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PLASMA TECHNOLOGY AND ITS APPLICATION TO EXTRACTIVE METALLURGY

SYNOPSIS

The present state of the technology relating to plasma generation and plasma furnaces is described, with particular reference to extractive metallurgy and refining techniques. A brief survey is presented of typical applications of plasma technology in metallurgical processing, and the work carried out on ferro-alloy applications is discussed in detail.

The feasibility of plasma furnaces for the reduction of iron oxide and vanadium oxide has already been demonstrated by the Bethlehem Steel Corporation. A preliminary evaluation is made of the use of plasma furnaces for the production of ferro-alloys.

INTRODUCTION

In the late 1950s, Sheer and Korman¹ carried out the first investigations into the carbothermic reduction of oxide ores using a plasma reactor. Since then rapid advances have been made in the technology of high-power plasma generation, and there has been a great increase in the number of investigations into the use of this technology in the chemical and metallurgical industries. Before 1971, when the use of plasma technology in the field of extractive metallurgy was reviewed by Sayce², little work had been reported in this field that involved ferro-alloy pyrometallurgy.

However, in the last eighteen months reports have become available of successful trials on the production of ferro-alloy in 1 MW-pilot plasma furnaces, and plasma installations of more than 10 MW are now available commercially.

The aim of this review article is:

- to describe the current state of plasma technology in detail,
- to review the applications of plasma technology to extractive metallurgy since 1970, and
- to describe the work carried out on the production of ferro-alloys in plasma furnaces.

PLASMA TECHNOLOGY

A plasma furnace can be defined as an electrically heated gas furnace in which the materials are subjected to high temperatures (greater than 2000 K) and undergo varying degrees of heat treatment and reaction according to their residence time in the furnace and the chemical nature and enthalpy of the plasma gas. A plasma is a partially ionized gas at atmospheric pressure that is sufficiently conducting to allow stable transfer of electric power between two or more electrodes.

Although, at the turn of the century, plasma discharges were used in Norway for the fixation of nitrogen from air³, present-day plasma technology has developed from the work done by physicists to develop methods of generating

higher and higher gas temperatures, and from the need for high-temperature gas flows for the testing of materials in the aerospace industry.

Three major technical developments in plasma generation contributed to the rapid growth in the application of plasma devices to the chemical and metallurgical industries.

- the high-intensity, consumable-anode plasma,
- the fluid-stabilized plasma, and
- the radio-frequency-induced (r.f.) plasma.

The high-intensity anode plasma, shown in Figure 1, which was discovered by Beck⁴ in 1921, developed by Finkelburg⁵ in the early 1950s, and perfected by Sheer and Korman¹ in the 1960s, was used for a series of applications in which the carbothermic reduction and chlorination of many oxide ores were attempted⁶. By prefabricating anodes from mixtures of graphite and oxides, Sheer and Korman¹ were able to carry out many oxide reductions by feeding the anode to the plasma as the anode was consumed by evaporation. The chemistry could be controlled

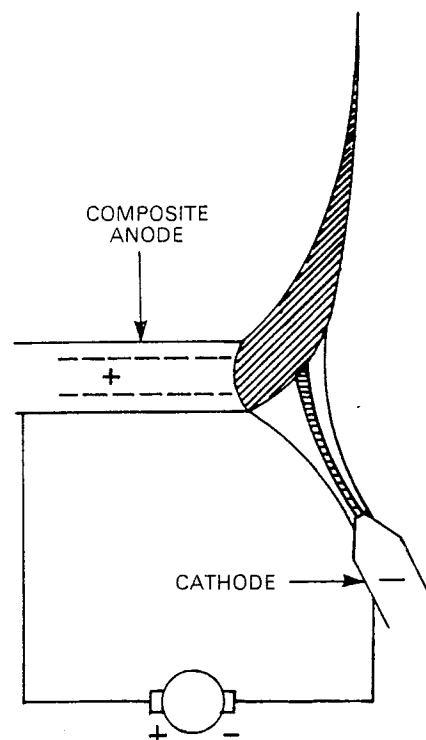


FIGURE 1 A high-intensity carbon arc.

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Dr Hamblyn graduated in chemical engineering from London University in 1965 and received his Ph.D. in chemistry from the University of Surrey for research carried out at the RTZ Borax Research Centre on plasma chemistry. In 1972 he joined the research department of LONZA AG in Switzerland where he was Project Leader in charge of the development of a plasma pilot plant for fumed silica production. In 1975 he took up a post as Research Scientist at the CSIR in South Africa and recently joined the National Institute for Metallurgy, where he is working on the application of plasma technology to extractive metallurgy. Dr Hamblyn has published several papers on chemical processing in plasma reactors.

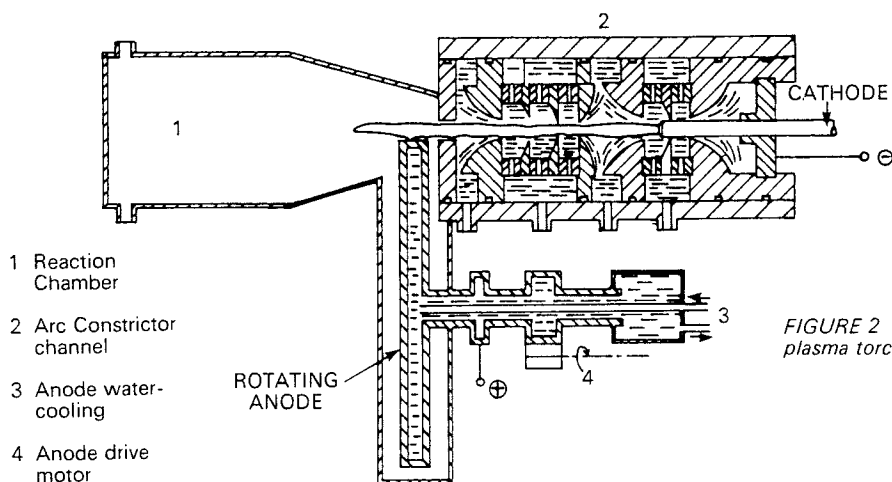


FIGURE 2 A liquid-stabilized direct-current plasma torch.

by the selection of the appropriate graphite-to-oxide ratio in the anode, and the conversions of oxides to elements or carbides were usually greater than 50 per cent. The elegance of this reduction technique was offset by the high cost of anode fabrication, and no major industrial use of this technique has developed. The high-intensity plasma remains a useful laboratory tool for investigation of the chemistry of carbothermic reductions, and was used recently for the preparation of boron carbide from borax⁷.

