

EFFECTS OF OXIDATION ON THE MICROSTRUCTURE AND REDUCTION OF CHROMITE PELLETS

B. Zhao¹ and P.C. Hayes²

¹ Pyrometallurgy Research Centre (PYROSEARCH), School of Chemical Engineering, The University of Queensland, Brisbane, Queensland, 4072, Australia; P.Hayes@uq.edu.au

ABSTRACT

Fine chromite ore can be made into pellets in preparation of feed material for use in submerged arc ferrochromium smelting. During the pelletising process the charge is subjected to a range of temperature and gas conditions. The aim of the study was to determine whether changes to pelletising practice that could improve pellet reducibility in the smelting furnace. To this end a series of experiments have been undertaken to determine the effects of preoxidation of chromite pellets in air on the product microstructure, and on the subsequent rates and extent of reduction in CO gas.

The principal findings of this research are

- *The rates of preoxidation of the chromite spinel M_3O_4 to M_2O_3 phase increase with increasing temperature.*
- *The rates of reduction of the pellets below 1200°C are enhanced by the oxidation to M_2O_3 . Low temperature reduction to form iron metal in addition reduces the effective particle size of the chromite grains with the potential to enhance the subsequent rates of dissolution in the slag.*
- *The rates of reduction above 1200°C are not influenced by preoxidation since above this temperature M_2O_3 is rapidly reduced back to spinel, and no advantage in preoxidation to reduction kinetics is obtained.*

The results indicate that optimum reduction and dissolution of the chromite in submerged arc smelting may be achieved by enhancing preoxidation of the pellets during pelletising to maximise M_2O_3 formation.

1 INTRODUCTION

Chromite ores used in the production of ferrochromium are charged as lump or pelletised fines submerged arc furnace. The reducibility of the ores in CO gas atmospheres is an important characteristic that can influence the energy efficiency and overall yield of chromium through decreasing the heat load on the furnace and influencing the structural modification and dissolution of the chromite grains in the slag. [1]

The reducibilities of lump chromite ores and pellets have been widely reported in the literature [2-21]. There appears to be general agreement that in the loose charge iron is preferentially reduced from the solid chromite grains by reaction with carbon monoxide gas produced in the lower furnace.

The rate limiting reaction mechanism during the gaseous reduction of dense chromite grains is the ionic diffusion of metal species in the solid spinel phase. Soykan et al [12] proposed that the reduction of chromite occurs by the following sequence of reactions;

- a) “Initially, Fe^{3+} and Fe^{2+} at the surface of the chromite particle are reduced to the metallic state. This is followed immediately by the reduction of Cr^{3+} ions to the divalent state.
- b) Cr^{2+} ions diffusing toward the centre of the particle reduce the Fe^{3+} ions in the spinel under the surface of the particle to Fe^{2+} at the interface between the inner and outer cores. Fe^{2+} ions diffuse towards the surface, where they are reduced to metallic iron.
- c) After the iron has been completely reduced, Cr^{3+} and any Cr^{2+} that is present are reduced to the metallic state, leaving an iron- and chromium- free spinel, MgAl_2O_4 ”.

The partially altered chromite contains a dispersion of fine iron/chromium metal alloy particles. The solid alloy, formed in the early stage of reduction as the charge descends and is heated through the loose charge in the upper furnace, contains principally iron. As the reaction time and temperature increases, the chromium concentration in the alloy increases.

Chromite fines are also used in ferrochromium alloy production. Green pellets consist of chromite concentrate fines, bentonite which acts as a binder and fine coke to provide heat source during firing. To provide the desired balance between mechanical strength and reducibility the pellets are fired in a moving grate furnace. The counter-current gas flow means the green pellets are preheated in an oxidising atmosphere as they move through the furnace. Ignition of the coke breeze in the pellets creates local reducing conditions within the pellet as the pellet approaches and reaches peak bed temperature. Partial fusion of the materials at temperature creates a porous yet mechanically strong material. The pellets are then cooled by the incoming fresh air that passes through the pellet bed.

The focus of the present study is to investigate ways in which the reducibility of the pellet charge can be further enhanced.

2 RESULTS AND DISCUSSIONS

2.1 As-received chromite lump and pellets

The microstructure of a typical South African lump chromite ore is presented in Figure 1. The dense lump ore consists of large (100 to 500 μm diam.) rounded chromite grains surrounded by a silicate matrix. In contrast, examples of the microstructures of typical South African “as-received” pellets are presented in Figures 2 and 3. Chromite pellets are porous and are made up of angular particles formed as a result of the size reduction processes that were carried out in the preparation of the chromite concentrates. The binder phase appears as a grey material in the micrographs. The black areas represent holes or voids in the material. The chromite particle sizes within the pellets range from approximately 10 to 100 μm .

The detailed microstructure of the particles differs with position within the pellet. It can be seen from Figure 2 that in the outer grains of “as-received” pellet a high proportion of acicular M_2O_3 (white phase) is present in the M_3O_4 chromite spinel grains. In contrast it can be seen from Figure 3 that in the material at the centre of the pellet grains of “as-received” FM pellets consist of only M_3O_4 chromite spinel grains, that is, no oxidation of the inner grains during pellet preparation.

The formation of the M_2O_3 during oxidation is thought to occur through a rapid shear transformation mechanism described previously for Fe_2O_3 to Fe_3O_4 reduction [22-24]. The nucleation of the product oxide starts at the particle surface and propagates along the close-packed planes of spinel and M_2O_3 phases, across and through the individual grains. The interface on the close packed planes is coherent, and the reaction is reversible. This is in sharp contrast to classical shrinking core mechanisms in which the incoherent reaction interface progresses uniformly from the particle surface towards the centre of the particle.

