REDUCTION OF TACONITE IN THE SUSTAINED SHOCKWAVE PLASMA (SSP)

K.J. Reid and J.J. Moore, Mineral Resources Research Center, University of Minnesota, Minneapolis, MN; J.K. Tylko, Plasmatech, Inc., and Mineral Resources Research Center, University of Minnesota, Minneapolis, MN.

ABSTRACT

The principle of the sustained shockwave plasma (SSP) is outlined. Initial reduction results are described in which Minnesota taconite concentrate is reduced "in-flight" in an open arc, laboratory-scale, 40 kW and a 100 kW enclosed SSP reactor using graphite and lignite char reductants. The degree of metallization and metallographic structures produced are evaluated and reduction mechanism(s) postulated.

1. INTRODUCTION

One of the main disadvantages of conventional pyrometallurgical extraction operations is the need for large slag-metal baths and associated increased energy requirements and refractory consumption problems.

In ironmaking, although there have been major technological advances and improvements in efficiency in blast furnace operation over the past two decades: in most recent cases of blast furnace installations the returns on the required multibillion dollar investments have been very low or zero.

However, energy costs and availability, the need for improved pollution control and the increasing requirement to extract metals from leaner sources demand radically new approaches in extractive metallurgy. One such approach is the use of plasma technology.

Although the benefits of improved kinetics at higher temperatures are well understood, reaction temperatures in conventional pyrometallurgical processes are often limited by combustion technology and refractory properties. Methods of using the higher temperatures obtainable in plasma systems have been sought by process engineers and have been reviewed by Sayce[1] and Hamblyn.[2]

All of these systems use the so-called low-temperature plasma (less than 100,000 K) and rely solely on the thermal characteristics of the plasma. Advantages over electric arc practice are mainly associated with the use of substantially nonconsumable cathodes and higher local temperatures within the plasma itself.

In these early plasma devices the treatment of particulate matter took place chiefly in the peripheral regions surrounding the plasma and the introduction of larger quantities of feedstocks resulted in the formation of molten layers adhering to the walls of the arc chamber. Expanding the plasma volume into a suitable reaction medium will take advantage of the high temperatures and activated states within the plasma to enable "in-flight" reduction of the mineral particle feedstock, remove the need for large slag-metal baths, and provide the basis of a low volume-high throughput, continuous processing reactor. Although some attempts[3-5] have been made to increase the effective volume of the plasma, they were not expanded sufficiently to fully intercept and process all the falling mineral particles, resulting in only partial reduction of the minerals. Therefore, previous LT plasma devices had to rely on transferring the arc column to a molten bath in which the final reduction was carried out with a consequent increase in energy input needed to maintain the molten condition.

2. THE SUSTAINED SHOCKWAVE PLASMA (SSP) REACTOR

In contrast to the above, the device used in the present investigation was a scaled-down version of a sustained shockwave plasma (SSP) reactor,[6] a new type of LT plasma reactor intended primarily for large- and medium-scale industrial applications. The chief characteristic of SSP systems is their ability to wholly entrain and process large quantities of particulate feedstock in a very fast orbiting and pulsating cone of nonlocal thermodynamically equilibrated (NLTE) plasma established between two stationary electrodes of a variety of designs.[7] An important feature shared by all SSP reactors is the way by which the actual orbiting of the arc is carried out. Instead of orbiting the whole arc column (as is frequently done), only the arc attachment is displaced, causing the arc to orbit. This technique has been shown to have three important advantages: firstly, it requires a minimal amount of energy; secondly, it does not affect to any measurable extent the plasma cone itself; and, thirdly, it can provide an accurately locked synchronization enabling orbiting speeds up to 60,000 rpm. Accordingly, orbiting may be carried out at the cathode or anode or at both arc attachments.

In summary, the three main features exploited in the SSP system are:

a) high rates of orbiting
b) imposition of electrically-produced pulsations;
c) high particle loading.

