucleation of metallic particles throughout the ore particles. Further reduction took place mainly at the surface of the ore particles, where the size of the metallic particles and the amount of slag increased. Increasing temperature and retention time at those temperatures had little effect on the relative proportions of the three phases in the interior of the ore particles.

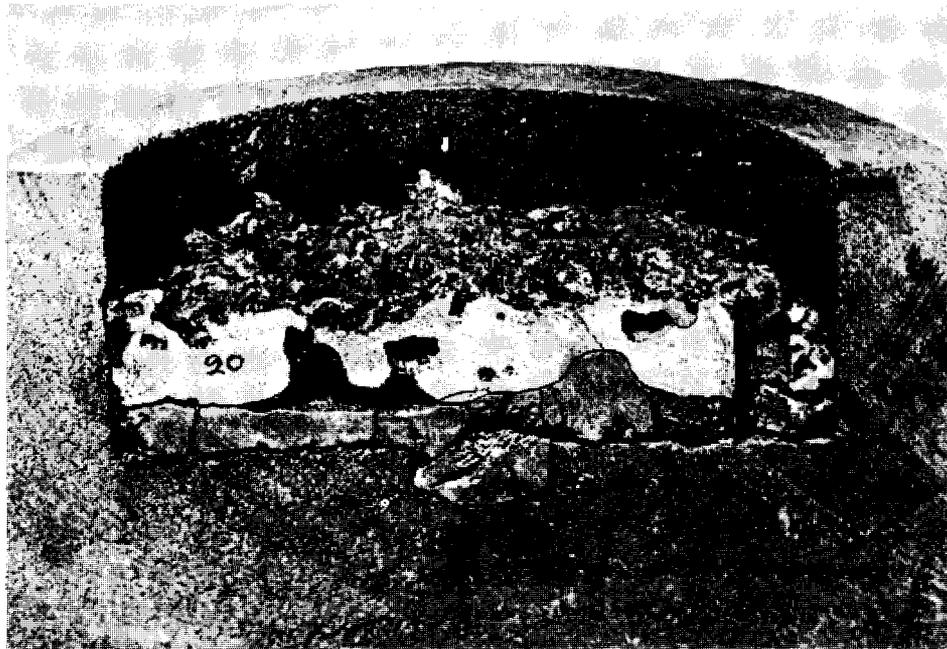


Fig. 3—Charge of ore and coal heated to 1600°C and held for 2 hours. (Note unreacted reducing agent on top of the slag layer)



Fig. 4—The appearance of a fractured particle of ore after it had been heated to 1400°C and then cooled. Grains of impure manganous oxide appear rounded and the slag is dendritic. SEM, 2000 X reduced 1460 X for reproduction, tilt 0°

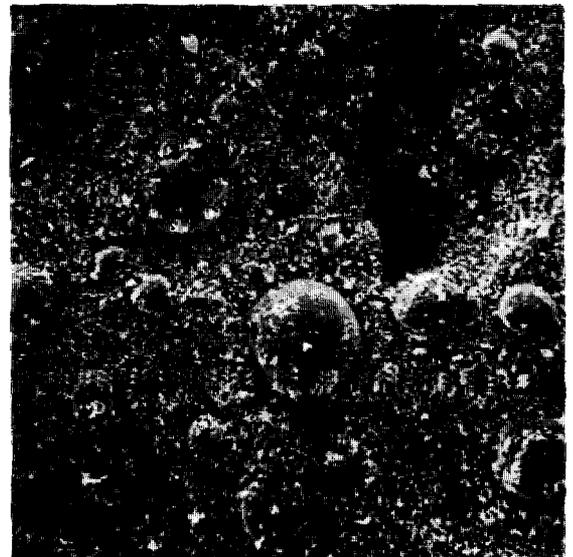


Fig. 5—Beads of alloy on the surface of an ore particle that was heated with coke to 1400°C and then cooled. A film of dendritic slag covers the ore particle. SEM, 100 X reduced 72 X for reproduction, tilt 30°

The early stages of reduction are shown in Fig. 4, which shows the fractured surface of an ore particle that was heated with coke to 1400°C and then cooled. The ore appeared porous, and the slag crystallized in the form of dendrites. Fig. 5 shows the metallic beads and slag that formed on the surface of an ore particle reacted under the same conditions.