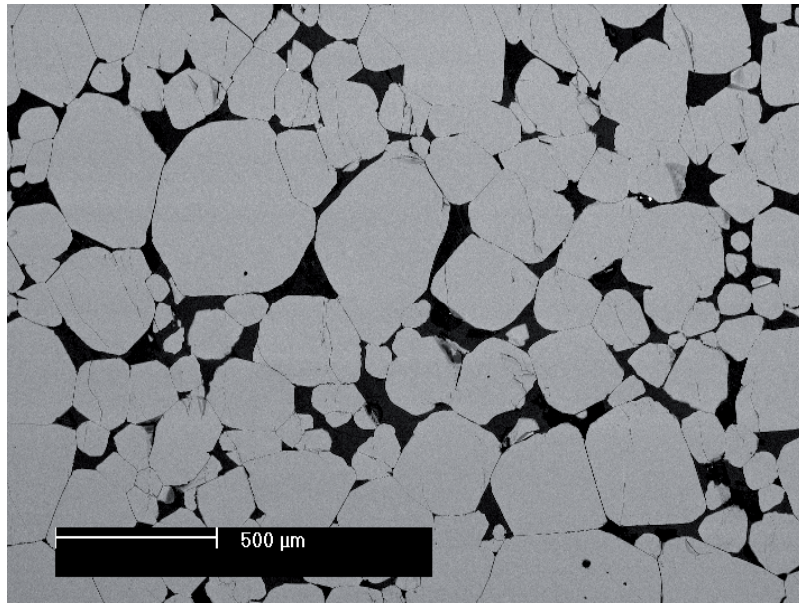


Figure 1: As-received South African chromite lump

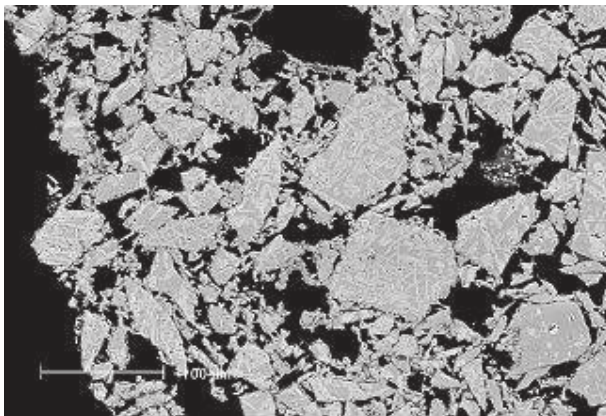


Figure 2: Outer of as-received FM pellet

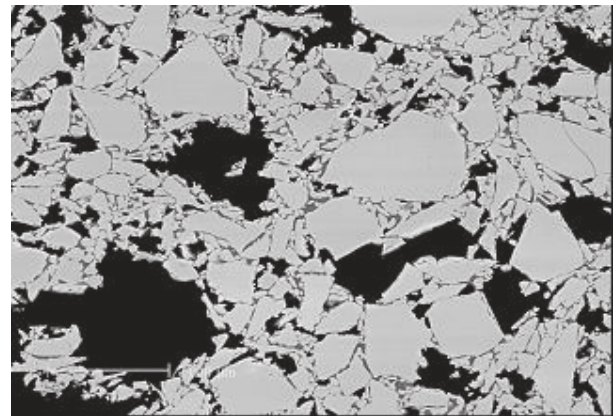


Figure 3: Centre of as-received FM pellet

The bulk compositions of as-received chromite lump and pellet are given in Table 1. All iron in the sample is calculated as FeO.

Table 1: Bulk composition of “as-received” chromite materials (wt%), all iron is reported as FeO

	CaO	MgO	Al ₂ O ₃	SiO ₂	“FeO”	Cr ₂ O ₃
lump	1	10.7	14.5	8.3	23.5	39.5
FM pellet	/	11.3	13.6	2.3	25.4	43.3

The results of the isothermal reduction tests undertaken in the laboratory of individual lump and pellets (single particles, 5g) in flowing CO gas at temperatures between 1200-1700 °C are shown in Figures 4 and 5 respectively. All samples were predried at 120°C. A separate sample was used for each experiment. It can be seen that at temperatures lower than 1500 °C the extents of reduction for lump materials are less than those obtained with pellet for the same reaction conditions. At these low temperatures typically encountered during descent through the loose charge zone of the furnace essentially no reduction takes place; same alloy is formed on the outer surfaces of the lump but there

is no reduction of grains in the centre of the lump material. However, above 1500 °C the reaction rate is greatly increased with increasing temperature. It can be seen that after 120 min at 1700 °C the weight loss for lump is 17.5% compared to 11% for pellet; this may be due to the different chemistries and melting temperatures of the matrix materials in each case but has not been investigated in detail in this present study.

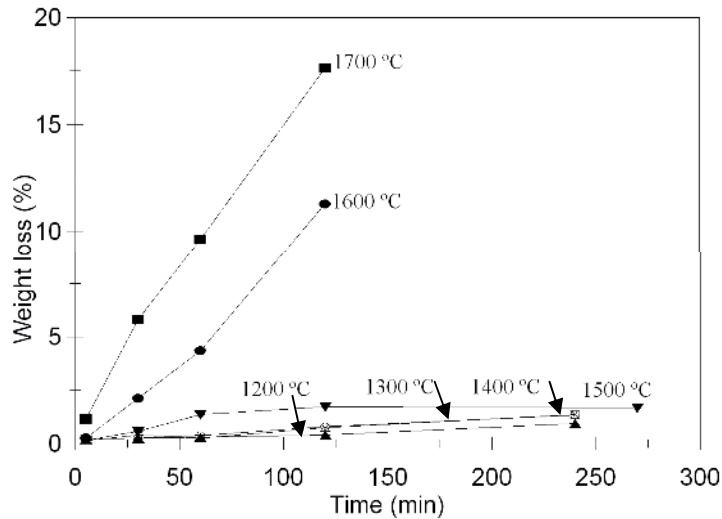


Figure 4: Plot of weight loss against to reaction time at different temperatures for chromite lump in CO gas

