THE BEHAVIOUR OF COKE IN SUBMERGED ARC FURNACE SMELTING OF FERROMANGANESE

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ABSTRACT

It has been observed that the productivity of ferromanganese furnaces, and the stability of metal and slag compositions, vary considerably according to the type of coke used as reductant. However, the desired properties of coke for optimum furnace performance are not well understood. In this investigation, the behaviour of four cokes, which exhibited a wide range of performance in ferromanganese production, was investigated by means of laboratory simulations of reducing conditions in the furnace.

The Stationary Charge in Controlled Environment (SCICE) technique was used to simulate the conditions in the furnace shaft. Batches of raw materials, mixed in the same proportions as used in practice, were heated at fixed rates to 900, 1100 and 1300°C then cooled. The mass loss was used as a measure of the degree of reduction. Conditions in the lower part of the furnace were simulated by means of melt-reduction experiments in which lumps of coke were drilled out to form crucibles in which enriched ferromanganese slags were reduced at 1500 and 1550°C then cooled.

An examination of the raw materials and the cooled, reacted charges using a variety of analytical and characterization techniques enabled the sequence of reaction and changes in morphology of the raw materials to be followed. This enabled an understanding of the behaviour of the cokes during reduction to be developed, which was then used to explain the observed performance of the cokes in practice. By relating the observed behaviour of the cokes in the laboratory tests to measurable properties of the unreacted cokes and to their observed performance in practice, it was shown that to achieve high productivity and good furnace performance, cokes should be selected to have moderately high reactivity towards CO_2 (Boudouard reactivity) relative to conventional iron blast furnace cokes.

1. INTRODUCTION

The reactions and changes in the burden materials during the submerged arc furnace production of high carbon ferromanganese have been extensively investigated through both plant and laboratory scale studies. The excavation of a frozen furnace at the Meyerton ferromanganese plant in South Africa in 1977 has provided considerable understanding of the changes in the burden materials and the nature of the reaction zones. Details of the excavation procedure are given by Barcza *et al*. [1], and studies by Koursaris [2-4] on the excavation products revealed that the interior of the furnace could be divided into nine zones of which three appear to be of most importance in reduction and metallurgical processing. These are: a cone of fast descending burden around each electrode; a coke bed directly below the electrodes; and a mixed coke-slag layer beneath the coke bed.

In some early laboratory studies of carbonaceous reduction of iron ores [5-7] a technique to simulate the processes that occur in the shaft of the iron blast furnace was developed which became known as the Stationary Charge In Controlled Environment (SCICE) technique. Urquhart [8] used the SCICE technique to study the production of high-carbon ferrochromium in a submerged arc furnace and the technique was subsequently used by Grimsley [9], Dewar and See [10] and Koursaris and See [11] to investigate the reduction of South African Mamatwan manganese ore at relatively low temperatures using Delmas and ISCOR cokes.

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Examination of samples from the “dig-out” the Meyerton furnace [1] by Koursaris and Finn [4] revealed that the mineralogical and morphological changes in the ore were similar to those that occurred in the SCICE investigations [11].

The major findings of that study were that between 1300 and 1600ºC reduction occurred in three main stages:

- rapid reduction of higher manganese oxides to MnO and of hematite to metallic iron (in the solid state) by carbon monoxide and formation of a primary slag consisting mainly of CaO and SiO_2;
- dissolution of MnO into the slag and reduction at the surface of ore lumps to form metallic beads; and
- reduction by lump carbon in contact with molten slag.

In all previous studies of reduction of manganese ores to form ferromanganese, most attention has been paid to the behaviour of the ore and little attention has been paid to that of the coke. Pistorius [12] recently reviewed the role of carbon in ferro-alloy production and highlighted the importance of the kinetics of carbon dissolution in the metal.

The objective of the present work was to investigate the behaviour of coke in ferromanganese production in order to identify the desirable properties of coke for optimum furnace performance. The investigation was undertaken to attempt to explain the different furnace performance observed by metallurgists at the TEMCO plant then operated by BHP Limited (now BHP Billiton Limited) in Tasmania, Australia. For ferromanganese production, TEMCO operates two Elkem closed top, rotating arc furnaces rated at 27,000 kVA and 29,000 kVA and an Elkem 36,000 kVA stationary closed furnace. The ferromanganese is produced from metallurgical grade lump manganese ore from Groote Eylandt in Australia’s Northern Territory, sinter produced from manganese ore fines on a Lurgi down-draught sintering machine at TEMCO, and iron ore for grade control.