The three phases (slag, oxide, and metal) and their general mode of occurrence in the interior of partially reduced particles of ore are shown in Fig. 6, which depicts a sample taken from a charge of ore and coke heated to 1500°C and cooled. It can be seen that the slag formed the continuous phase, and that the metallic nuclei adhered to the oxide grains, which appeared to be coalescing.

As already mentioned, the colour of the ore changed to green when it was heated with coal or coke to 1300°C or above. This change in colour was associated with the formation of green haloes round the grains of impure manganous oxide. Scanning electron microscopy showed that the haloes were caused by a reaction rim, the appearance of which is shown in Fig. 7.

The slag layer that formed on the surface of ore particles at an advanced stage of reaction is shown in Fig. 8. The larger metallic particles at the slag-oxide interface and the random nature of the metallic nuclei in the interior of the ore particles are apparent. The amount of slag in the interior of the ore particle is very small.

Fig. 9 shows a particle of ore breaking up in the slag layer that formed in a charge of ore and coke heated to 1600°C and held at that temperature for 1 hour. The smaller size of the oxide grains in the slag matrix indicates that the oxide is dissolving in the slag. An increase in the retention time from 1 to 2 hours at 1600°C caused a significant decrease in the amount of unreduced oxide in the slag. The shape of the oxide grains changed from rounded to elongated as shown in

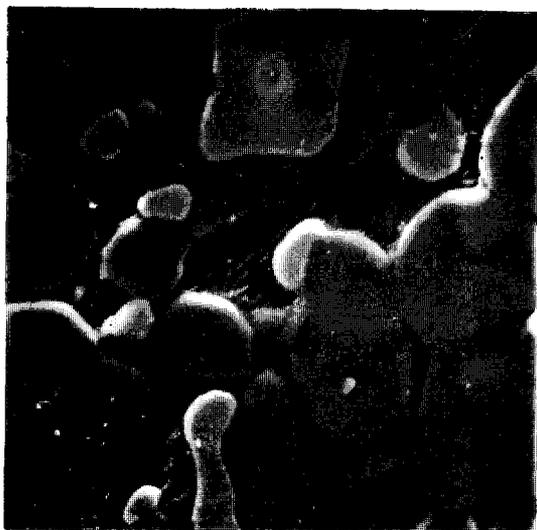


Fig. 6—The interior of an ore particle heated with coke to 1500°C and then cooled. The continuous phase is made up of slag. The grains of impure manganous oxide appear grey, and the metallic beads light grey. SEM, polished, 2700 X reduced to 1890 X for reproduction, tilt 45°

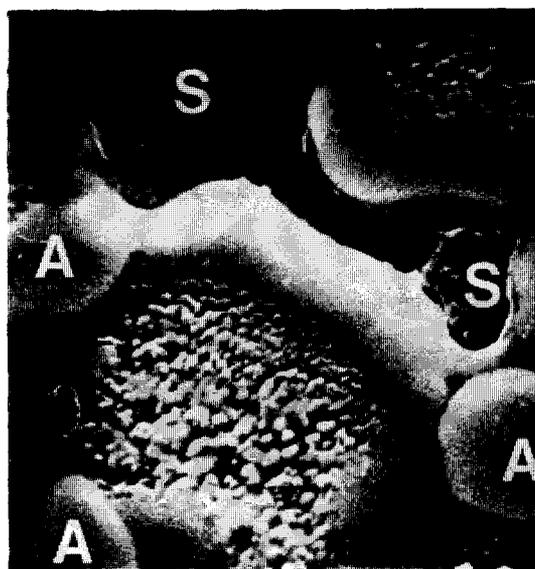


Fig. 7—The reaction rim that formed around grains of impure manganous oxide when ore and coke were heated to 1400°C and then cooled. Areas of slag (S) and metallic globules (A) are indicated. SEM, etched 2 per cent HCl, 10 000 X reduced 7000 X for reproduction, tilt 30°

Fig. 10. Electron-microprobe analysis by the EDS system showed that these grains were depleted in manganese and enriched in magnesium. Fig. 10 illustrates that the slag also contained particles of graphite, which probably originated from the alloy.