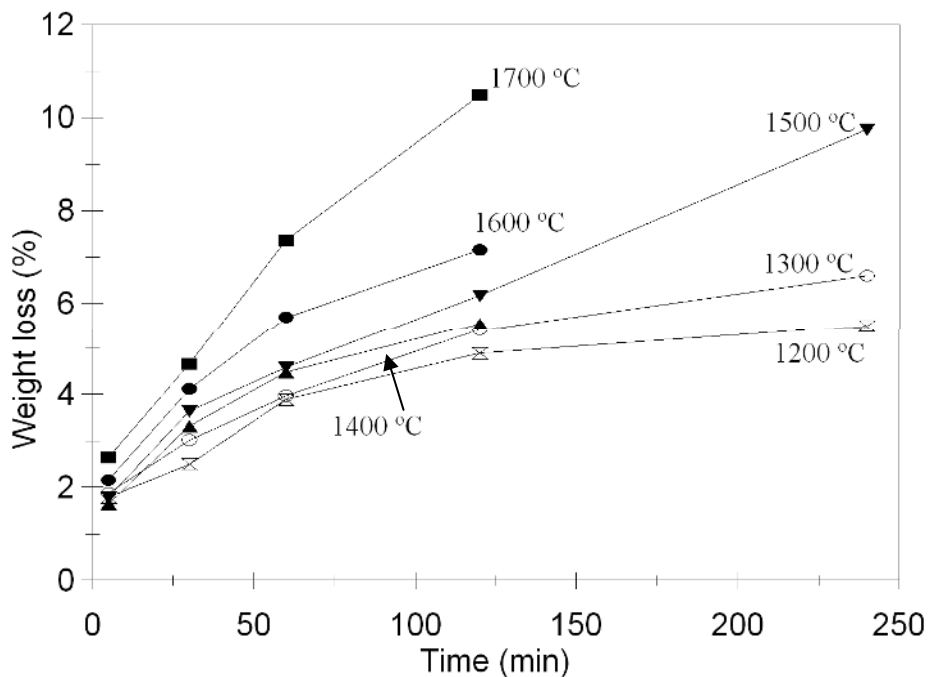


Figure 5: Plot of weight loss against to reaction time at different temperatures for FM pellet in CO gas

Microstructural examination of the pellets following reduction in CO gas at 1200 °C reveals that the grains at the outer regions of the pellets are readily reduced to form alloy within 5 minutes. The alloy was found to be dispersed throughout these grains and the grains are progressively broken up into sub-grains as reduction proceeds (Figure 6). On the other hand substantial alloy is not observed to form in the centre of the pellets until greater than 60 minutes reduction, and in this case the alloy nucleates and grows only on the outer surfaces of the original chromite grains (Figure 7).

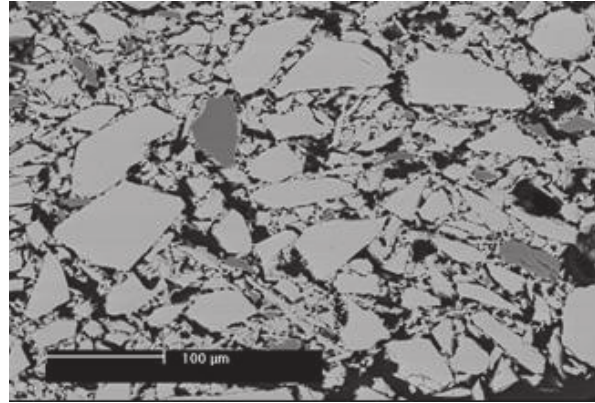
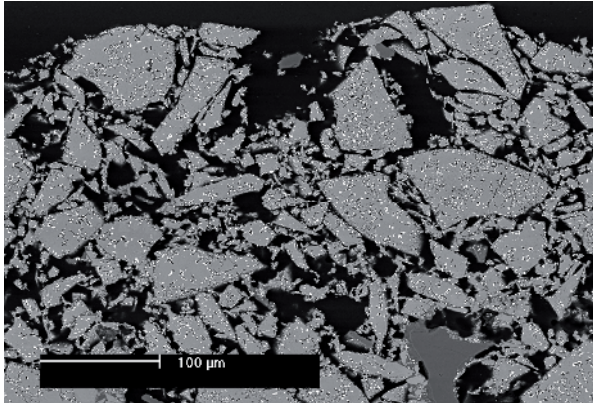


Figure 6: Outer of FM pellet reduced at 1200 °C for 60 min in CO gas

Figure 7: Centre of FM pellet reduced at 1200 °C for 60 min in CO gas

These observations indicate a) the reducibility of the porous fine particulate pellets is greater than lump ore, especially at low temperatures, and b) there is potential for increasing the reducibility of the chromite pellets through further oxidation of the pellets during cooling stages of pellet manufacture. The results of further detailed studies on the pre-oxidation of chromite pellets and effects of these pre-treatments on subsequent reduction in CO gas are presented in the following sections.

2.2 Oxidation Microstructures

FM pellets (diam. 16-18 mm) were oxidised at 800, 1000 and 1200 °C in air for 15 min respectively. The treatment time was selected on the basis of residence times that might be reasonably achievable in current pelletising plants. Figures 8 to 13 show the microstructures of the FM pellets following oxidation in air at 800, 1000 and 1200 °C. Following treatment at 800 and 1000 °C some oxidation of the outer grains of the pellets is observed but the grains at the centre of the pellets are unaltered. At 1200 °C it is clear that there is extensive conversion of M_3O_4 to M_2O_3 throughout the pellets.

2.3 M_2O_3 Formation

Quantitative metallographic analysis of “as received” and air-treated pellets was undertaken to determine the volume % M_2O_3 vs. penetration across the section of the pellet. The results of these measurements are presented in Figures 14 to 17 It was found that the “as received” pellets contain approximately 40% M_2O_3 in the outer grains and no M_2O_3 in the centre of the pellets.

The phase proportions are not significantly changed following oxidation of the FM pellets in air at 800 °C for 15 minutes. Oxidation of the FM pellets in air at 1000 °C results in an increase in the % M_2O_3 in the centre of the pellets to approximately 30%. After treatment at 1200 °C the % M_2O_3 in the centre of the pellets is increased to approximately 40%, and is essentially uniform across the complete section of the pellets.