In the late 1980s, TEMCO metallurgists ran a series of campaigns using cokes from different sources and observed a range of furnace performance.

For some cokes, the furnace was stable and productivity was high while for others productivity was low and the furnace behaved poorly; for example,

- The temperature of the top of the furnace increased by more than 300ºC.
- The furnace off-gas was high in hydrogen and sometimes contained volatilised manganese.
- The slag and alloy composition varied over a wide range.
- Graphitised coke was tapped from the furnace with the slag.
- Coke, electrode and power consumption rates were high.

A selection of coke samples which exhibited a range of behaviours from good to bad furnace performance was supplied by TEMCO for the purpose of attempting to identify the characteristics of the cokes which caused the variation in performance. The investigation involved characterising the cokes to determine their range of properties and performing a series of experiments in the laboratory to simulate the reduction of burden materials.

2. COKE CHARACTERISATION

The composition of the coke samples is given in Table 1. The Newcastle, Port Kembla and Whyalla cokes are blast furnace cokes prepared at the respective steel works in Australia (the Newcastle plant has subsequently closed). The source of the Japanese coke is not known. Use of the Japanese and Newcastle cokes was found by TEMCO metallurgists to result in better furnace performance than use of the Port Kembla and Whyalla cokes.

A microscopic examination revealed that the Japanese coke contained large quantities of isotropic and anisotropic fusible materials. The anisotropic material had the widest variety of mosaic textures, ranging from fine to medium and course grain. It was concluded that the Japanese coke was made from a blend of low, medium and high rank coals and coke breeze. Newcastle coke contained a smaller amount of fusible material than the Japanese coke. The fusible materials also contained a narrower variety of mosaic textures;

there was little isotropic material and no flow/patch mosaic texture. This indicates that the Newcastle coke was made from a blend of low and medium rank coals with no added coke breeze. The Port Kembla and Whyalla cokes were micro-texturally similar and both contained larger quantities of non-fusible materials than the Newcastle and Japanese cokes. The blend from which they were produced contained a larger quantity of medium to high rank coal as revealed by the coarser mosaic textures. The non-fusible components in the Port Kembla, Whyalla and Newcastle cokes exhibited both isotropic and anisotropic properties. Fewer non-fusible grains were present in the Japanese coke than the Port Kembla and Whyalla cokes, while Newcastle coke contained fewer non-fusible grains than Japanese coke.

Table 1. Composition of Coke Samples (wt%).

	Japanese	**Newcastle**	**Port Kembla**	**Whyalla**
Fixed Carbon	87.9	86.6	88.5	85.7
Volatile Matter	0.60	0.50	0.30	1.04
SiO_2	6.07	3.72	6.54	7.58
Al_2O_3	3.07	2.01	4.35	3.91
CaO	0.32	0.50	0.26	0.40
Fe_2O_3	2.20	1.24	1.14	1.37
S	-	0.40	-	0.36
P	0.09	0.07	0.05	0.04
Mn	0.09	0.32	0.01	0.05
K_2 O	0.13	0.17	0.13	0.15
MgO	0.12	0.10	0.02	0.11
TOTAL	101.6	95.6	101.7	99.3

Rounded, oval and elongated pores were present in all the cokes. The rounded and oval pores were formed by degasification during coking while the elongated pores were formed by interconnection of degasification pores, also during coking, or originated from the original coal. The Japanese coke contained the largest degasification pores and their walls were relatively thin. Pore size in the Whyalla coke was larger than in Port Kembla coke but smaller than in the Newcastle and Japanese cokes. The pores in the Japanese coke occurred predominantly in the fusible components while they were present in both the fusible and non-fusible grains in the other three cokes.

Table 2. Average force (and Standard Deviation) required to break coke particles under compression.

Coke Type	**Size Range (mm)**	**Force (N)**	**S.D. (N)**
Japanese	50-200	760	185
	20-50	200	75.0
	6-19	100	40.0
Newcastle	50-200	530	200
	20-50	110	60.0
	6-19	125	55.0
Port Kembla	50-200	940	285
	20-50	210	60.0
	6-19	105	40.0
Whyalla	50-200	2060	315
	20-50	185	105
	6-19	170	85.0

2.1 Strength

A Tinius Olsen hardness testing machine was used to determine the strength of coke particles. The apparatus had two plates which were free to rotate in all directions so that the force exerted on particles was through their flattest faces. The tests were carried out on coke samples between 6 and 200 mm in diameter. Particles were tested individually and, for each coke size fraction, 10 measurements were made then averaged. The values are shown in Table 2.