The water-stabilized arc, originally conceived by Gerdien and Lotz⁸ to increase the current density of the direct-current arc column, was further developed by Weiss⁹, who required a stable jet of plasma that could be used as a source for spectrographic measurement of temperature. This device led directly to the development of the 250 kW liquid-stabilized plasma torch now used for plasma spraying¹⁰, and indirectly to the development of the high-powered, gas-stabilized, direct-current plasma devices that are used for the testing of materials in the aerospace industry. Many facilities for testing with direct-current gas-stabilized plasma of megawatt capacity are operated on a routine basis in America, among which the most powerful is probably that of General Electric, which has a 25 MW plasma generator¹¹.

The r.f. plasma, originally developed by Reed¹² in 1960 as a new crystal-growing technique, revived interest in the field of plasma chemistry. The ability of the r.f. plasma reactor, owing to the absence of metal electrodes, to handle virtually any chemical, opened up the way to investigations of many chemical processes that could previously not be studied in this way because of the rapid corrosion of plasma-torch materials¹³. Since the r.f. plasma is limited to laboratory-scale operation, it has found its main use as a diagnostic tool in the measurement of the properties of plasmas and in the elucidation of the mechanisms involved in chemical reactions. Commercial spectrometers using low-power r.f. plasmas as the light source are now available.

Direct-current plasma generators

Either liquid-stabilized or gas-stabilized plasma is used for direct-current plasma generators.

Liquid-stabilized plasma jets

A typical water-stabilized plasma jet of 250 kW is

shown schematically in Figure 2. Water is pumped tangentially into and out of a cylindrical channel, and a direct-current arc is struck between an axial graphite cathode and a disc anode rotating at 3000 rev/min. The direct-current column is stabilized by the water vortex, and a hydrogen-oxygen plasma jet is formed by rapid evaporation from the surface of the water. This type of plasma jet has a thermal efficiency of between 80 and 90 per cent and gas enthalpies of 70 MJ/kg can be obtained at mean gas temperatures¹⁴ of 8000 K. The main applications of this type of torch are for plasma spraying, where water is used as the stabilizing liquid, but in other applications where a reducing atmosphere is required, ethanol has been used¹⁴.

Gas-stabilized plasma jets

Many different types of gas-stabilized, direct-current plasma jets have been successfully developed and marketed over the years. All the devices are basically similar in that the plasma is struck between a tungsten cathode and a copper anode, and a flow of plasma-stabilizing gas is injected between the electrodes, as shown in Figure 3. The velocity of the exit gas at the nozzle is typically from mach 1 to 2, and gas temperatures in excess of 20000 K have been measured¹⁵ in this region. Many different gases have been used in this device, although the most common are argon, nitrogen and hydrogen.

Direct-current plasma jets alone, whether stabilized by gas or liquid, are of limited use except for welding, cutting, and spheroidization. When used for processes involving mass transfer and reaction of particulate solids or melts, a reactor or furnace is required that effectively utilizes the energy and reactivity of the plasma gas stream.

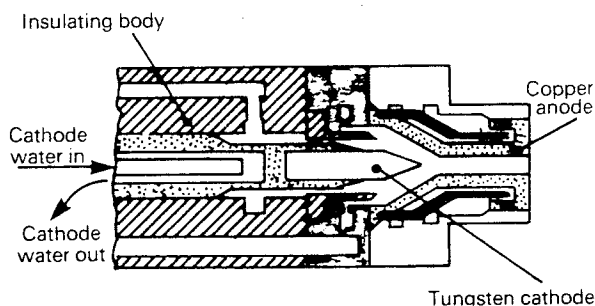


FIGURE 3 A gas-stabilized direct-current plasma torch (after Sayce²).

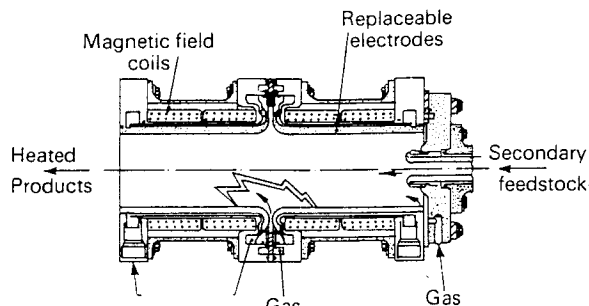


FIGURE 4 A 3.5 MW single-phase alternating-current arc heater (after Fey¹⁷).

Alternating-current plasma generators

Alternating-current plasma generators use a single-phase or three-phase power supply.

Single-phase alternating current

Plasma generators of 50 Hz were originally operated¹⁶ at 100 kW and are now commercially available¹⁷ at 3.5 MW. The 100 kW generators consisted of a pair of coaxial water-cooled copper electrodes across which a plasma discharge was maintained by a 1 MHz ignition unit. This type of generator was reported¹⁸ to have a 60 per cent thermal efficiency at 100 kW.

The 3.5 MW single-phase plasma generator developed by Westinghouse and shown schematically in Figure 4 is a highly sophisticated device in which the plasma is maintained between two water-cooled copper-ring electrodes spaced approximately 1 mm apart. This small inter-electrode gap permits self-ignition when the current is zero and also minimizes electrode erosion by the combination of high-velocity gas purge between electrodes (200 m/s) and rotation of the plasma round the electrode gap at 60 000 rev/min by an external electromagnetic field.

The Westinghouse plasma generator is essentially a highly efficient (80 per cent quoted) gas heater that can supply medium-enthalpy gas streams (approximately 20 MJ/kg for air).