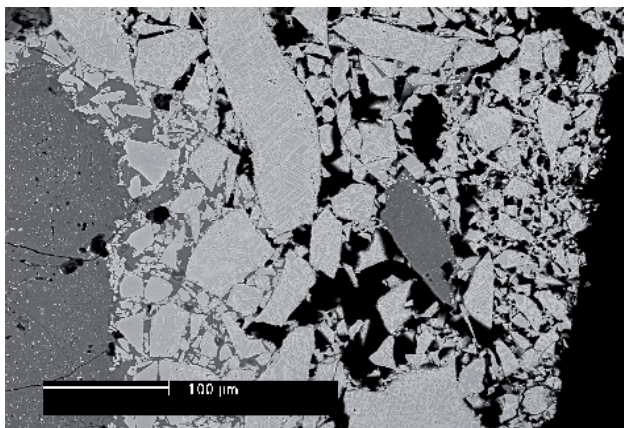


Figure 8: Outer of FM pellet treated at 800 °C for 15 min in air

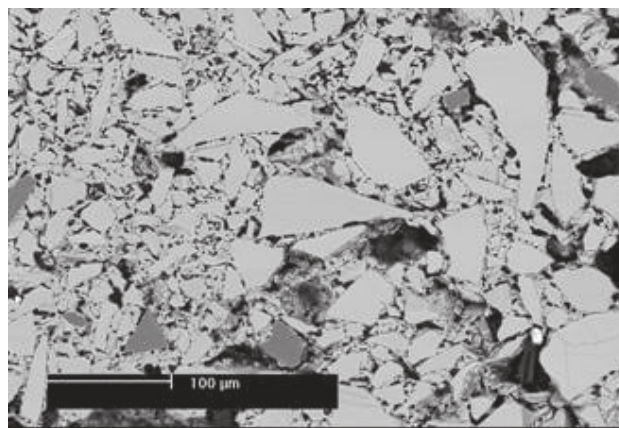


Figure 9: Centre of FM pellet treated at 800 °C for 15 min in air

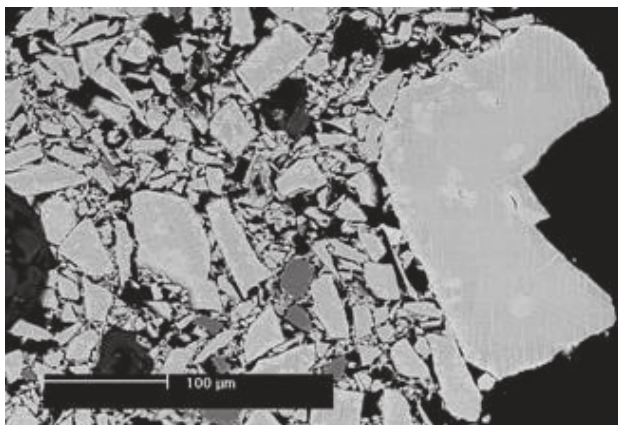


Figure 10: Outer of FM pellet treated at 1000 °C for 15 min in air

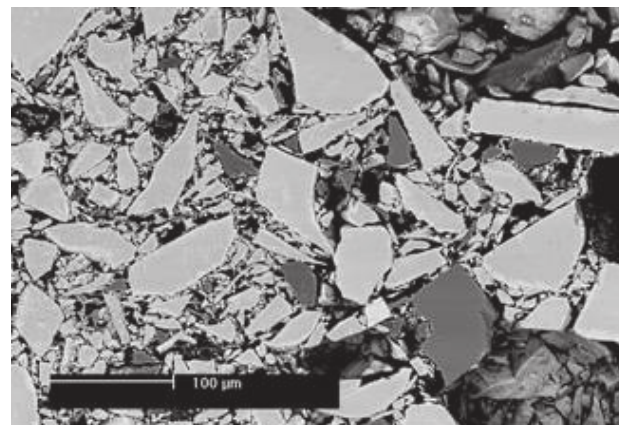


Figure 11: Centre of FM pellet treated at 1000 °C for 15 min in air

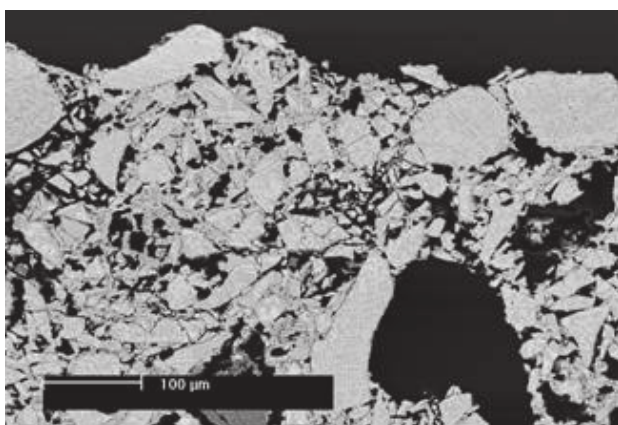


Figure 12: Outer of FM pellet treated at 1200 °C for 15 min in air

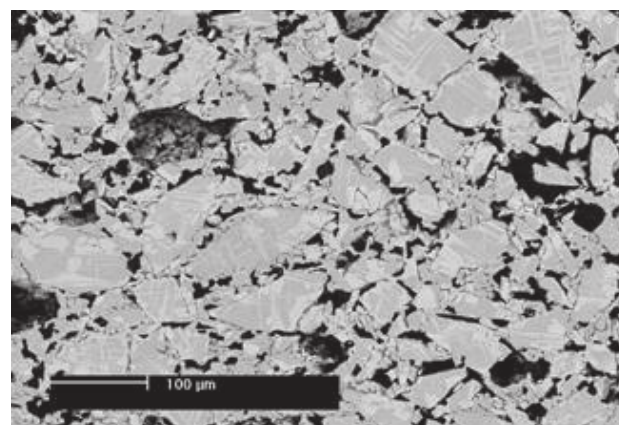


Figure 13: Centre of FM pellet treated at 1200 °C for 15 min in air

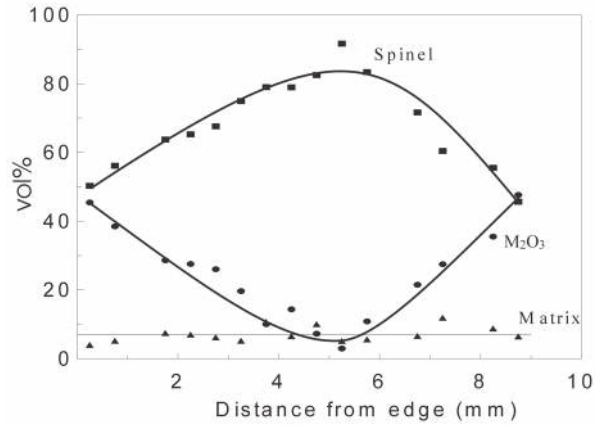


Figure 14: Penetration of phases in as-received FM pellet

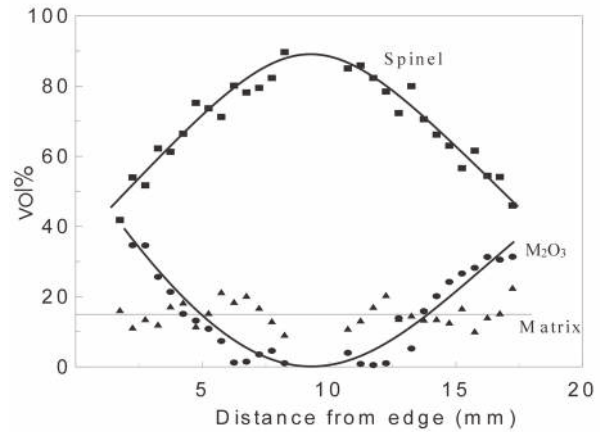


Figure 15: Penetration of phases in FM pellet treated at 800 °C in air for 15 min

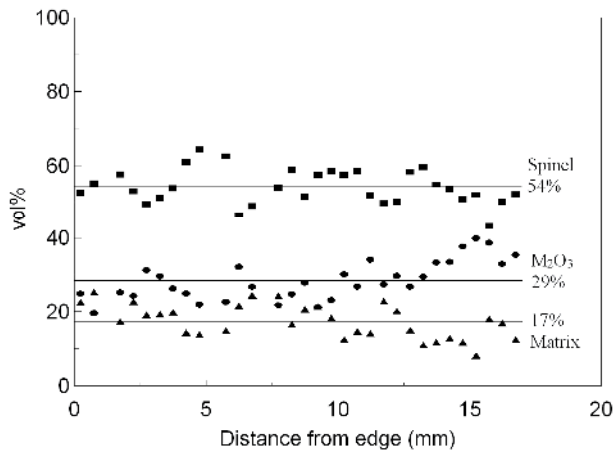


Figure 16: Penetration of phases in FM pellet treated at 1000 °C in air for 15 min

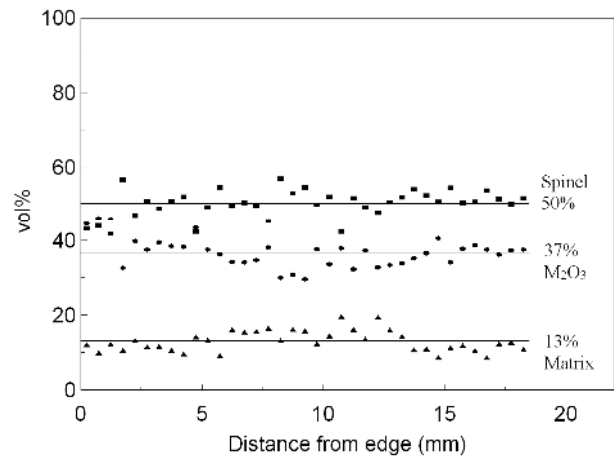


Figure 17: Penetration of phases in FM pellet treated at 1200 °C in air for 15 min

2.4 Phase Compositions

The compositions of the M_2O_3 and M_3O_4 phases were measured using electron probe X-ray microanalysis (JEOL8800) with wavelength detectors. Quantitative analysis was performed at an accelerating voltage of 15 kV and a probe current of 15 nA. The ZAF correction procedure was applied. The standards used for analysis were from Charles M. Taylor Co. (Stanford, California): Al_2O_3 for Al, $CaSiO_3$ for Ca and Si, chromite for Cr, Fe_2O_3 for Fe and MgO for Mg. There is some grain-to-grain variation of the chromite composition in the original pellets and this leads to variations in M_2O_3 composition in the “as-received” and pre-oxidised samples.

The average M_3O_4 composition in the original chromite grains is approximately 28.2 mol% FeO, 18.8 mol% MgO, 12.8 mol% Al_2O_3 and 40.3 mol% Cr_2O_3 . Following oxidation of the samples in air the average M_2O_3 composition measured in the present study is approximately 22 mol% Al_2O_3 , 45 mol% Cr_2O_3 , 33 mol% Fe_2O_3 . The average composition of the “new M_3O_4 ” in the oxidised samples is approximately, 23 mol% FeO, 27 mol% MgO, 7.5 mol% Fe_2O_3 , 18.5 mol% Al_2O_3 , 34 mol% Cr_2O_3 . The measurements show that in addition to the shear transformation, transfer and partitioning of MgO occurs between the “new M_3O_4 ” phase and the M_2O_3 .