The magnitude of the standard deviation indicates there was a large variation in strength, which is to be expected for non-homogenous materials of irregular shape. The averaged results show that, for each coke type, strength increased considerably with increasing size of particles. In the size range used by TEMCO (6 – 19 mm) Whyalla coke was the strongest followed by Newcastle coke with the Japanese and Port Kembla cokes having about the same strength.

2.2 Porosity

Porosity in coke is of two forms: open (pores that are interconnected and which lead to the surface of the grain) and closed. Open porosity was measured using a mercury porosimeter. Preliminary measurements indicated that the bulk of open porosity was in the size range 10 – 100 μm. Closed porosity was measured using an IBAS 2000 optical image analyser to examine polished sections of coke. The pores were discriminated from coke on the basis of reflectivity and closed pores were defined as all pores with radius less than 10 μm. One hundred images were examined for each sample, which were processed separately then averaged. The results are shown in Table 3.

The total porosity of all the cokes was around 40 percent, with open porosity being the larger component in all cases. There was not much variation between the four coke types of the open and closed porosity though the Japanese and Newcastle cokes had slightly lower open porosity and slightly higher closed porosity than the Port Kembla and Whyalla cokes.

Table 3. Open and closed porosity of the cokes “as received” (vol. %).

	Open Porosity (%)	**Closed Porosity (%)**	**Total**
Japanese	24.6	15.3	39.9
Newcastle	22.6	16.5	39.1
Port Kembla	27.2	12.2	39.4
Whyalla	29.3	13.4	42.6

2.3 Reactivity

The reactivity of the cokes with respect to carbon dioxide (the Boudouard reactivity),

$$CO_2(g) + C(s) = 2\,CO(g) \tag{1}$$

was determined at 1000ºC on two size ranges of particles. The results are presented in Table 4. Reactivity is defined as the volume of CO_2 (at STP) that reacts with 1.0 g of coke per second. In practice the reaction was carried out over a period of time and the reactivity averaged over the first 30 minutes and over the first 45 minutes are given in the table. The weight loss of the coke samples after 55 minutes of reaction with CO_2 is also given. The results show there are no significant differences between the reactivities of the cokes determined after 30 and 45 minutes, nor are there any significant differences between the reactivities determined on the two size fractions except for the Whyalla coke; it is slightly more reactive in the smaller size range. Japanese coke is clearly the most reactive followed by Newcastle coke. The Port Kembla coke is more reactive than the Whyalla coke in the smaller particles size range but is about equal in reactivity in the smaller size range. The trends in weight loss after 55 minutes reaction are similar to the trends in reactivity.

Table 4. Coke Reactivity Index at 1000 ºC for the “as received” cokes.

	0.6 – 1.2 mm Particles			**1.00 – 3.00 mm Particles**		
	Reactivity ($cm^3g^{-1}s^{-1}$)		**Weight loss (%)**	**Reactivity ($cm^3g^{-1}s^{-1}$)**		**Weight loss (%)**
	30 min	**45 min**	**55 min**	**30 min**	**45 min**	**55 min**
Japanese	0.36	0.34	13.5	0.32	0.29	10.40
Newcastle	0.23	0.21	7.40	0.20	0.20	8.40
Port Kembla	0.15	0.15	4.40	0.15	0.14	3.50
Whyalla	0.18	0.19	3.90	0.08	0.08	3.10

3. EXPERIMENTAL INVESTIGATION OF REDUCTION OF SINTER BURDEN

The coke characterisation results suggest that strength and initial porosity of the cokes are not related directly to the performance of the cokes in the furnace. However the reactivity of the cokes correlates well with the behaviour of the cokes in the furnace, the more reactive cokes being reported to perform better than the less reactive cokes. An experimental program was designed to assess whether coke reactivity could affect the reduction behaviour of the manganese burden. The program involved laboratory scale SCICE tests to examine the reduction of furnace burden up to 1300ºC and a series of reduction-from-melt experiments to investigate reduction in the higher temperature mixed slag-coke zone of the furnace.