Three-phase alternating current

The use of three-phase plasma reactors is well established in the petroleum industry. Knapsack-Griesheim

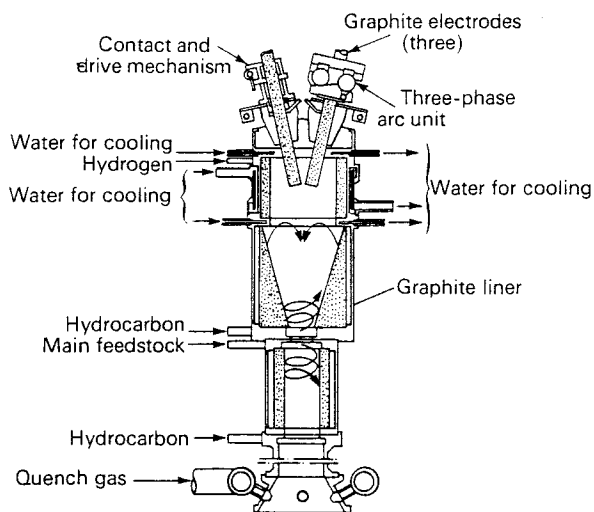


FIGURE 5 A 4 MW three-phase alternating-current plasma reactor (after Schallus et al¹⁹).

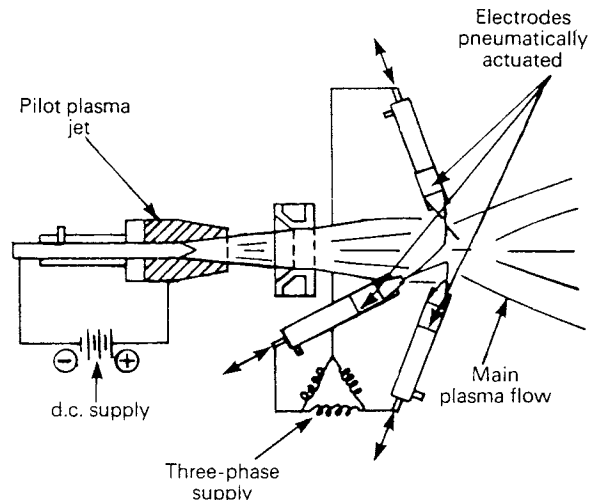


FIGURE 6 A 200 kW three-phase alternating current plasma system with direct-current stabilization (after Bonet et al²⁰).

have operated a series of 4 MW three-phase plasma reactors for many years for the production of acetylene from hydrocarbon feedstock¹⁹, a mixture of acetylene and ethylene being produced that requires 4 500 kW.h/t. The reactor shown schematically in Figure 5, consists of three carbon electrodes mounted vertically in a cylindrical

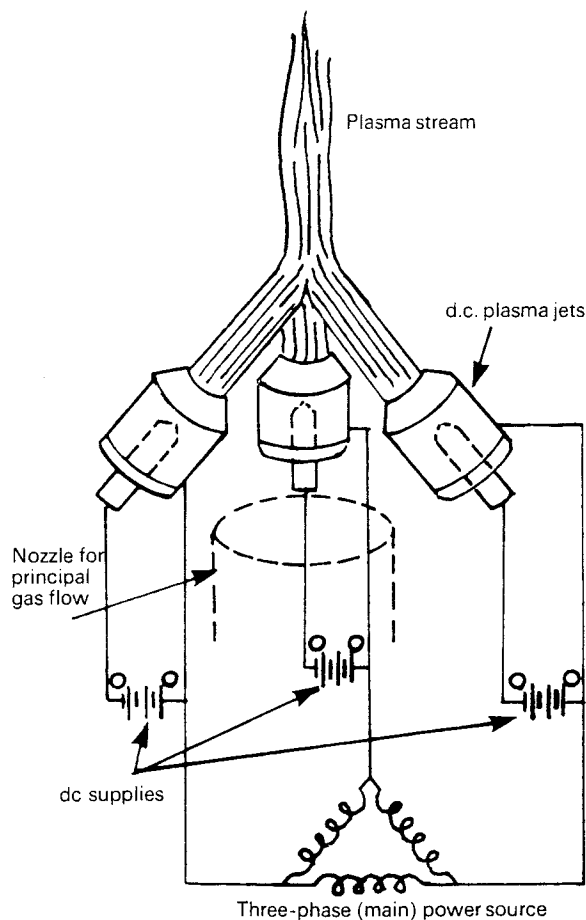


FIGURE 7 A 200 kW three-phase alternating-current plasma system with superimposed direct-current supply (after Arcos SA²¹).

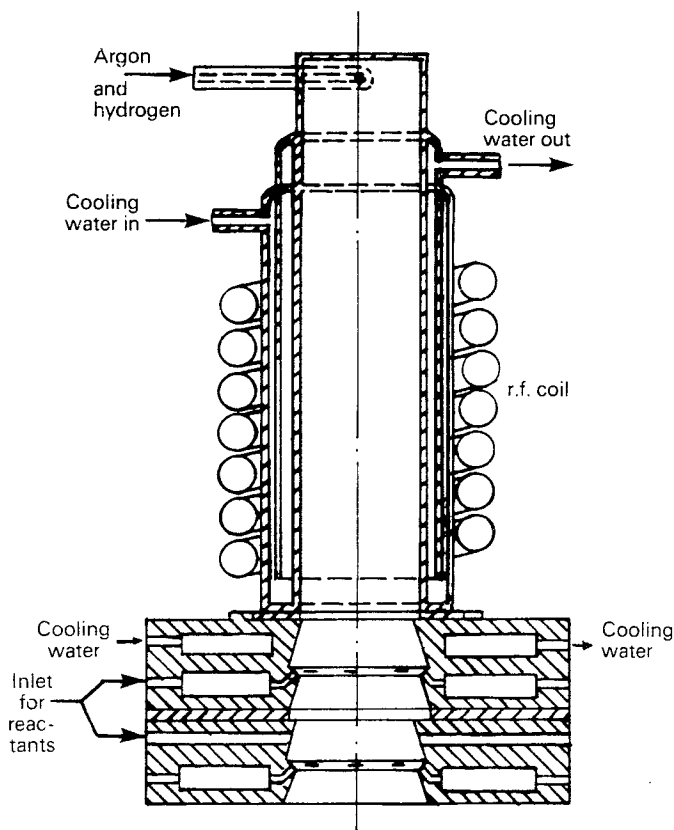


FIGURE 8 A 30 kW radio-frequency plasma reactor (after Hamblyn *et al*²⁴).

graphite reactor. A constant electrode gap can be maintained by an electrode drive mechanism. Three plasma arcs are stabilized by a tangential flow of hydrogen into which hydrocarbon feedstock is injected. Acetylene conversions are conserved by quenching downstream with a stream of recycled hydrocarbon.