The results demonstrate that, for the particular pellets tested, treatment at 1200 °C in air for 15 mins. results in complete oxidation throughout the pellet; treatment below these temperatures and times does not provide significant extent of oxidation of the pellets beyond that already present in the “as received” pellets.

2.5 Reduction Microstructures

To ensure uniformity in starting materials all pre-oxidised pellets were prepared by oxidation at 1200 °C in air for 15 min. Individual sample were then treated in a flowing CO gas stream at different temperatures (1200 to 1600 °C) for 60 min. There is no significant difference in weight loss between peroxidised sample and as-received sample as the proportion of the M_2O_3 phase formed during the oxidation is small. Typical microstructures of the pre-treated, reduced FM pellets are shown in Figures 18-27.

Oxidation at 1200 °C followed by reduction at 1200 °C results in the reduction of the M_2O_3 present in both the outer and inner grains of the pellet. There is some evidences of physical breakup or fissure formation of the chromite grains at the centre of the pellet prior to alloy formation (see Figure 19). The formation of the Fe-Cr alloy appears to occur preferentially initially at the sites where the M_2O_3 intersects with the external surface of the particles. As reduction proceeds the alloy forms across the whole width of the particle following the path previously transformed to M_2O_3 . The preferential nucleation and growth of alloy on the M_2O_3 may be attributable to the absence of MgO in this phase; MgO stabilises thermodynamically both spinel and monoxide (wustite) phases making reduction of these phases difficult. The presence of M_2O_3 is demonstrated to have a positive impact on the reducibility through the further break up of the spinel particles into sub-grains; increasing the surface area available for metal formation and reducing the diffusion path length in the oxide.