3.1 SCICE Experiments

The objective of the SCICE test is to provide conditions that simulate a batch of raw material descending through the upper part of the furnace shaft. For a test, a batch of approximately 500 g of charge, made up of the raw materials used by TEMCO and in the same proportion, was heated in an alumino-silicate crucible in an induction furnace at the rate of 350ºC per hour to a predetermined temperature (up to 1300ºC), held at temperature for one hour, then cooled under nitrogen. To obtain a reasonably homogenous charge the particle sizes of the raw materials used in the experimental program were approximately one tenth that used in practice at TEMCO.

The composition of the raw materials used in the tests is given in Table 5 and the charge mixture used for standard conditions is shown in Table 6. The experimental set up is illustrated in Figure 1. Considerable effort was devoted to developing a procedure that gave reproducible temperature profiles. The crucible, with charge and thermocouple, was weighed before each test and again after cooling at the completion of each test.

Table 5. Composition of raw materials used in the SCICE tests (mass percent).

Constituent	**Sinter**	**Mn Ore**	**Fe Ore**	**Limestone**
MnO	56.30	48.10	0.55	0.08
SiO_2	6.80	7.10	2.43	2.00
Al_2O_3	4.60	4.20	0.84	0.30
CaO	0.09	0.07	0.30	52.70
MgO	-	0.12	0.16	1.80
BaO	1.60	0.93	-	-
Na_2O	0.10	0.22	-	0.10
K_2O	1.20	1.65	-	0.10
Fe	5.90	4.40	65.60	0.30
TiO_2	0.23	-	0.04	0.02
P_2O_5	0.09	0.09	-	<0.01
Cr_2O_3	-	-	-	-
ZnO	-	-	-	<0.01
Free H_2O	-	-	1.26	-

At the completion of a test, the contents of the crucible were emptied onto a metal tray and sieved to separate out the unreacted coke, which could be easily separated due to its smaller size fraction. Limestone, identified by its white colour, was then separated by hand, and the unreacted iron ore was separated using a magnet. Sinter and manganese lump ore were not easily distinguishable and generally both were greenish in colour after reaction. However the porous structure of the sinter helped to distinguish it from manganese ore. Each component recovered was weighed and representative samples of each were taken for analysis and characterisation.

Table 6. Masses and sizes of raw materials used in the SCICE experiment.

Charge	**Mass (g)**	**Wt%**	**Size (mm)**
Sinter	342.4	68.6	2.36 – 7.5
Mn lump ore	20.7	4.5	2.36 – 7.5
Limestone	32.5	6.5	2.36 – 7.5
Iron ore	18.0	3.6	2.36 – 7.5
Coke	103.0	16.8	0.6 – 1.2
TOTAL	516.6	100.0	

3.1.1 Mass loss results

The mass loss results for the crucibles and contents due to reactions releasing volatiles, predominantly CO_2 and CO, are shown graphically in Figure 2. Coke mass loss is shown in Figure 3. As expected, the total mass loss, and mass loss by the coke, increased with the final temperature achieved but, interestingly, there is a significant difference in the mass loss achieved at each temperature depending on the coke type used in the experiment. The trends for total mass loss and coke mass loss are consistent and strongly indicate that the rate of reduction of the burden materials in the experiments was controlled by the Boudouard reaction since the order of the degree of reduction is similar to the order of the reactivity of the coke towards CO_2 at 1000ºC (Table 4).