A three-phase plasma unit of smaller scale was developed by Bonet *et al*²⁰ in France. This device, shown in Figures 6 and 7, is capable of supplying up to 200 kW of three-phase power to three water-cooled copper electrodes producing a plasma stabilized by a small 30 kW direct-current unit. This equipment is being produced commercially and is now available in Belgium²¹. A homogeneous volume of plasma is produced by this device, which has been used mainly for theoretical studies of heat transfer to refractory oxides in a fluidized-bed reactor²².

A three-phase plasma reactor of 600 kW has been used by Fey *et al*²³ for spheroidization of magnetite, in which 280 kg of magnetite per hour was treated at an energy requirement of 2000 kW.h/t. This device uses the two annular electrodes of the single-phase Westinghouse torch together with a coaxial ring electrode.

Radio-frequency-induced plasma

A plasma can also be stabilized within a cylinder of non-conducting material (e.g. quartz, boron nitride) by induction from a magnetic field oscillating a radio-frequency (2 to 10 MHz). Figure 8 shows the design of a laboratory-scale plasma reactor²⁴ used for the reduction of volatile metal chlorides, which is capable of operation up to 30 kW. The oscillating magnetic field is produced by

an external induction coil that forms part of the tuning circuit of the radio-frequency generator.

The main advantage of this type of plasma reactor is that there are no electrodes within the reaction chamber and consequently any gas that is non-corrosive to quartz can be used. This feature greatly extends the usefulness of the reactor for chemical and metallurgical studies, and has made it possible for chlorine-based systems to be studied²⁵.

Unfortunately, scale-up of the r.f. plasma reactor has proved difficult and expensive, and, although successful scale-up to 800 kW has been reported²⁶ and work on a 1 kHz toroidal discharge is being carried out²⁷, this device remains essentially a laboratory tool.

PLASMA FURNACES FOR METALLURGICAL PROCESSING

Expanded plasma furnaces

Attempts to obtain longer contact times between particulate solids and the current-carrying plasma gas, and higher particle densities, in the plasma gas, have resulted in the development of several techniques for expanding plasma gas streams.

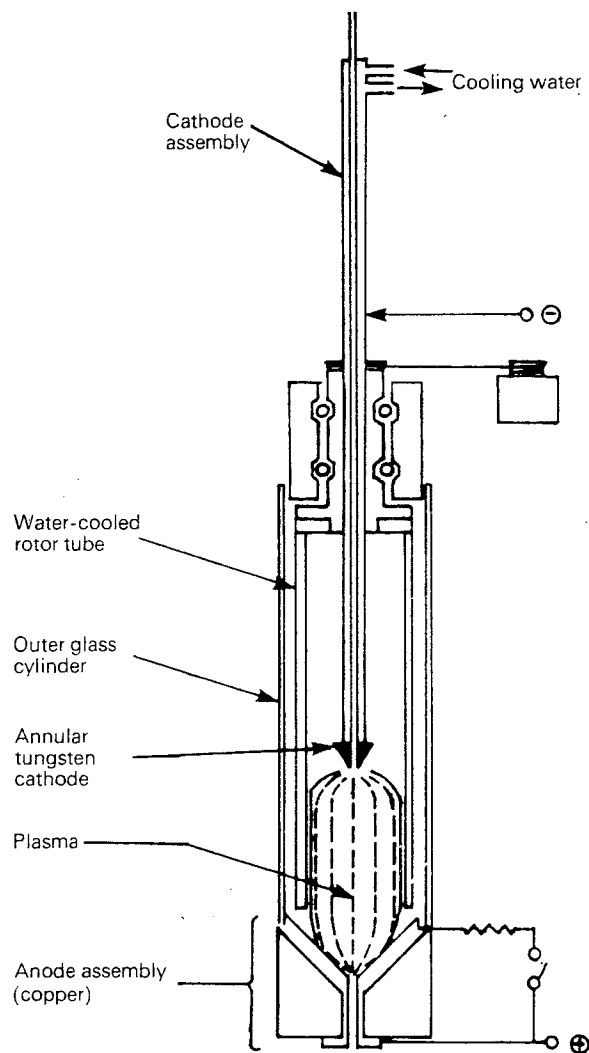


FIGURE 9 A 30 kW rotating-wall, direct-current plasma furnace (after Whyman²⁸).

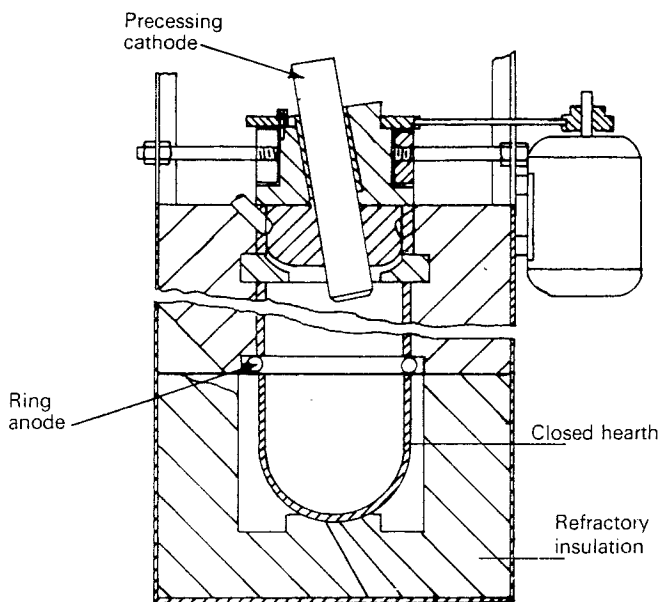


FIGURE 10 A 200 kW precessing-cathode, direct-current plasma furnace (after Tylko³⁰).