When reduction is carried out temperatures above 1300 °C (Figures 20 and 21), however, most of alloy appears to be formed directly on the outer surfaces of the spinel grains. Oxidation at 1200 °C followed by reduction at temperatures above 1200 °C does not provide any advantage in either extent of reduction or change in microstructure. Despite the successive phase changes accompanying the oxidation and reduction, and the reversible M_3O_4 to M_2O_3 transformation, break-up of the chromite grains does not occur. Examination of the microstructures indicates that the M_2O_3 is reduced back to spinel before reduction to metallic iron can take place. As indicated previously the M_2O_3/M_3O_4 transformation occurs through a solid state shear process and is reversible. If no reduction of oxide and alloy formation has occurred in the M_2O_3 there is no impediment to the reversion of M_2O_3 to M_3O_4 .

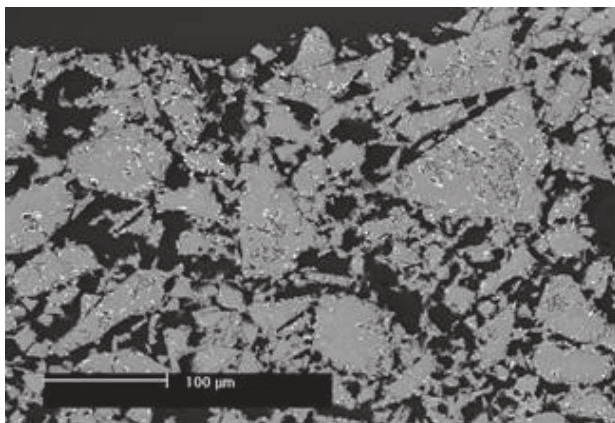


Figure 18: Outer of FM pellet treated at 1200 °C for 15 min in air and then reduced at 1200 °C for 60 min in CO gas

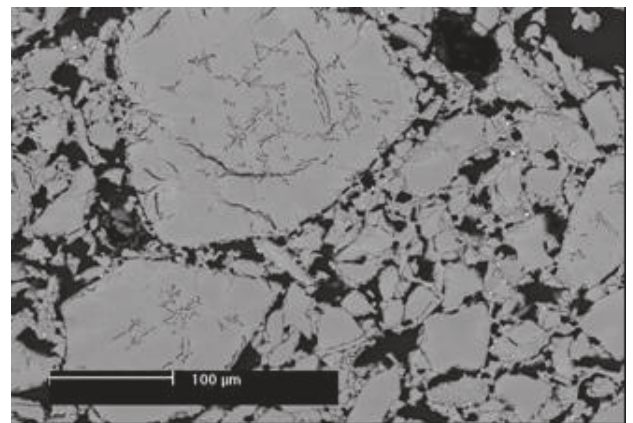


Figure 19: Centre of FM pellet treated at 1200 °C for 15 min in air and then reduced at 1200 °C for 60 min in CO gas

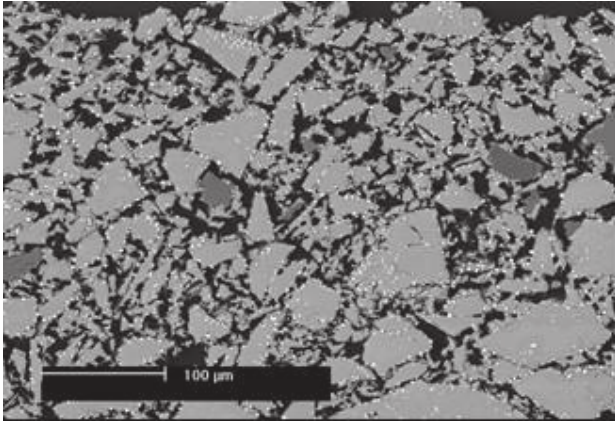


Figure 20: Outer of FM pellet treated at 1200 °C for 15 min in air and then reduced at 1300 °C for 60 min in CO gas

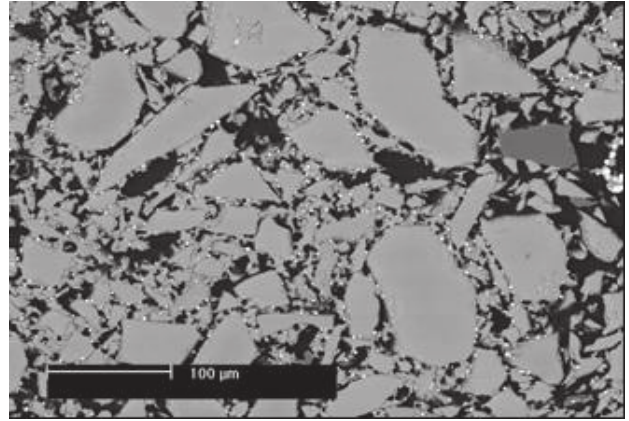


Figure 21: Centre of FM pellet treated at 1200 °C for 15 min in air and then reduced at 1300 °C for 60 min in CO gas

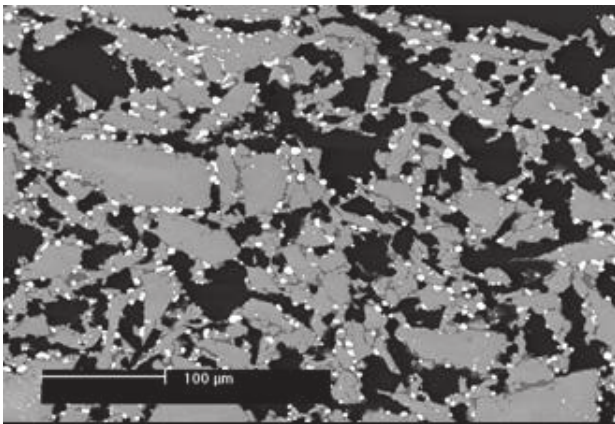


Figure 22: Outer of FM pellet treated at 1200 °C for 15 min in air and then reduced at 1400 °C for 60 min in CO gas