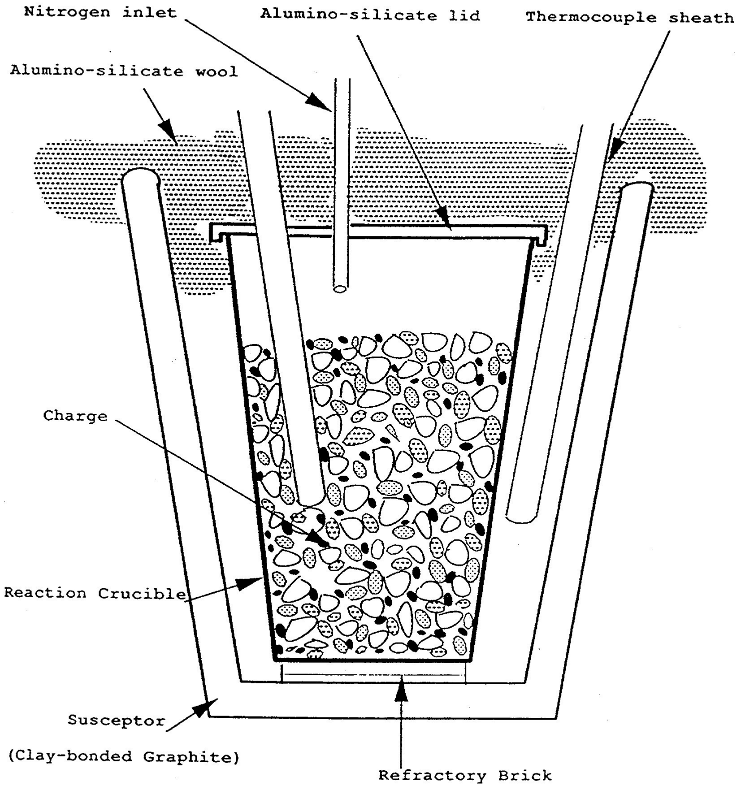

Figure 1. Schematic diagram of the crucible assembly used for the SCICE experiments.

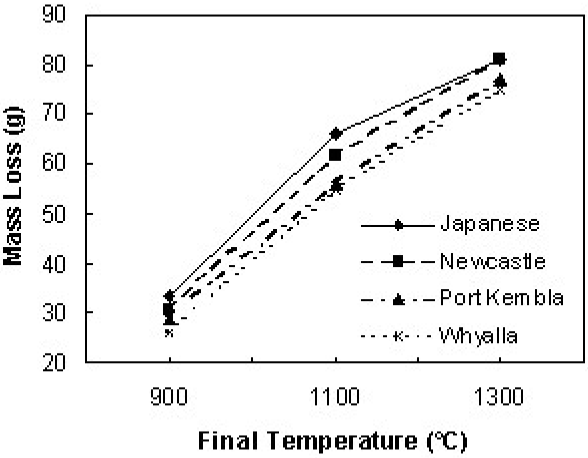

Figure 2. Total mass loss of crucible contents in the SCICE experiments.

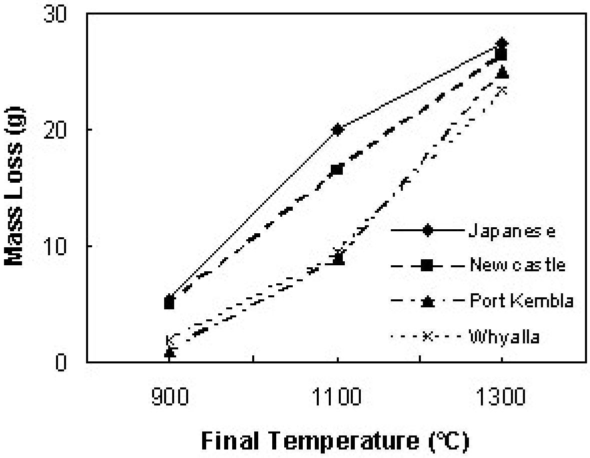

Figure 3. Mass loss of the coke component of the SCICE experiment.

3.1.2 Changes in limestone, iron ore, and sinter

Examination of the products from the 900ºC series of tests revealed that all the limestone had decomposed to CaO and the iron ore (which was initially hematite and goethite) had partially transformed to magnetite and wustite. At 1100°C some reduction of the iron ore to metallic iron had occurred in all cases. For Japanese coke all the iron ore had been reduced to metal and for Newcastle coke iron oxide that remained unreduced had converted fully to wustite, whereas for the other cokes some magnetite remained. At 1300ºC all the iron ore had been reduced to globules of metal for all four cokes. The metal globules typically contained about 16 wt% Mn and 4 wt% C.

The unreacted sinter consisted of Hausmanite (Mn_3O_4), Jacobsite $(Mn,Fe)_3O_4$, tephroite (Mn_2SiO_4) and some MnO. At 900 ºC the Hausmanite and Jacobsite in the sinter from Japanese and Newcastle coke tests had converted to MnO while those reacted with the other cokes had only partially converted. At 1100ºC, all remaining Hausmanite and Jacobsite had converted and some metallic "prills" of Fe, containing 10 – 30 wt% Mn, had formed. These were typically 35 – 50 µm in diameter and the relative amount of metal was highest for the Japanese and Newcastle cokes. At 1300ºC partial fusion of the sinter had occurred, the amount of metal had increased further (though the relative amounts were higher for Japanese and Newcastle cokes), and the metallic "prills" had increased in size to typically 50 – 100 µm and contained 30 – 40 wt% Mn.