Rotating-wall expansion

The first significant progress in plasma expansion was reported by Whyman²⁸, who developed a direct-current plasma reactor, shown schematically in Figure 9. In this device, the direct-current column was expanded by viscous-drag forces exerted on its periphery by a water-cooled copper cylinder, rotating at speeds up to 1000 rev/min. Initiation of plasma was effected by lowering the cathode to the anode level and striking a conventional d.c. arc. By raising the cathode and increasing the speed of rotation of the annular wall, a plasma of approximately three litres in volume could be stabilized (10 cm ϕ by 40 cm long) at power levels of 40 kW. Temperature distributions within the expanded arc column were reported to be flat and residence times of particles within the expanded plasma were much longer than in conventional plasma jets. This reactor was used to study the evaporation of several refractory materials including alumina, silica and zirconia by use of a special cathode assembly²⁹. Bryant *et al*²⁹ reported that injection of 150 μm alumina particles into a 30 cm long argon plasma resulted in only partial evaporation, whereas complete evaporation of 100 μm agglomerates of 1 μm alumina particles at rates of approximately 20 g/min was possible. The inherent difficulty in this design of expanded plasma reactor was the anode constriction which inevitably blocked up with solid deposits after a short operating period, thus limiting the furnace to batch operation.

Rotating cathode expansion

A more advanced concept of the expanded plasma reactor, developed by Tetronics Ltd³⁰ is that of the expanded precessive plasma (E.P.P.) formed between an orbiting cathode and a ring anode set in a refractory shell as shown in Figure 10. The term 'precessive' simply describes the motion of the cathode tip relative to the anode arc root, i.e. the cathode tip precedes the arc root in its rotation. Speeds of precession of up to 2000 rev/min are used, enabling an extremely stable plasma flow to be maintained which can readily accept high solid feed rates. The plasma configuration, i.e. speed of precession and

height of cathode above the anode ring, is controlled automatically according to the loading of solids feed in the plasma volume. Solids are introduced into the furnace from a multiple outlet powder feeder as a circular curtain around the precessing cathode.

This furnace has been operated at 200 kW for various extractive metallurgical applications, including concentration of low-grade ilmenite ores, reduction of magnetite concentrates to iron using powdered coke as reductant, and thermal treatment of zircon sand to facilitate leaching of silica from zirconia. Other uses of the expanded, precessive plasma furnace are spheroidisation of 5 μm iron and nickel powder, and the extraction of copper from copper-containing minerals. This furnace is now in commercial operation, producing low-tonnage products and a 1.4 MW furnace is being constructed in association with Foster Wheeler Ltd³¹.

Fluid-convection expansion

A method for expansion of a plasma without mechanical rotation has also been successfully developed and is reported to be used commercially for the melting of zircon sand³². This method of plasma expansion was developed from an observation by Maeker³³ that a zone of low pressure exists around the cathode tip into which surrounding gas and solids are rapidly entrained. Sheer *et al*³⁴ developed a plasma reactor that used this phenomenon and described the device as a 'fluid convection cathode reactor'. The plasma was stabilized between the fluid convection cathode and three transpiration anodes, as shown in Figure 11. By altering the relative positions of the three anodes and the cathode while increasing power supplied to the plasma, they were able to obtain an expanded volume of plasma.

The zircon sand treatment furnace³² developed by Ionarc Smelters Ltd uses an expanded plasma flow that is stabilized between a fluid convection cathode and three graphite anodes, which are fed continuously into the

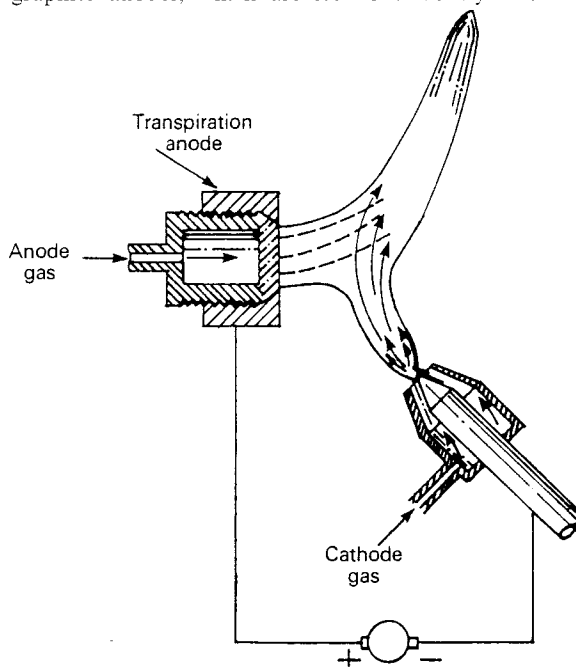


FIGURE 11 A 50 kW fluid-convection cathode plasma system (after Sheer *et al*³⁴).

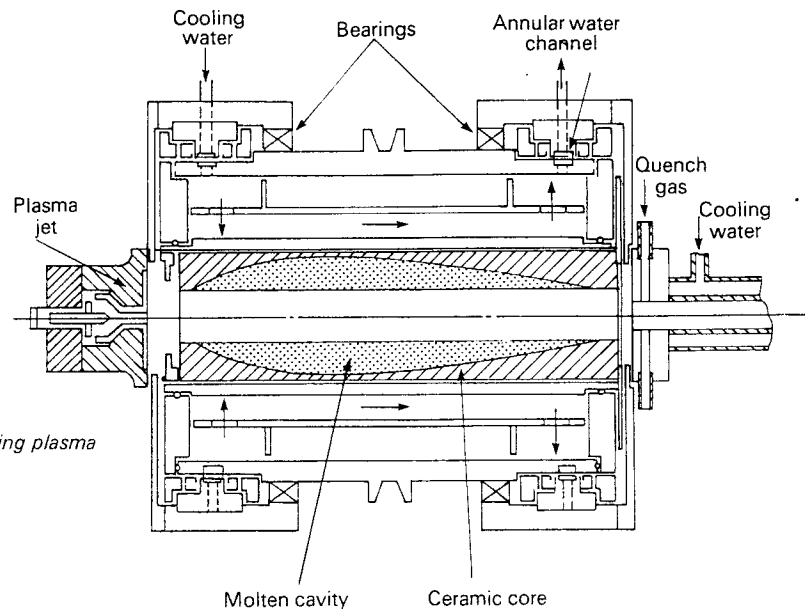


FIGURE 12 A 30 kW horizontally-rotating plasma furnace (after Howie and Sayce⁴⁰).

plasma zone to compensate for anode loss by evaporation. An alternative anode configuration for this type of plasma furnace has also been successfully developed at the National Physical Laboratories in the UK where three direct-current plasma jets are used as anodes³⁵.