All of these effects appear to be closely interacting and in some respect synergistic.

The SSP technique is of particular interest since the whole volume of the generated plasma is utilized as the reaction medium. The inherent advantages over other plasma devices include the absence of rotating parts, the ease of scaling-up to virtually any required size and low refractory wear resulting from the separation of the refractory walls from the high temperature regions by the curtain of falling feedstocks. Other advantages include the very short treatment time, the ease of starting up and shutting down the installation and the possibility of utilizing a wide range of reductants: gaseous, solid and atomized liquid. A more detailed account of the SSP system is given elsewhere.[8]

3. EXPERIMENTAL INVESTIGATION

The main intention of this initial work was to evaluate the SSP principle for in-flight reduction and its potential ability to perform as a continuous low volume, high throughput reactor. An investigation of the possible reduction mechanism(s) pertaining within the plasma medium would also aid in an understanding of the potential application of the SSP principle to the processing of mineral concentrates.

The degree of in-flight reduction achieved in less than 100 milliseconds in the reactor will be largely controlled by the entrainment and interaction of reactants within the plasma medium. This was observed by placing a mirror above and at a slight angle to the generated SSP arc in an open 40 kW reactor. From this experimental set-up it was possible to determine favorable plasma orbiting conditions during feeding of the mixture into the SSP medium. The products were quenched by a free fall through a wide column and were collected as solids. There was no final treatment in a molten pool. Once the reactor conditions necessary to achieve substantial taconite concentrate reduction had been established in this open 40 kW reactor a second set of experiments was conducted in an enclosed 100 kW reactor (Figures 1 and 2).

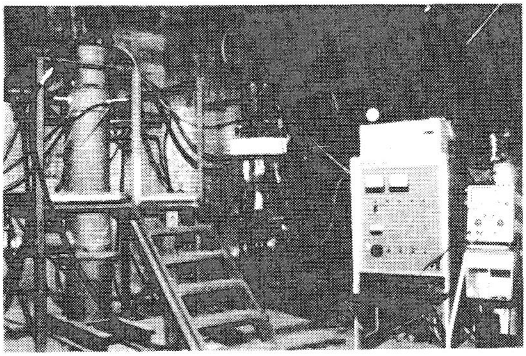


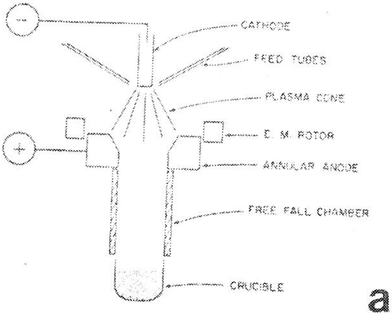
FIGURE 1 EXPERIMENTAL SSP REACTORS
(a) LEFT, ENCLOSED 100 kW REACTOR
(b) CENTER, OPEN 40 kW REACTOR WITH A MIRROR PLACED ABOVE CATHODE,
(c) RIGHT, REACTOR CONTROL UNIT.

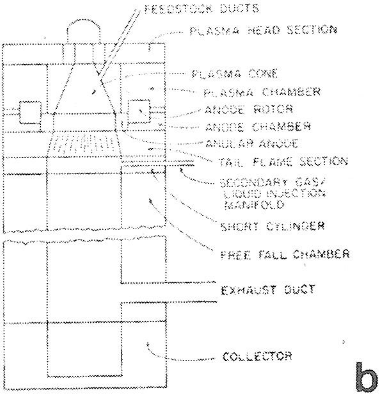
In each SSP reduction run, the reductant was ground to -300 microns and thoroughly mixed with the fine, as received, taconite concentrate. The mixture was dried at 120°C for 60 minutes prior to feeding into the SSP reactor. The effect of reductant reactivity on SSP processing was evaluated using the relatively unreactive graphite and the reactive lignite char as reductants. The latter reductant was also used to determine the effect of a high sulfur (2.06% S) reductant.