X-ray-diffraction Analysis

Charges of ore and coke reacted at 1300°C and held at that temperature for up to 2 hours consisted mainly of impure manganous oxide, α -iron, and a slag very similar to calcium orthosilicate (α -Ca₂SiO₄). The major peaks of the impure manganous oxide were displaced to higher angles by about 0,5° (2 θ). The same phases occurred in charges reacted at 1400°C (temperature maintained for 0 to 4 hours), although minor diffraction peaks began to appear owing to the formation of carbides. Identification of the carbides was difficult because of the low intensities and breadth of the peaks.

Examination of the charge heated to 1500°C and then cooled showed a small increase in the amount of alloy and slag. Quantities of α -iron could still be detected.

Charges reacted at 1600°C for 0 to 2 hours showed a significant increase in the amounts of alloy and slag, and a corresponding reduction in the amount of impure manganous oxide. The α -iron was present as small globules in the interior of particles of ore, but the major peak of this phase was obscured by reflections from the carbides.

Alloys from charges that had been reacted at 1400°C for 2 to 4 hours, or at 1600°C (temperature maintained for 0 to 2 hours), were analysed. Slag from charges reacted at 1600°C (temperature maintained for 0 to 2 hours) was also analysed.

The phases in the alloy were similar irrespective of the experimental conditions. The alloy from charges that had been reacted at 1400 and 1500°C was picked from the surface of ore particles and was of a different composition from the metallic globules that formed in

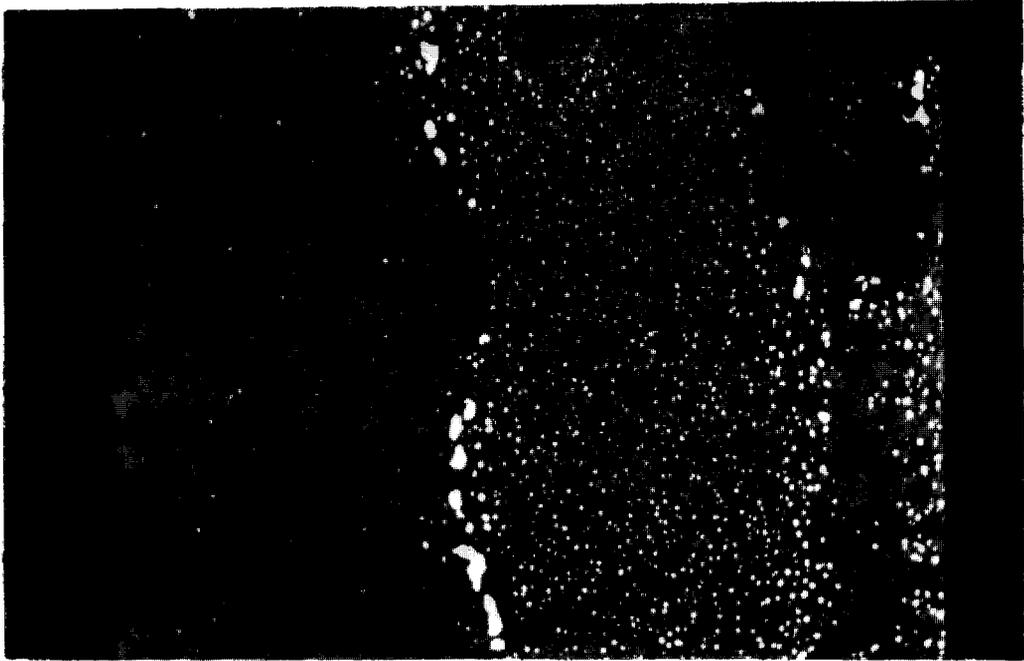


Fig. 8—A particle of ore heated with coke to 1600°C and then cooled. The metallic phase appears bright and is distributed randomly throughout the matrix. A film of slag can be seen to the left of the larger metallic beads. The pores appear black. Polished, reflected light, 320 X