The use of these fluid-convection plasma-furnaces for heat treatment of particulate solids, whether it be a melting or an evaporation process, depends primarily on the success of the powder feed system in attaining uniform flows of powder into the entrainment region surrounding the cathode tip. Once a successful powder feed system has been developed for a particular application then large powder feed rates to the current-carrying plasma can be obtained. Wilks *et al*³² report complete dissociation of zircon at rates of up to 140 kg/h at 300 kW operation of the Ionarc furnace, which is similar to the performance of the NPL furnace that can melt up to 70 kg/h of zircon at 150 kW³⁵.

The merits of the three different anode configurations are not clearly established at present. The disadvantage of the graphite anode system, i.e. necessity for control of the anode feed rates, is to a certain extent offset by the radiation of heat from the hot anode tips to the particles in the plasma gas, which could mean slightly reduced energy requirements, especially when the system is scaled up. The use of transpiration anodes which enable relatively cool gas to be supplied to the plasma tail flame is of use in evaporation processes, where quenching of the evaporated species is important.

For example Sheer *et al*³⁴ have evaporated many refractory oxides in their fluid convection cathode device and have successfully prepared a commercial surface-active silica at power requirements of 11 000 kW.h/ton silica by controlled quenching of the silicon monoxide and oxygen evaporation products. Another benefit of the transpiration anode system is that the transpiring gas prevents deposition of oxides on the anode face which can cause insulation and lead to arc instability.

The major disadvantage of all the fluid convection cathode systems as opposed to the expanded precessing plasma is that they demand a rigorous powder feeding control system to ensure that the powder passes through

the current-carrying region of the plasma, whereas in the precessing plasma all the powder passes through the current-carrying plasma by virtue of the furnace wall, which supports the ring anode and hence bounds the system.

Rotating plasma furnaces

Plasma-fired rotating furnaces have developed from the use of flame-fired and solar-heated rotating furnaces for melting of glasses and refractory oxides.

Horizontal-drum furnaces

Grosse *et al*³⁶ reported the use of a centrifugal plasma furnace for melting various metals in the presence of molten oxides. The furnace was fired with a 30 kW direct-current plasma jet and was operated at rotation speeds of between 500 and 1 500 rev/min. Grosse *et al*³⁶ prepared mixtures of alumina and various metals by melting an alumina charge in the furnace and then melting a rod of metal such as aluminium or iron in the oxide melt. The molten metal was reported to float on the molten alumina surface within the rotating furnace.

Foex *et al*³⁷ developed a rotating furnace for melting batches of special refractory oxides. The furnace was heated by an axial plasma column transferred between two direct-current plasma jets situated at either end of the furnace. Refractory powder mixtures were melted in the rotating furnace and the melt poured into a water quench, where homogeneous prills of mixed oxides were formed. Supplementary power could be supplied to the transferred plasma column from an external power source up to a maximum of 120 kW. A typical power requirement for melting a zirconia/5 per cent lime mixture was 12.4 MJ/kg of melt poured from the furnace (or 5.1 MJ/kg oxide melted).

The use of a horizontally rotating plasma furnace for evaporation of refractory oxides was reported by Sayce and Selton³⁸. They developed a semi-pilot scale rotating plasma furnace, fired by a 30 kW d.c. plasma jet (shown in Figure 12) in which evaporated species were quenched at the furnace outlet and the resultant fine powders separated from the gas stream in an electrostatic precipitator.

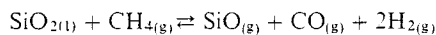
Mixtures of carbon and refractory oxides, such as alumina, silica, magnesia, and titania were prepared and fired in the rotating furnace, which was heated by the 30 kW argon plasma jet, and gaseous reduced oxide species were quenched to form high-surface-area products. The average energy requirements and surface area of products prepared in this furnace are shown in Table 1.

TABLE 1
EVAPORATION IN ROTATING FURNACES³⁸

Feed oxide	evaporating species	quench gas	product	SA m ² /g	kW.h/kg
Al ₂ O ₃	Al ₂ O	air	Al ₂ O ₃	80	15,5
SiO ₂	SiO	N ₂	SiO/SiO ₂	—	13,8
MgO	Mg	air	MgO	44	34,72

The work of Sayce and Selton³⁸ on reduction of refractory oxides in a rotating furnace was limited to batch operation at a relatively small scale.

The principle of the rotating plasma was further developed for continuous operation at 200 to 250 kW power levels for the production of fumed silica by Schnell *et al*¹⁴. This furnace consisted of a water-cooled mild steel drum (400 mm in diameter and 700 mm in length) containing silica. The furnace was rotated horizontally at speeds up to 500 rev/min and fired with a direct-current plasma jet of the type shown in Figure 2. The plasma jet, which was stabilized with a 70 per cent mixture of ethanol and water, was capable of continuous operation by means of a continuous graphite cathode feed assembly. Silica sand (0,1 to 0,3 mm) and methane gas were fed continuously to the reactor through inlets adjacent to the plasma jet. Sand feed rates of up to 15 kg/h were possible and methane/sand ratios were maintained at approximately 20 per cent stoichiometric for the reaction:



The silicon monoxide vapour, diluted in a mixture of hydrogen and carbon monoxide, was quenched and reoxidized with steam that was expanded from a 2000 kPa supply line via mixing jets located at the furnace outlet.

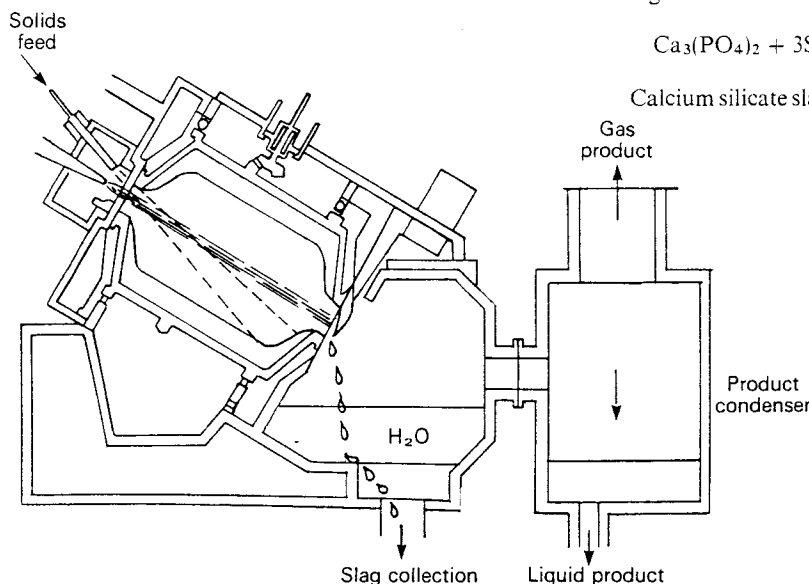


FIGURE 13 A 100 kW sloping rotating plasma furnace (after Yerouchalmi *et al*³⁹).