4. EXPERIMENTAL RESULTS

Favorable SSP conditions, as determined by the 40 kW open reactor, are given in Table I and the chemical analysis of the taconite concentrate is given in Table II. The taconite concentrate consisted of approximately 92% magnetite with small amounts of free hematite, quartz, minnesotaite, chert and carbonate minerals and was used with as received sizing of 100% passing 150 microns and 77.3% passing 44 microns. The graphite reductant had a fixed carbon of 98.5% while that of the lignite char was 61.28%. The char also assayed 17.5% volatiles and 2.06% S.

In initial runs at low orbiting





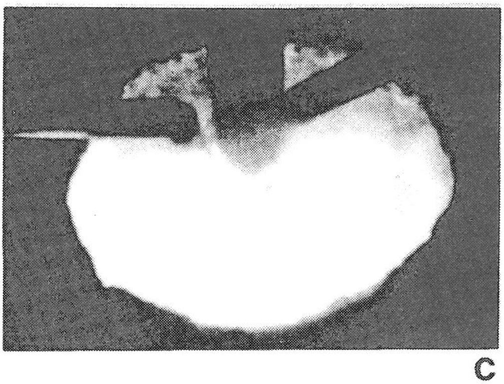


FIGURE 2 SCHEMATIC DIAGRAM OF (a) THE 40 kW OPEN ARC REACTOR (b) THE ENCLOSED 100 kW REACTOR (c) OPEN ARC SSP REACTOR. TACONITE GRAPHITE FEED AT AN ORBITING RATE OF 34,000 RPM.

TABLE I. 40 kW LABORATORY-SCALE SSP REACTOR REDUCTION VARIABLES

Expanded Plasma Arc Cone							Argon
Diameter (mm)		Length	Volt	Current	Rotation	Coil Power	Flow Rate
Top	Bottom	(mm)	(V)	(A)	(rpm)	(kW)	(m^3hr^{-1})
20	90	90	100	300	30,000	0.1	0.8

TABLE II. CHEMICAL ANALYSIS OF TACONITE CONCENTRATE (%)

Total Fe	Fe^{3+}	Fe^{2+}	FeO	Fe_2O_3	Fe_3O_4	Metallic Fe	SiO_2	S	C
66.81	44.49	22.16	28.5	63.6	92.1	0.16	6.23	0.004	0.37

speeds the amount of graphite reductant used was varied from zero to a 200% stoichiometric level based on the reduction reaction:

$$Fe_3O_4 + 4C = 3Fe + 4CO \tag{1}$$

The degree of metallization and percentage reduction of Fe^{3+} to Fe^{2+} (whether in the form of FeO or metallic Fe) is plotted in Figure 3. In subsequent experiments orbiting speeds in the region of 30,000 rpm were used and resulted in increased metallization of the taconite as shown in Figure 3. The relationship between degree of metallization and degree of reduction of Fe^{3+} to Fe^{2+} is given in Figure 4. This indicates that metallization becomes prominent once approximately

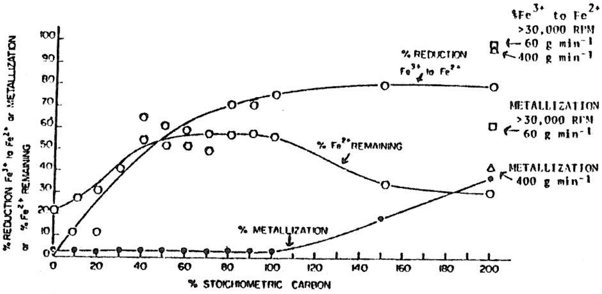


FIGURE 3 TACONITE REDUCTION DATA AT VARIOUS STOICHIOMETRIC CARBON LEVELS AT LOW RPM (<30,000 RPM) ORBITING SPEEDS UNLESS OTHERWISE STATED.