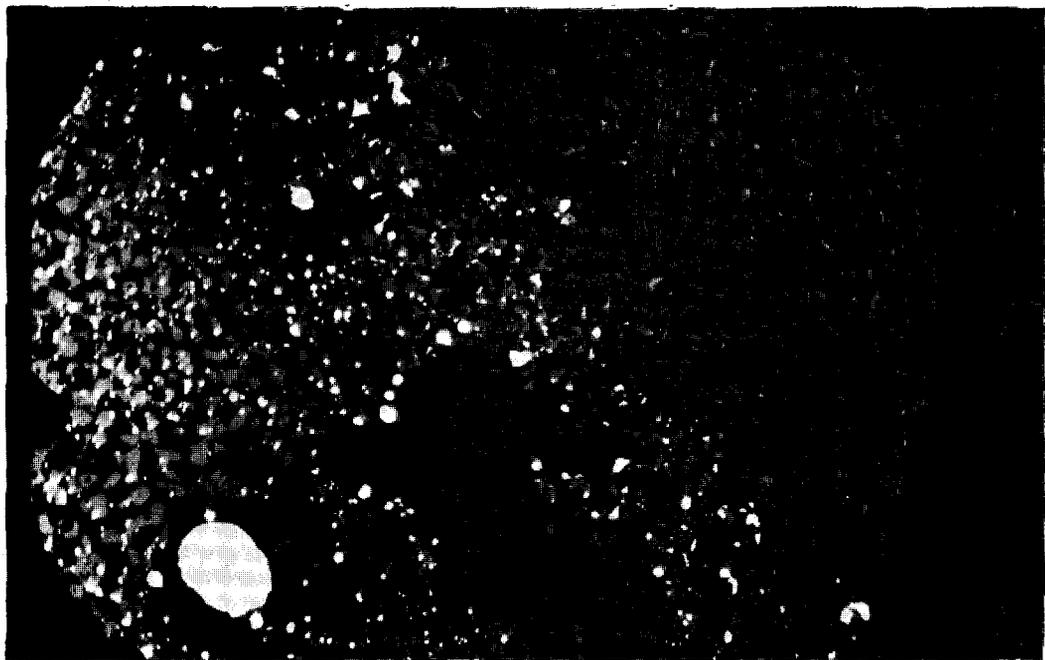


Fig. 9—A particle of ore breaking up in the slag matrix that formed by the reacting of ore and coke at 1600°C for 1 hour. The metallic phase appears bright, and the impure manganous oxide grey. Polished, reflected light, 120 X

the interior of particles of ore. Precise identification of the individual phases was not possible.

The d -spacings of the carbides agreed to some extent with those given for Mn_5C_2 and Fe_3C for values of d between $3,34\text{\AA}$ and $1,59\text{\AA}$. However, these traces showed many peaks, with d -values between $1,59\text{\AA}$ and $1,103\text{\AA}$, which could not be matched with the d -values of any of the carbides listed in the ASTM file. It is probable that the carbides that formed were mixed carbides of iron and manganese. Microscopic examination showed that the metallic component was in two main phases, while small quantities of material might have been in a third phase.

The traces of the non-metallic component of the charges showed that impure manganous oxide was still present in small quantities. The amount was reduced significantly when the retention time at 1600°C was increased from 0 to 2 hours. Some manganese was present in solution in the slag, as was indicated by the green colour of the slag. Precise identification of the slag phases was not possible owing to the complexity of the tracings obtained.

The X-ray-diffraction analysis was also carried out on samples taken from charges of ore and coal. A comparison of the tracings obtained with those discussed above showed that no significant differences existed between charges that had been reacted under comparable experimental conditions.

Mass Losses, and Alloy and Slag Compositions

The mass losses under different SCICE conditions varied from a minimum of 23 per cent for heating to 1300°C with Iscor coke and then cooling, to a maximum of 43 per cent for heating to 1600°C with Delmas coal and holding for 2 hours. Very little change in mass occurred during retention at temperatures below 1500°C . The rate of reduction was slow up to 1400°C , increased rapidly between 1400 and 1500°C , and decreased again above 1500°C . The composition of the alloys that formed under different conditions of temperature, retention time, and reducing agent is shown in Table IV. These results should be examined in the light of the fact that the amount of alloy formed at temperatures below 1500°C was very small, and that particles of alloy (about 2 to 5 g) were picked from the surface of ore particles. These alloys, therefore, cannot be said to have been representative of the entire metallic component present in any one charge. The alloy that formed in charges of ore and coke at 1300°C was analysed by EDS area-analyses on globules that had been mounted and polished.

The variations in the manganese and iron contents of the alloys formed by the heating of charges of ore and coke, and of ore and coal, between 1300 and 1600°C are plotted in Fig. 11. The alloy formed in the early stages consisted mainly of iron. Its manganese content increased with temperature, changing at a slower rate at temperatures greater than about 1450°C , owing to the increased volume of alloy present. The composition of the alloys was not affected significantly by the type of reducing agent used.