3.1.3 Changes in coke properties

At 900ºC, Japanese coke had the greatest and Port Kembla coke the least changes in micro-structure and texture. Both the fusible and non-fusible materials of the Japanese coke showed signs of reaction whereas in the other cokes only the fusible materials showed signs of reaction. At 1100ºC, the micro-structural changes were greater than at 900ºC and the pores sizes were usually much larger. Serration occurred in the fusible and non-fusible materials of the Japanese coke while in the other cokes only the lower rank non-fusible material became more reactive. At 1300ºC, most of the Japanese coke had eroded to small fragments due to serration on the pore peripheries. The non-fusible materials in the other cokes were the initial points of reaction leading to erosion and fragmentation. The change in open porosity of the reacted cokes is shown in Figure 4.

The reactivity towards CO_2 (at 1000ºC) of the four cokes reacted at 1100 and 1300ºC was determined and the results are presented Table 7 as mass loss after 55 minutes reaction with CO_2. The results show that the cokes from the 1100ºC SCICE series had reactivities about 2 to 3 times higher than the "as received" cokes and that the reactivities increased further in the 1300ºC series but tended to converge in value. This is consistent with the results in Figure 3 which show that there was greater spread in the mass loss values of the four varieties of coke at 1100ºC compared to 1300ºC (9 – 20 g compared with 23 – 27 g, respectively). This would be expected if the Boudouard reaction was rate-limiting in the temperature range 900 to 1300ºC.

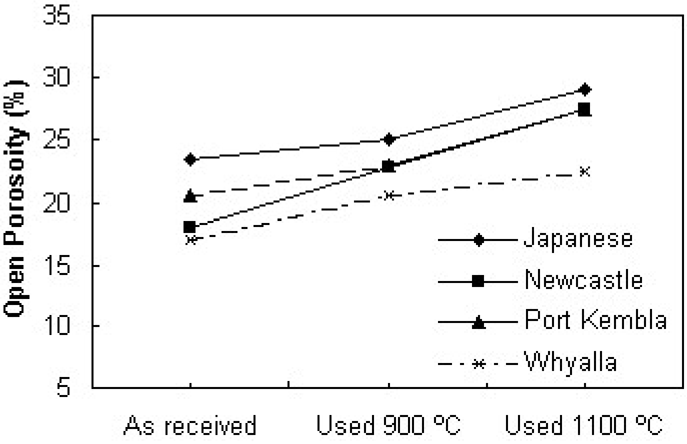

Figure 4. Open porosity of reacted cokes determined by mercury porosimetry.

Table 7. Reactivity, as % weight loss of coke after 55 minutes reaction with CO_2 at 1000ºC, of coke samples from the SCICE experiments.

	Coke "as received"*	**COKE AFTER REACTION WITH RAW MATERIALS**	
		Reacted at 1100ºC	**Reacted at 1300ºC**
Japanese	13.5	26.4	31.6
Newcastle	7.4	18.7	37.3
Port Kembla	4.4	14.4	27.1
Whyalla	3.9	13.3	34.1

*from Table 4

3.2 Reduction-From-Melt Experiments

To simulate conditions for reduction of MnO-rich slag in the lower part of the furnace, higher temperatures than could be achieved in the SCICE experiments are needed. An upper limit of about 1300ºC was imposed on the SCICE experiments because, above that temperature, the crucibles were excessively attacked by the slag, contaminating the slag and, at higher temperatures, failing to contain the slag. An approach was used in which "enriched" slags of the composition likely to occur in the first-formed slag were reacted in hollows created by drilling into lumps of coke. In this way the coke acted as the container for the slag as well as being the reductant. "As received" coke was used for these tests because the coke recovered after the SCICE experiments was too porous and weak.