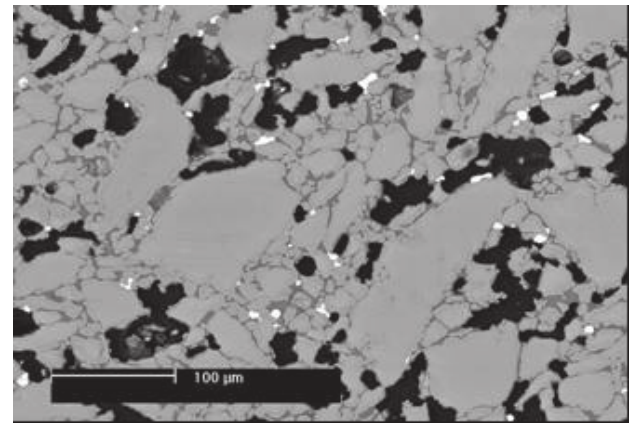


Figure 23: Centre of FM pellet treated at 1200 °C for 15 min in air and then reduced at 1400 °C for 60 min in CO gas

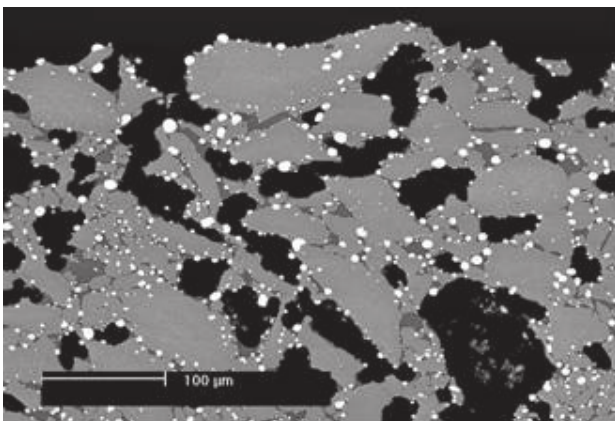


Figure 24: Outer of FM pellet treated at 1200 °C for 15 min in air and then reduced at 1500 °C for 60 min in CO gas

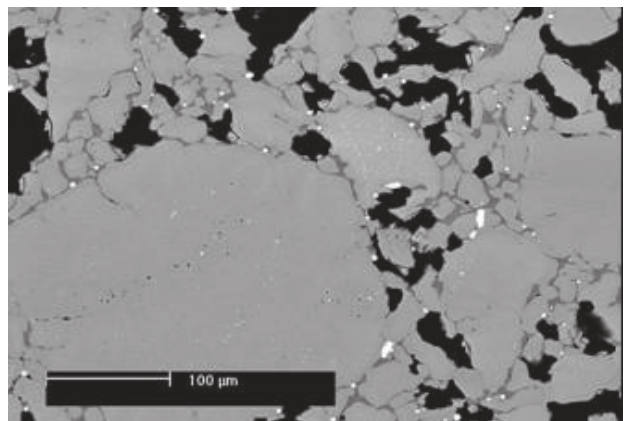


Figure 25: Centre of FM pellet treated at 1200 °C for 15 min in air and then reduced at 1500 °C for 60 min in CO gas

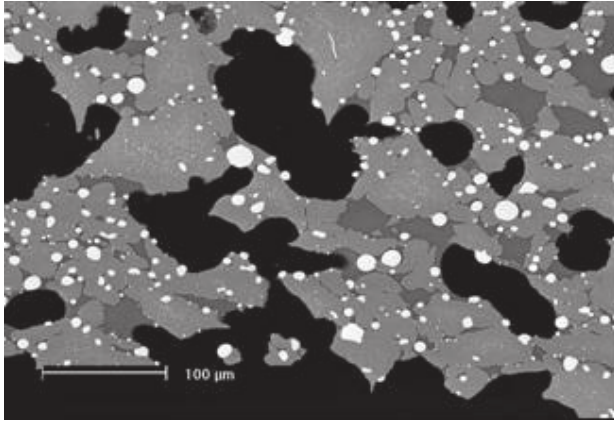


Figure 26: Outer of FM pellet treated at 1200 °C for 15 min in air and then reduced at 1600 °C for 60 min in CO gas

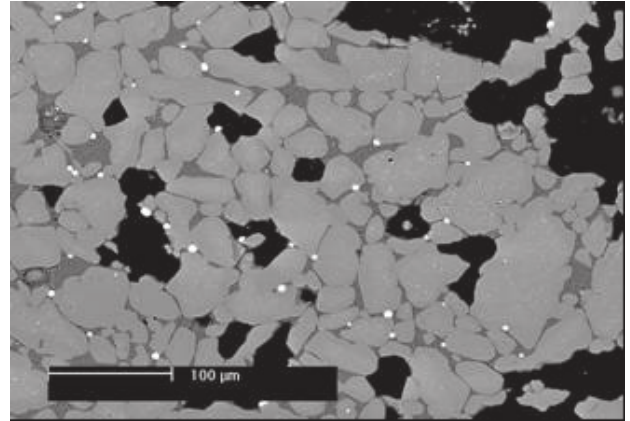


Figure 27: Centre of FM pellet treated at 1200 °C for 15 min in air and then reduced at 1600 °C for 60 min in CO gas

Reduction above 1400 °C (Figures 22 and 23) results in liquid silicate formation in the pellets and liquid phase sintering takes place, visible in the form of shape change of the grains and the elimination of fine grains through solution and reprecipitation of the chromite grains.

Above 1500 °C (Figures 24 to 27) significant rounding of the chromite grains, densification and grain growth have occurred. At 1600 °C reduction clearly takes place throughout the pellet as evidenced by the formation of alloy prills on the chromite grain boundaries.

2.6 Industrial Implications

The experiments reported above have been conducted under isothermal conditions. In metallurgical practice pellet feed to a submerged arc furnace would be charged at ambient temperature, and simultaneously heated and pre-reduced as the burden descends through the furnace to the hot zone.