The influence of retention time on the manganese

content of the alloys is shown in Fig. 12. The alloys formed at 1600°C with Iscor coke and Delmas coal had very similar compositions. The alloys formed at 1400°C with Iscor coke appeared to be richer in manganese than the corresponding alloys formed with Delmas coal for retention periods of less than 4 hours. The discrepancy is believed to be due to errors in sampling.

The composition of the slags formed at 1600°C for retention periods of 1 or 2 hours is shown in Table IV. A drastic reduction in the proportions of manganous oxide and ferric oxide occurred owing to an increase in

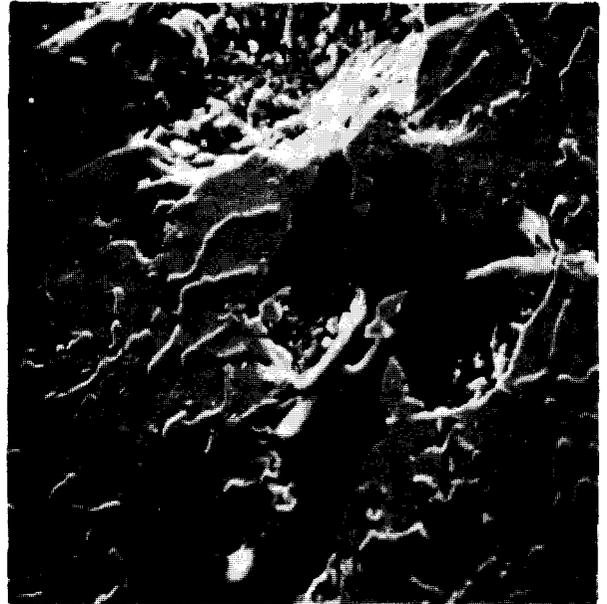


Fig. 10—Elongated grains of impure manganous oxide and particles of graphite in a matrix of slag, which formed by the reacting of ore and coke at 1600°C for 2 hours. SEM, polished, $575\times$ reduced $385\times$ for reproduction, tilt 45°

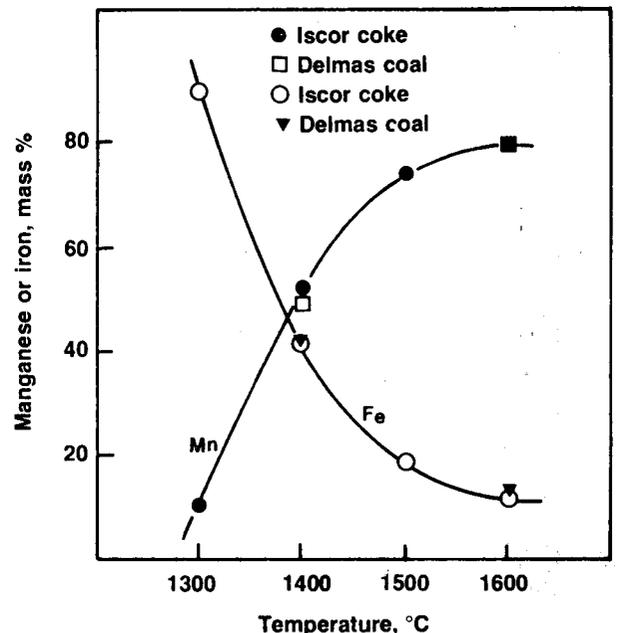


Fig. 11—Variation of manganese and iron in the alloy with temperature

the retention time at 1600°C from 1 to 2 hours. The slags contained lumps of partially reduced ore and dispersed grains of impure manganous oxide. The iron was present mainly as metallic globules in the slag and partially reduced lumps of ore.