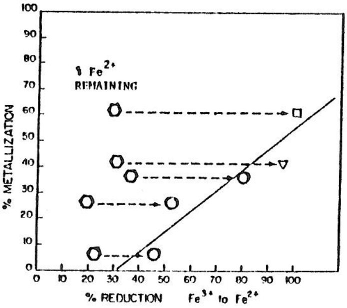


FIGURE 4 DEGREE OF METALLIZATION VERSUS REDUCTION OF Fe^{3+} (Fe_2O_3) TO Fe^{2+} (FeO) (SAME SYMBOLS AS FIGURE 3).

30% reduction of Fe^{3+} (Fe_2O_3) to Fe^{2+} (FeO) has been achieved under the 200% stoichiometric carbon conditions used. Increasing the feed rate to 400 g min^{-1} and using the more reactive lignite char reductant only reduced metallization to 41.7%. This is considered to be very encouraging for such a high feed rate into this small laboratory-scale SSP reactor. At 100% reduction of Fe^{3+} to Fe^{2+} only 63% metallization has been achieved under these initial experimental conditions indicating that there is still substantial reduction of FeO to Fe required to provide a highly metallized product.

Typical photomicrographs of the reduced taconite are given in Figure 5.

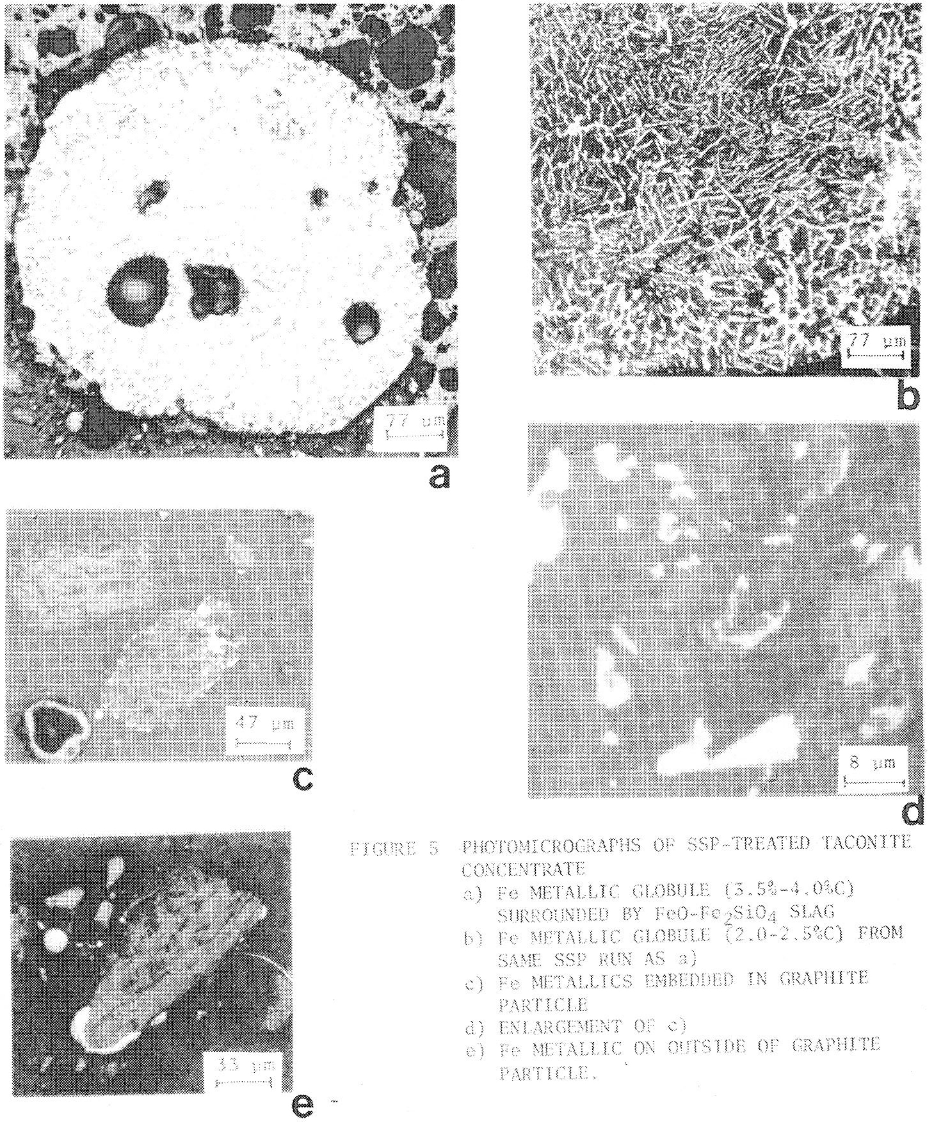


FIGURE 5 PHOTOMICROGRAPHS OF SSP-TREATED TACONITE CONCENTRATE
a) Fe METALLIC GLOBULE (3.5%-4.0%C) SURROUNDED BY FeO-Fe_2SiO_4 SLAG
b) Fe METALLIC GLOBULE (2.0-2.5%C) FROM SAME SSP RUN AS a)
c) Fe METALLICS EMBEDDED IN GRAPHITE PARTICLE
d) ENLARGEMENT OF c)
e) Fe METALLIC ON OUTSIDE OF GRAPHITE PARTICLE.

The rapid heating and cooling rates (of the order of 10^6°C s^{-1}) result in highly metastable metallic structures as indicated in Figures 5(a) and (b).

Point analyses were obtained using SEM and EPMA techniques and indicated that the metallic product contained only Fe and C. It is of particular significance that no sulfur was found in any of the metallic globules examined. Figure 5(a) shows a typical metallic globule surrounded by a FeO-Fe_2SiO_4 duplex structure which was produced by reducing taconite with 150% stoichiometric carbon in the form of graphite. From microhardness testing it was determined that the white phase was cementite and the duplex dark phase was pearlite (Figures 5(a) and (b)). From an evaluation of the relative amounts of cementite to pearlite it was possible to deduce that the carbon level varied from about 1.0 to 4.0% in these metallics. Occasionally, metallic phases were found situated inside a reductant particle as shown in Figure 5(c) and (d) and on the outside as shown in Figure 5(e).