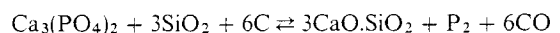
By control of the quench/oxidation process, the production of a surface-active silica was possible at energy consumptions of approximately 13 000 kW.h/ton SiO₂. The surface-active silica so-formed had surface areas up to 300 m²/g and was equivalent to commercially available fumed silicas in most of its surface properties.

Several problems remain to be overcome in the design and operation of rotating plasma furnaces for chemical reductions such as the reduction of quartz sand. The use of a gas phase reductant imposes a mass transfer limitation on the reaction rate, which would be overcome by using a solid reductant such as coke or carbon. The use of solid reductant in the fumed silica process was precluded by the purity specification of the product, in which no carbon could be tolerated. For other applications it may well be possible to use solid reductants and hence avoid the limitation of mass transfer of gaseous reducing species to the rotating melt. Another difficulty which remains to be overcome is loss of molten reactant in both particulate and bulk forms from rotating furnaces, under the influence of momentum transfer from the plasma gas. This can probably be overcome by use of larger size ranges of feed materials or by use of higher rotation speeds. Operation of rotating plasma furnaces with off-axis plasma burners could also be beneficial, as the higher surface area of melt thus obtained would provide for higher heat transfer rates from the plasma gas to the rotating melt.

Sloping-drum furnaces

The use of a rotating plasma furnace with a sloping drum for the continuous treatment of tricalcium phosphate ore was proposed by Yerouchalmi *et al*³⁹. The design of this furnace is shown in Figure 13, is essentially the same as that of Foex *et al*³⁷, but the furnace is operated at an angle of 45° to the horizontal and is enclosed in a sealed chamber to prevent the entry of air to the system. Tricalcium phosphate, silica, and coke are introduced to the top end of the rotating furnace, which is fired by a 150 kW transferred arc maintained between electrodes at each end of the furnace.

The tricalcium phosphate is reduced by the coke in the presence of silica to produce phosphorus vapour according to the following equation:



Calcium silicate slag is tapped continuously from the lower

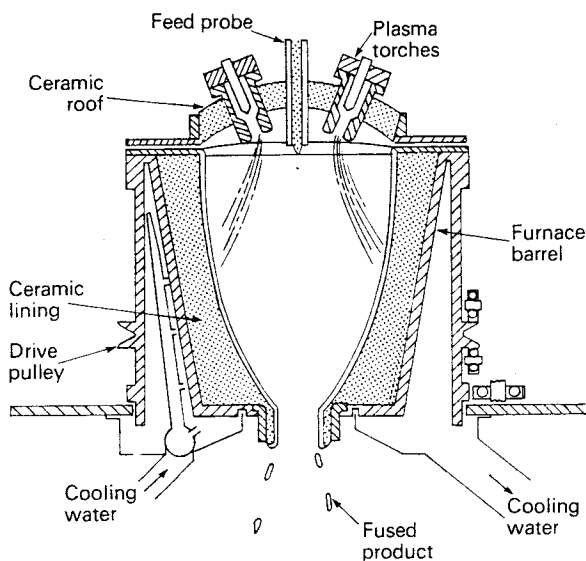


FIGURE 14 A 60 kW vertically-rotating plasma furnace (after Barrett et al⁴¹).

end of the rotating furnace, while phosphorus vapour, carbon monoxide, and plasma gas are drawn into a water quencher where phosphorus is condensed and collected.

This proposed process overcomes some of the problems encountered in the use of the rotating plasma furnace for production of fumed oxides by virtue of the continuous off take of molten material. It offers a method of separating unreacted feed materials from the gas phase product, when quenching of the product is not critical (as with phosphorus).

Vertical-drum furnaces

In an attempt to improve continuous feeding of materials to, and continuous withdrawn of both liquid and vapour products from rotating plasma furnaces, Howie and Sayce developed a 60 kW, vertical-drum rotating furnace. This furnace, shown in Figure 14, has been found most suitable for the study of the fusion of refractories and glasses⁴⁰ and extractive metallurgical processes, such as slag fuming⁴¹.

The furnace consists of an inverted conical barrel welded into an outer cylindrical shell. The furnace roof is fabricated from a castable refractory (e.g. mullite, alumina, or stabilized zirconia) and supports two d.c. plasma jets which are operated in the transferred mode. Ceramic linings are precast from the material under study and set in the furnace barrel and the inner surface fused *in situ* by firing the two d.c. plasma jets. When operated in the transferred mode, the two jets repel each other and are deflected towards the rotating ceramic wall, thus increasing heat transfer and melting rates. After initial melting, there was some evidence of resistance heating of the liquid furnace linings, as occurs in conventional arc melting of metals and slags.

Melting experiments were carried out on a mixture of 50 per cent silica, 40 per cent alumina, and 10 per cent baria, in which glass droplets of 3 to 5 mm in diameter were produced continuously at rates up to 4.5 kg/h, at an energy requirement of 12 200 kW.h/ton. The bubble content of the glass droplets was observed to decrease during the course of an experimental run, as fusion of the ceramic lining approached completion. Howie and Sayce⁴⁰

concluded that the vertical rotating melting furnace, in which the inner wall consists of the material to be melted, offers advantages over conventional static carbon-arc and plasma melting furnaces, in that there is a higher ratio of melt area to roof area available for heat transfer. Also there are no refractory walls in contact with the furnace atmosphere and hence no erosion of refractory linings can occur. When compared with the horizontal or sloping rotating drum plasma furnaces, the vertical drum furnace has a larger melt diameter at the feed end, which facilitates both a multi-torch configuration and feeding of materials to the rotating melt. However, the increase area of refractory roof could lead to higher heat losses and to additional materials problems.