Discussion

The results of the X-ray-diffraction and EDS

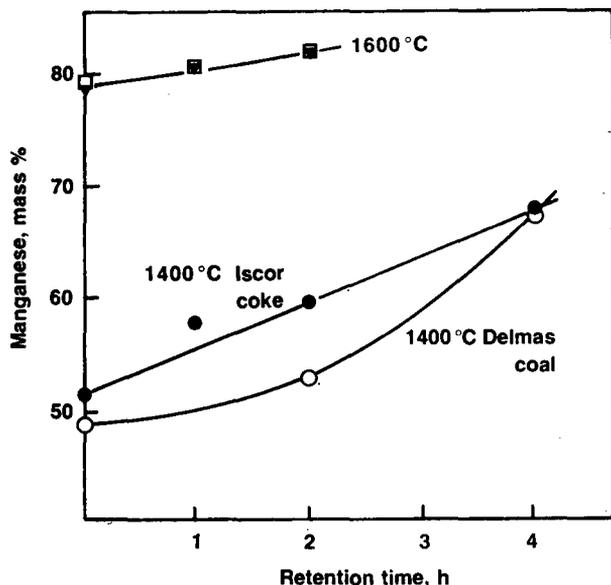


Fig. 12—Variation of manganese in the alloy with retention time

analyses show that the reduction of iron oxide to α -iron precedes the reduction of manganous oxide. This could be expected in view of the higher stability of manganous oxide at all temperatures¹².

From the composition of the alloys produced by the retention of the SCICE charges at 1600°C from 0 to 2 hours, it is evident that the degree of reduction achieved was similar for the two reducing agents. This result is in general agreement with the findings of Grimsley⁵, who studied the rate of reduction of Mamatwan ore fines with graphite and activated char between temperatures of 1000 and 1300°C. He found that the rate of reduction was faster with activated char during the initial stages, but that the degree of reduction achieved after 90 minutes was the same for the two reducing agents.

The following reactions result in the formation of the final alloy and slag.

The decomposition of the calcite and dolomite at temperatures⁶ between 600 and 900°C makes the ore porous, permitting rapid reduction to occur throughout the ore particles by reaction with carbon monoxide. This results in the formation of coarse grains of manganous oxide (Fig. 4) and a primary slag, which consists essentially of calcium oxide and silica. The primary slag forms a film on the surface of the ore particles (Fig. 5) and a continuous network in the interior of the ore particles (Fig. 6). The hematite in the ore is reduced to metallic iron, which forms globules that adhere to the oxide grains (Fig. 6). The magnesium oxide released from the dolomite goes into solution in the manganous oxide grains.

TABLE IV

COMPOSITION OF THE ALLOYS AND SLAGS FORMED UNDER DIFFERENT EXPERIMENTAL CONDITIONS

Temperature of reaction °C	Retention time h	Reducing agent*	Element					S
			Mn	C	Fe	Si	P	
<i>Alloys</i>								
1300†	0	I.C.	10,63 ±2,66	—	89,37 ±2,66	—	—	—
1300†	1	I.C.	13,37 ±8,73	—	86,63 ±8,73	—	—	—
1300†	2	I.C.	10,83 ±5,22	—	89,17 ±5,22	—	—	—
1400	0	I.C.	51,4	6,1	41,1	0,13	—	—
1400	1	I.C.	57,8	6,0	31,5	0,36	0,09	0,04
1400	2	I.C.	59,6	5,5	31,9	0,30	0,09	0,05
1400	4	I.C.	67,5	6,1	23,8	0,34	0,07	0,04
1400	0	D.C.	48,9	5,6	41,0	0,59	0,17	0,06
1400	2	D.C.	53,0	6,0	39,6	0,12	0,08	0,02
1400	4	D.C.	67,1	6,1	23,0	0,45	0,09	0,13
1500	0	I.C.	73,6	6,9	18,2	0,15	0,09	0,02
1600	0	I.C.	79,1	7,0	11,2	0,23	0,06	0,04
1600	1	I.C.	80,3	7,5	10,1	0,19	0,06	0,02
1600	2	I.C.	81,3	7,4	10,5	0,05	0,06	< 0,01
1600	0	D.C.	78,7	7,1	12,0	0,22	0,07	0,03
1600	1	D.C.	80,5	7,7	10,5	0,13	0,06	0,02
1600	2	D.C.	81,5	7,2	11,0	0,03	0,05	0,01
			MgO	Al ₂ O ₃	SiO ₂	CaO	MnO	Fe ₂ O ₃
<i>Slags</i>								
1600	1	I.C.	8,98	6,59	16,70	34,92	30,02	3,62
1600	2	I.C.	11,19	8,63	22,51	45,32	10,43	2,27
1600	1	D.C.	8,33	5,25	16,23	33,70	35,55	5,21
1600	2	D.C.	10,64	9,30	23,54	43,95	10,41	1,41

*I.C. = Iscor coke, D.C. = Delmas coal.