Table III provides a summary of the maximum levels of metallization achieved for both the open 40 kW and enclosed 100 kW SSP reactors.

TABLE III MAXIMUM LEVELS OF METALLIZATION ACHIEVED IN THE LABORATORY-SCALE SSP REACTORS

SSP Reactor	Power Used, kW	Reductants	Feed Rate g m^{-1}	Degree of Metallization %
Open, 40 kW	30	Graphite	60	63.0
Open, 40 kW	30	Lignite Char	400	41.7
Enclosed, 100 kW	60	Lignite Char	76	74.6

5. DISCUSSION

The results achieved by in-flight reduction of taconite will first be discussed in light of conventional direct reduction research and, subsequently, in light of those conditions which are thought to exist under SSP conditions.

Research[9-14] on the direct reduction of iron oxide with a solid carbon reductant at conventional reduction temperatures has concluded that the reduction mechanism follows the two-stage sequence:

i) $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$ and ii) $FeO \rightarrow Fe$

However, this solid-solid reaction represented as:

$$Fe_3O_4 + 4C = 3Fe + 4CO \tag{1}$$

can take place only at the points of contact.

Once a small amount of metallic iron is formed it produces a barrier and from this point, reduction is more likely to proceed by the kinetically more favorable solid-gas reaction:

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2 \tag{2}$$

In this case the rate controlling step of the overall reaction has been determined to be the gasification of carbon by the Boudouard reaction,[11-14] i.e.,

$$CO_2 + C = 2CO \tag{3}$$

which is catalyzed by the presence of metallic iron[11,15-17] produced initially by reaction (1). Therefore, once the initial metallic iron is produced via reaction (1) the reduction proceeds by reactions (2) and (3) which, on addition, equate to reaction (1).