Finely ground ferromanganese slag from TEMCO was doped with MnO_2 and Fe_2O_3 powders (mixed with a stoichiometric amount of powdered carbon to form MnO and FeO) and remelted under nitrogen. The resulting slag, of composition shown in Table 8, was reground and used in the Reduction-from-Melt experiments. In an experiment, about 10 g of the enriched slag was poured into the hole in a lump of coke which was placed on a bed of alumina powder in a silicon carbide tray then covered with an inverted alumino-silicate crucible. The assembly was placed in an electrically heated muffle furnace, programmed to heat at 1500ºC/hour, and heated to 1500 or 1550ºC. It was held at that temperature for 15 minutes, for the 1500ºC tests, or 30 minutes, for the 1550ºC tests, then the furnace was switched off. The cooling rate of the furnace at high temperatures was about 80 ºC/min which ensured that the crucible contents solidified in less than 5 minutes after switching off the furnace. The reacted "crucibles" were sectioned, one section being used for microscopic examination, the other for chemical analysis. A typical section of a "crucible" is shown in Figure 5. An equilibrium experiment was also performed using a Port Kembla coke "crucible" which was heated to 1500ºC and held for 12 hours.

Table 8. Composition of the "enriched" slag used for reduction-from-melt tests (wt%).

MnO	**FeO**	**SiO_2**	**Al_2O_3**	**CaO**	**MgO**	**BaO**	**K_2O**	**TiO_2**	**P_2O_5**	**S**
57.4	5.1	11.0	7.6	5.9	2.5	1.7	2.8	0.28	0.13	0.35

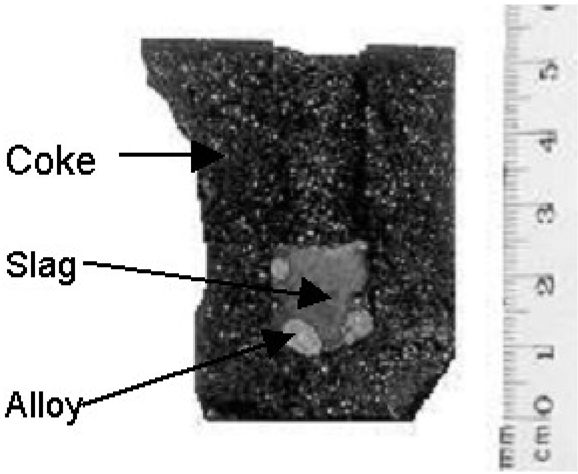

Figure 5. Photograph of the products of a typical melt reduction test.

Table 9. Composition of alloys produced in the reduction-from-melt experiments (wt%).

	1500ºC					1550ºC			
	Japanese	**Newcastle**	**Port Kembla**	**Whyalla**	**Equilibrium**	**Japanese**	**Newcastle**	**Port Kembla**	**Whyalla**
Mn	-		-	-	70.9	-		-	-
Fe*	-	-	-	-	13.9	-		-	-
C*	7.1	-	7.2	-	4.7	7.2		7.4	-
Si*	0.1	-	0.6	-	7.6	0.6		0.1	-
Mn/Fe	5.4$^+$	3.9$^+$	1.8$^+$	2.3$^+$	5.1*	5.1$^+$	4.1$^+$	3.8$^+$	4.0$^+$

*bulk chemical analysis of alloy recovered from crucible
$^+$average of 3 microprobe point analyses

The degree of reduction can be followed by the Mn-to-Fe mass ratio as shown in Table 9. FeO is more easily reduced than MnO and hence the higher the Mn/Fe ratio the greater the degree of reduction achieved. The results show that for the 1500ºC series, the degree of reduction follows the initial order of reactivity of the cokes, with a range of Mn/Fe ratios of 1.8 for Port Kembla coke to 5.4 for Japanese coke. The Mn/Fe ratio for Japanese coke is similar to that for the equilibrium test. However, for the 1550ºC series, the effect of the initial reactivity of coke is small; the range of final Mn/Fe ratios being only 3.8 for Port Kembla to 5.1 for Japanese coke, and closer to the equilibrium value. The results indicate that attainment of the equilibrium of the reaction

$$(MnO) + Fe = Mn + (FeO) \tag{2}$$

is rapid once molten phases are formed, with Japanese coke attaining the equilibrium Mn/Fe ratio at 1500ºC within a little over an hour of total reaction and the other cokes approaching the equilibrium ratio in the 1550ºC tests. Silicon reduction was far from the equilibrium value and this is consistent with the knowledge that silicon equilibrium in iron making is slow to attain [13]. Note that the carbon content of the alloy from the equilibrium test is lower than for the other tests because silicon suppresses the solubility of carbon.