†These analyses were carried out by the EDS method. The figures given are the means of 3 determinations and their standard deviation.

The formation of the primary slag impedes further reduction by carbon monoxide in the interior of the ore particles, and no substantial increase in metallization occurs with increasing temperature or retention time. The size of the metallic beads on the surface of the ore particles increases rapidly owing to the reduction of manganous oxide by carbon dissolved in the metal. The discontinuous nature of the oxide (Fig. 9), the reaction rim on the surface of oxide grains (Fig. 7), and the changes in shape (Fig. 10) and composition of the oxide grains suggest that manganous oxide is transported to the metal by dissolution into the slag.

With further reduction, the bigger metallic beads drain to the bottom of the crucible, the volume of slag increases, and contact between the slag and the reducing agent is improved. At that stage, reduction occurs from the slag mainly by solid carbon. Reduction at the interface between the slag and the alloy layer is also possible.

A number of reactions⁸ could describe the reduction of manganous oxide in solution from the slag. Thermodynamic considerations show that the most probable reactions are as follows:



$$\Delta G_T^\circ = 265,7 - 0,18T \text{ kJ (reference 15)}$$



$$\Delta G_T^\circ < 1500 = 273,4 - 0,16T \text{ kJ (reference 15)}$$

$$\Delta G_T^\circ > 1500 = 287,9 - 0,17T \text{ kJ (reference 15)}$$

The standard free energy change for the reduction to manganese metal and carbide equals zero at 1420 and 1280°C.

The co-existence of small areas of iron and green impure manganous oxide can be explained by use of the observations of Davies and Richardson¹⁴. These investigators measured the extent to which manganous oxide departs from the stoichiometric composition as the partial pressure of oxygen is raised from 10^{-8} or 10^{-9} kPa to 10 kPa at temperatures between 1500 and 1600°C. It was suspected that the composition of manganous oxide varies because, in experiments involving solid manganous oxide at 1500 to 1600°C, it was observed that the colour of the manganous oxide changed from green to black as the partial pressure of oxygen in the system was increased.

At temperatures between 1300 and 1550°C, manganous oxide is formed from manganic oxide at partial pressures of oxygen below 10,133 kPa (10^{-1} atm) and below approximately 0,1 kPa (10^{-3} atm) respectively¹⁵.

Based on data from Kubaschewski *et al.*¹⁶, calculations of the partial pressure of oxygen for the reduction of ferrous oxide to iron give values of about 2×10^{-9} and 6×10^{-7} kPa at temperatures of 1300 and 1600°C respectively. Thus, the value of oxygen partial pressure in the system must have been lower than 2×10^{-9} and 6×10^{-7} kPa at temperatures of 1300 and 1600°C respectively if metallic iron formed in the ore. These values for the partial pressure of oxygen are consistent

with the formation of green impure manganous oxide¹⁴.

The primary slag is dicalcium silicate as this silicate is more stable¹⁷ than silicates such as $\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$, $\text{MnO} \cdot \text{SiO}_2$, and $2\text{MnO} \cdot \text{SiO}_2$ at temperatures between 1300 and 1600°C. The composition of the slag changes as reduction progresses owing to the incorporation of the ash constituents in the reducing agent and the liberation of magnesia from solid solution in the manganous oxide. The final slag has a composition in the system Al_2O_3 -CaO-MgO-SiO₂-MnO.

Conclusions

The reactions that occur during the reduction of Mamatwan manganese ore with either Iscor coke or Delmas coal are not significantly different.

Reduction of the ore at temperatures between 1300 and 1600°C appears to occur in three main stages.

The first stage involves the rapid reduction of higher manganese oxides to manganous oxide and of hematite to metallic iron by carbon monoxide. A primary slag forms that contains mainly calcium oxide and silica.

The second stage involves the dissolution of manganous oxide into the slag and reduction at the surface of ore particles by carbon dissolved in the metallic beads.

During the third stage, reduction occurs mainly by solid carbon in contact with the molten slag. Some reduction may occur from the slag in contact with the layer of alloy at the bottom of the crucible.

The final slag has a composition in the Al_2O_3 -CaO-MgO-SiO₂-MnO system.

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