Appreciable metallization of magnetite did not commence with less than 100% stoichiometric carbon level [based on equation (1)] even though the reduction of Fe^{3+} (Fe_2O_3 in the magnetite spinel, $FeO \cdot Fe_2O_3$) to Fe^{2+}(FeO) was almost 80% at the 100% stoichiometric carbon level. At carbon levels exceeding the 100% stoichiometric level the degree of Fe^{3+} to Fe^{2+} remained roughly constant while the level of Fe^{2+} iron decreased and the degree of metallization increased. These results support the generally recognized theory of a two-stage reduction sequence. However, the presence of 6.23% SiO_2 in the taconite produces a certain amount of liquid fayalite slag which will lower the activity of FeO and reduce the thermodynamic driving force for reduction. The $FeO-SiO_2$ binary phase diagram (Figure 6) indicates that, under equilibrium conditions, the ratio of wustite:fayalite is approximately 22:6, i.e., 78.6% FeO in a $FeO-Fe_2SiO_4$ slag. It may therefore be assumed that the metallic Fe had been produced by reduction of wustite rather than by the thermodynamically less favorable reduction of fayalite. Under these conditions maximum metallization achievable would be 77.7% compared with 63% actually achieved in the open 40 kW reactor and 74.7% in the 100 kW enclosed reactor. Therefore, it may be postulated that the SSP in-flight reduction of magnetite takes place in two stages:

i) reduction of Fe^{3+} to Fe^{2+}

i.e.,

$$FeO \cdot Fe_2O_3 + CO = 3FeO + CO_2 \qquad (4)$$

The FeO will also be present as fayalite depending on the SiO_2 content.

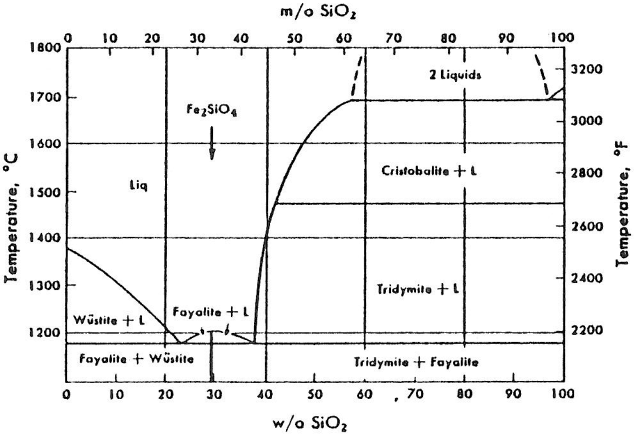


FIGURE 6 $FeO-SiO_2$ BINARY PHASE DIAGRAM

ii) reduction of Fe^{2+} iron (FeO) to metallic iron (fayalite remaining unreduced),

$$FeO + CO = Fe + CO_2 \qquad (5)$$

Reaction (4) requires only 25% of the stoichiometric carbon reductant compared with reaction (1) and may be used to account for the initial shape of the curve in Figure 4 which shows a maximum reduction of Fe^{3+} to Fe^{2+} at about 40% stoichiometric carbon. The excess amount of carbon over the theoretical 25% required for this reaction is probably due to the nonequilibrium conditions existing in the sustained shockwave plasma medium.

Initially, reaction (1) takes place by direct reaction between solid carbon and magnetite producing very small areas of liquid iron in active areas of the graphite particle surface. Evidence of this has been found and substantiated by optical microscopy [Figure 5(d) and (e)] and electron probe microanalysis. This metallic iron can then act as a catalyst for the production of CO via the Boudouard reaction (3) for continuation of reduction by reactions (4) and (5). However, the extremely short residence time, i.e., less than 100 ms, requires excessive amounts of carbon and CO in order to effect these reduction reactions to any great extent, therefore necessitating carbon reductant levels in the order of 200% stoichiometric based on reaction (1). It should be possible to improve the maximum level of reduction achieved in-flight to above 80% by adding CaO to remove the restricting effect of a silicate slag formation.