Improved performance of the process can be achieved by ensuring that iron reduction is complete before the pellets arrive at the softening and melting zones of the furnace, since this minimises the heat load in the hot zone. In addition since the pellets will dissolve and disintegrate in the hot zone, the smaller the effective particle size the more likely the chromite will be reduced, the residual spinel dissolved in the slag and therefore the greater the chromium recovery.

In this context there is potential to improve the low temperature reducibility of pellets through pre-oxidation during pelletising and to improve subsequent ferro-chromium smelting furnace productivity.

3 CONCLUSIONS

Experimental studies have shown that the oxidation of chromite spinel, M_3O_4 , in air results in the formation of the M_2O_3 phase. The rapid transformation to the M_2O_3 phase occurs through a solid state shear mechanism that results in the preferential growth on close packed planes in the crystals. The induced strain at the M_3O_4/M_2O_3 phase boundary and preferential reduction of M_2O_3 can result in the mechanical break up of the grains, increasing the effective surface area for reaction and reducing the grain size of the material.

This pre-oxidation of chromite pellets can improve the low temperature reducibility of these materials. Oxidation of pellets at 1000 to 1200 °C in air has been shown to be effective for particular commercially produced pellets. There is potential to enhance the extent of this oxidation during pellet manufacture through modification of existing pelletising processes.

ACKNOWLEDGEMENTS

The authors would like to acknowledge financial support for this study from Samancor Cr, Johannesburg. Ms Ying Yu and Ms Ruilan Liu, who provided general laboratory assistance and undertook much of the careful sample preparation and measurement work.

4 REFERENCES

- [1] Hayes, P.C., "Aspects of SAF Smelting of Ferrochrome", Proc. Intl. Symp. on Ferroalloys, INFACON X, Cape Town, 2004, SAIMM, Johannesburg, pp.1-14.
- [2] Rankin W.J., "The reduction of chromite by graphite and carbon monoxide", Trans. IMM., 88(1979), C107-113.
- [3] Katayama H. G. and Tokuda M., "The reduction behaviour of synthetic chromites by carbon", Trans ISIJ, 20(1980), pp.154-162.
- [4] Kinloch E.D., "The role of mineralogy in pilot plant prerelution of chromite ores in South Africa", Proc. Intl. Cong. App. Miner. Geol. Soc. S. Afr., Johannesburg, South Africa, 1983, pp.337-49.
- [5] Searle M.J. and Finn C.W.P., "Mathematical modelling of the reduction behaviour of chromite from the upper chromite layer of the Bushveld Complex", MINTEK Report No. M96, Randburg, South Africa, 1983.
- [6] Algie S.H., Rankin W.J. and Finn C.W.P., "Some aspects of the reduction of chromite with carbon", Trans ISIJ, 24(1984), pp.141-142 and MINTEK Report No.157, Randburg, South Africa, 1984.
- [7] Kucukkaragoz C.S. et al., MINTEK Report No.154, Randburg, South Africa, 1984.
- [8] Searle M.J., M.Sc. thesis, University of Witswatersrand, Johannesburg, South Africa, 1984.
- [9] Fernandes T.R.C., Lee W.E. and Mitchell T.E., "Microstructural aspects of reduction of Zimbabwe chromite to high carbon ferrochrome", Trans IMM, 103(1994), C177-C187.
- [10] Fernandes T.R.C., "Chromite mineralogy and metallurgical behaviour", MINTEK 50, Sandton, 1984, pp. 913-922.
- [11] Perry K.P.D., Finn C.W.P. and King R.P., "Ionic diffusion mechanism of chromite reduction", Metall. Trans B, 19B(1988), pp.677-684.
- [12] Soykan O., Eric R.H. and King R.P., "The reduction mechanism of a natural chromite at 1416 °C", Metall. Trans B, 22B(1991), pp.53-63, 801-809.
- [13] Niayesh M.J. and Dippenaar R.J., "The solid state reduction of chromite", INFACON 6, Cape Town, 1992, vol. pp.57-63.
- [14] Van Vuuren C.P.J., Bodenstein J.J., Sciarone M. and Ketsens P., "The reduction of synthetic iron chromite in the presence of various oxides – a thermo-analytical study", INFACON 6, Cape Town, 1992, vol.1, pp.51-55.
- [15] Weber P. and Eric R.H., "The reduction mechanism of chromite in the presence of a silica flux", Metall. Trans. B, 24B(1993), pp.987-995.
- [16] Ringdalen E. and Olsen S.E., "The effect of chromite ore mineralogy on reduction mechanisms and reducibility", INFACON 8, China Science and Technology Press, 1998, pp.147-152.
- [17] Vazarlis H.G., Lekatou A., "Pelletising-sintering, prerelution, and smelting of Greek chromite ores and concentrates", Ironmaking and Steelmaking, 20(1993)1, pp.42-53.
- [18] Kekkonen M., Xiao Y. and Holappa. L., "Kinetic study on solid state reduction of chromite pellets", INFACON 7, Trondheim, Norway, 1995, pp.351-360.
- [19] Kekkonen M., Syynimaa, A., Holappa. L and Niemela P., "Kinetic study on solid state reduction of chromite pellets and lumpy ores", INFACON 8, Beijing, 1998, pp.141-146.
- [20] Xiao Y. and Holappa. L., "Kinetic modelling of solid state reduction of chromite pellet with CO", INFACON 8, Beijing, 1998, pp.135-140.
- [21] Xiao Y., Reuter M. and Holappa. L., "Reduction of chromite pellet with CO", INFACON IX, Quebec, 2001, pp.147-156.
- [22] Swann P.R. and Tighe N.J., "High voltage microscopy of hematite to magnetite", Metall. Trans B., 7B(1977), pp.479-487.
- [23] Hayes P. C. and Grieveson, P, "Microstructural changes on the reduction of hematite to magnetite", Metall. Trans. B, 12B(1981)3, pp.319-326.
- [24] Baguley P., St.John D.H. and Hayes P.C., "The conditions for the formation of lath and porous magnetite on reduction of hematite in hydrogen/water gas mixtures", Metall. Trans. B, 14B(1983)3, pp.513-514.