4. DISCUSSION

Carbothermic reduction of MnO and FeO are endothermic reactions but MnO reduction requires more heat than FeO reduction,

$$MnO(s) + C(s) = Mn(l) + CO(g); \quad \Delta H^\circ = 276 \text{ KJ (at 1200ºC)} \tag{3}$$

$$FeO(l) + C(s) = Fe(s) + CO(g); \qquad \Delta H° = 149 \text{ KJ (at 1200ºC)} \qquad (4)$$

MnO reduction also requires a higher minimum temperature (where $\Delta G° = 0$): 1400ºC for MnO and 720ºC for FeO. In practice, the thermodynamic activities of Mn and Fe are less than unity due to alloy formation so the actual minimum temperatures will be slightly lower. In ferromanganese production, therefore, it is thermodynamically possible for the iron ore to be reduced to iron, the higher manganese oxides to be reduced to MnO, and some of the MnO to be reduced to Mn dissolved in the metallic iron (at low thermodynamic activity) in the solid state under the conditions in the shaft using the sensible heat and reducing capacity of the gases produced in the slag-coke zone. This would leave only the reduction of the remaining MnO to occur in the high temperature mixed slag-coke zone.

The results of the SCICE and Reduction-from-Melt experiments reveal that the rate of reduction of iron oxide to metal and the reduction of the higher oxides of manganese to MnO are strongly controlled by the Boudouard reaction under conditions that exist in the shaft of the submerged arc furnace at temperatures up to about 1300ºC. The rate of reduction of MnO to alloy is much less controlled by the Boudouard reaction since, at temperatures where most of the MnO is reduced (>1300°C), the reactivities of the cokes, irrespective of the initial values, tend to converge to broadly similar values (Table 7).

The height of the shaft of a submerged arc furnace is much less than that of an iron blast furnace and the residence time of the burden in the shaft is proportionately less. Typically, reduction of oxides to metal must be performed in a few hours compared with 6 to 8 hours in an iron blast furnace. Use of a reactive coke in submerged arc furnace production of ferromanganese allows the iron oxide to be reduced to metal, the higher oxides of manganese to be reduced to MnO and a small amount of the MnO to be reduced to Mn dissolved in iron by the time the burden reaches the mixed slag-coke layer below the electrodes. The lower height of the shaft relative to that of an iron blast furnace also means that the strength of coke is a less critical property in submerged arc furnace smelting of ferromanganese than in iron blast furnace smelting.

It is now possible to postulate a model to explain the observed poor performance at TEMCO when the lower reactive cokes were used. When a low reactive coke is used, less reduction of iron oxide and of the higher oxides of manganese will occur in the shaft and a higher proportion of coke will survive and accumulate around the electrodes resulting in a deeper coke bed. This will decrease the burden resistivity and lead to higher temperatures and greater heat generation in the hearth. This in turn will lead to volatilisation of manganese metal, an increased off-gas temperature, and greater reduction of silica. At the same time, power and electrode consumption will increase and coke particles will graphitise and become less reactive. Due to the less reactive nature of the coke and the relatively short residence time of charge materials in the hearth, incomplete reduction of MnO will occur, leading (with the increased silica reduction) to poor alloy and slag chemistry control, and to unreacted coke being tapped.

5. CONCLUSIONS

Previous studies on the behaviour of burden in the submerged arc furnace production of high carbon ferromanganese have focussed on the metal-forming constituents. Little attention has been given to the properties of coke required for good furnace performance.

The overall conclusion of this study is that coke selected for use for ferromanganese production in submerged arc furnaces should be more reactive (as measured by the conventional Boudouard reactivity test at 1000°C) than those normally used in the iron blast furnace. Use of these cokes should result in stable furnace operation and good productivity. The reason for this is that more reactive cokes will enable Boudouard-controlled reactions to be completed higher in the shaft, thereby more effectively utilising the sensible heat and reducing capacity of the gases from lower in the furnace, and enabling the final, high heat demand reduction of MnO to Mn to be the major reaction in the high temperature mixed slag-coke zone. Conversely, less reactive cokes may lead to poor reducing conditions and larger coke beds in the furnace, resulting in poor furnace control, unstable alloy and slag compositions, and higher power consumption.

Based on an examination of the cokes studied it is further concluded that cokes with the desirable attributes could be produced under appropriate coking conditions from a blend of low, medium and high rank coals. This will produce cokes of intermediate strength, high porosity and high reactivity (relative to iron blast furnace cokes).

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