In conjunction with the above discussion it must be realized that the plasma medium provides its own unique conditions which favor rapid in-flight reduction. To this end rapid dissociation, gasification and ionization of reactants will take place to some degree depending on the thermodynamics and kinetics of the plasma-solids interactions. The dissociation temperatures of the main constituents of the taconite concentrate under standard thermodynamic conditions are as follows:

$6Fe_2O_3 \rightleftarrows 4Fe_3O_4 + O_2; \quad T_D \simeq 1,700$ K

$2Fe_3O_4 \rightleftarrows 6FeO + O_2; \quad T_D \simeq 2,400$ K

$2FeO \rightleftarrows 2Fe + O_2; \quad T_D \simeq 5,100$ K

$SiO_2 \rightleftarrows Si + O_2; \quad T_D \simeq 4,400$ K

At the same time, some degree of gasification and ionization of these species will take place at temperatures in excess of 10,000 K, depending on their relative thermodynamic stabilities and the heat transfer rates existing within the SSP medium.

Also, at these high temperatures various carbon forms, C*, which are not found at conventional reduction temperatures, have been detected[18] via spectroscopy and mass spectrometry. In plasma processing of graphite,[18] C* has been found in five types of molecular form, i.e., C_1, C_2, C_3, C_4, C_5, each of which can be considered as a molecular gas at plasma temperatures greater than 2000°C. The relative proportion of these gaseous carbon molecules varies as other chemical and mineral species are reacted with carbon in the plasma medium.

These active forms of gaseous carbon should readily reduce iron oxide and form carbon monoxide.

Plasma temperatures have been found to be sufficient to break the molecular bonding of diatomic gases (CO in this investigation) which, due to high thermal gradients existing in the plasma medium, can reassociate providing high thermal conductivity. Again, at the high temperatures existing in the SSP medium, ionization of the gaseous molecules of carbon and carbon monoxide can be produced.[19] These high temperature states will result in increased reaction rates. However, the SSP is specifically designed to exploit nonthermally equilibrated conditions and the pulsating electron temperatures may be an order of magnitude higher than those of the ions. Therefore, collisions between electrons and ions will produce further heat transfer. These SSP features produce a nonuniform condition within which the plasma-solid interactions take place and make any study of the reaction mechanisms and kinetics extremely speculative. However, these highly favorable but variable reduction conditions can qualitatively account for the in-flight reduction of minerals and for the variation in degree of reduction and metallic structures observed.

The relatively high level of reduction of taconite with lignite char at 400 g/min, as compared to graphite at 60 g/min, is thought to be due not only to the greater reactivity of the lignite char but also due to the larger amount of volatiles which aids the plasma gas production and therefore improves reaction kinetics. Enclosing the reactor and increasing the power have resulted in an increase in the metallization to 74.7%. This is presumably due to the improved reduction potential achieved under these conditions making reoxidation less likely while increase in power will increase the plasma volume and improve mineral-plasma interaction. It is thought that a similar continuous trend will result as work progresses with further power increases in the enclosed SSP reactor.

6. CONCLUSIONS

In-flight reduction of Minnesota taconite concentrates has been achieved in small SSP reactors. The extent of reduction depended on SSP operating conditions, feed rate, concentration of reductant and the type of reductant used. Increased reduction was achieved with lignite char compared with graphite while no sulfur was detected in the metallics using a reductant containing 2.06% sulfur.

There was a wide variation in structure and composition of the metallic products ranging from hypereutectoid steels to high carbon irons. The stability of the plasma was improved by the introduction of the mineral particles.

This is the initial work in a long-range program aimed at investigating the application of plasma techniques to in-flight reduction and processing of minerals. Improvements in the degree and control of reduction are to be expected by scaling up the operation in an enclosed reactor chamber and by incorporating in-stream gas analysis and plasma spectroscopy diagnostic techniques.

7. ACKNOWLEDGMENTS

This project on novel direct reduction technology is funded by the Legislative Commission on Minnesota Resources, and their support is gratefully acknowledged.

The establishment of the new Process Technology Division within MRRC and the initial setting up of the Plasma Technology Laboratory were partially supported by federal funds from the Mineral Institute Program, and this support is also acknowledged.

Finally, we would like to thank Plasmatech Inc. and J.K. Tylko for making details of the new SSP technology available for this study.

8. REFERENCES

1. I.G. Sayce, Plasma Processes in Extractive Metallurgy, Advances in Extractive Metallurgy, Inst. Min Met, p 241, 1972.
2. S.M.L. Hamblyn, Plasma Technology and Its Application to Extractive Metallurgy, Minerals Sci Engng, Vol 9, No. 3, July 1977, p 151.
3. D.R. McRae, R.G. Gold, C.D. Thompson, W.R. Sandall, Ferrovanadium Production by Plasma Carbothermic Reduction of Vanadium Oxide, 34th Electric Furnace Conference, Iron and Steel Society of AIME, December 1976, St. Louis.
4. D.K.A. Donyina, J.D. Lavers, A. McLean, R.S. Segsworth, Plasma Processing of Ferromanganese Slags, 37th Electric Furnace Conference, Iron and Steel Society of AIME, December 1979, Chicago.
5. J.K. Tylko to Tetronics R & D Co., Ltd., U.K. Patents No. 1,390,351-3.
6. J.K. Tylko to Plasma Holdings, N.V., U.K. Patent Application No. 7913337.
7. J.K. Tylko, Expanded Low Temperature Plasmas, Address to Bulg. Acad. Sc. (Phys.), Nov. 11, 1972, Sofia.
8. J.K. Tylko, J.J. Moore, K.J. Reid, Reduction of Lean Chromite Ore Using a New Type Plasma Reactor, Proceedings of Symposium on Extractive Metallurgy of Refractory Metals, Annual AIME Meeting, Chicago, 1981, published by TMS-AIME.
9. H.L. Saunders, H.J. Tress, Interaction of Carbon and Iron Ore, Journal of Iron and Steel Institute, 157, (215), 1947.
10. B.G. Baldwin, The Mechanism of the Reduction of Iron Oxides by Solid Coke, Journal of Iron and Steel Institute, 179, (30), 1955.
11. K.J. Oksuka, D. Kumii, Reduction of Powdery Ferric Oxide Mixed with Graphite Particles, Journal of Chemical Engineering of Japan, 2, (1), 1969, p 46.
12. Y.K. Rao, The Kinetics of Reduction of Hematite by Carbon, Metallurgical Transactions, 2, (5), 1971, p 1439.
13. R.J. Fruehan, The Rate of Reduction of Iron Oxides by Carbon, Metallurgical Transactions, 8B, 1977, p 279.
14. M.C. Abraham, A. Ghosh, Kinetics of Reduction of Iron Oxide by Carbon, Ironmaking and Steelmaking, 6, (1), 1979, p 14.
15. P.L. Walker, Jr., M. Sfelef, R.A. Anderson, Chemistry and Physics of Carbon, P.L. Walker, ed., Vol. 4 (New York: Marcel Dekker, Inc. 1968), p 258.

16. J.B. Lewis, Modern Aspects of Graphite Technology, L.C.F. Blackman, ed., (London: Academic Press, 1970).

17. L.S. Darken, E.T. Turkdogan, Heterogenous Kinetics at Elevated Temperatures, G.R. Belton, W.L. Worrell, ed., (New York: Plenum Press, 1970).

18. B.R. Brontin, The Application of Plasmas to Chemical Processing, R.F. Baddour, R.S. Timmis, ed., (Oxford: Pergamon Press, 1967).

19. T.B. Reed, ibid. p 26.