In general all types of rotating plasma furnaces, although overcoming the problem of very short particle contact times with the plasma, are nevertheless limited by the fixed area of melt in contact with the plasma. This is not a problem for a heat transfer (i.e. melting) application, where heat transfer rates are sufficiently high because of the high bulk gas temperature and velocity, but can be a serious limitation in a gas-phase reduction application in which mass transfer of reductant from plasma gas to the bulk melt will be considerably lower than for a particulate melt system, where the surface area/unit mass of molten material will be much higher.

In order to combine the advantages of the treatment of fine particulate material in expanded plasma furnaces (high surface area/unit mass material) and those of the rotating plasma furnace (extended contact times of material with plasma gas) Bonet⁴² has proposed a mixed function reactor, in which the rotating cylinder of melt is the containing wall for a conventional plasma particle heater. This system would have the additional advantage of reducing radiation losses, because radiation between particle and the wall would occur at the same temperatures, thus minimizing the formation of cold zones, in the reactor. A further conceptual design of Bonet's mixed reactor would be a furnace in which the plasma could be transferred from a primary plasma cathode of the fluid-convection type described by Sheer³⁴, through the rotating melt to an anode ring at the base of a vertically rotating furnace. This would combine the advantages of both the expanded plasma concept and the rotating plasma furnace with the additional advantage of resistive heating of the liquid wall of the rotating furnace.

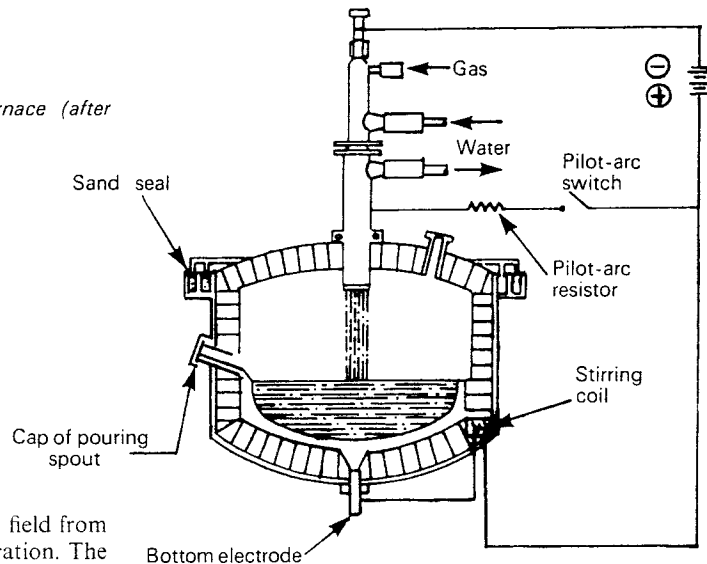
Molten-pool plasma furnaces

The use of molten-pool plasma furnaces in metallurgical melting and remelting processes was reviewed⁴³ in 1972 and has recently been the subject of a report by the U.S. National Academy of Sciences⁴⁴.

Closed-hearth furnaces

One of the first reports of the use of plasma heating in conjunction with a molten pool for the remelting of steel was the plasma arc furnace. Magnolo⁴⁵ described the operation of this furnace (shown in Figure 15) in which a direct-current plasma torch of 60 kW power was fired into a 0.6 m diameter furnace hearth, which was lined with conventional refractories. The furnace was operated on 150 kg batches of AISI 4340 steel, and electrical power was transferred from the cathode of direct-current plasma torch to the molten metal pool via the plasma column. The direct-current supply was connected through a stirring

FIGURE 15 The 60 kW LINDE Plasmarc furnace (after Magnolo⁴⁵).



coil set in the base of the hearth, the magnetic field from which inductively stirred the melt during operation. The chemical and physical properties of steels melted in the Linde furnace were claimed to be equal to those of vacuum-melted steels (e.g. oxygen contents of 8 to 25 p.p.m., hydrogen 1 to 2 p.p.m., and nitrogen 10 to 30 p.p.m.) but no energy requirements for batch melting were given.

The use of a plasma remelting furnace, having a capacity of 10 t. for remelting nickel-alloy scrap, stainless-steel scrap and tool-steel scrap was reported by Lachner *et al*⁴⁶ and Fiedler *et al*⁴⁷. The furnace was lined with rammed chrome-magnesite bricks and fired with three direct-current plasma torches of 3 MW each, running on either argon or mixtures of argon and nitrogen. The power consumption of the furnace during melt-down of scrap was reported as being from 600 to 800 kW.h/ton, and during the melt-finishing period, 100 to 200 kW.h/ton. The quality of the final remolten alloy was limited because it was cast into conventional air moulds, but it was nevertheless equivalent to quality of alloys produced in vacuum-induction or vacuum-arc remelting furnaces.

The use of a combined plasma-remelting furnace and an induction-heated remelting furnace is under development in Japan⁴⁸. The plasma torch operates at 200 kW in the transfer mode and is supplemented by a 200 kW induction heater coil. The tungsten cathode of the plasma jet used in this furnace is reported to have an operating life of up to 1000 h. Successful desulphurization and deoxygenation of steels (oxygen contents of less than 20 p.p.m.) have been reported using this combined furnace. The furnace has also been successfully used for the purification of titanium, chromium, and silicon and for the melting of copper alloys in batches up to 1.2 tons.

Esser *et al*⁴⁹ carried out simulation computations on the performance of plasma remelting furnaces in terms of the charge melt down time, t_N and the complete melting time t_E , where t_N was defined as the time in which 10 per cent of the charge material is melted. By relating t_N and t_E to important operating parameters, as indicated in the following equations:

$$t_N = a_0 + a_1 \left(\frac{M}{F_0} \right) a_2 \theta_B - a_3 E_S^n$$

$$\text{and } t_E = b_0 + b_1 d_B - b_2 \alpha_B - b_3 B_B$$

where M = mass of charge (kg)
 F_0 = surface area of bath (m^2)
 θ_E = preheating temperature of charge (c)
 E_S = electrical power input, kW
 d_B = bath depth (m)
 α_B = induced convection of melt bath
 (kcal./ m^2 .h.deg)
 B_B = plasma arc length (m)

Esser *et al*⁴⁹ were able to compute the power requirements for remelting in terms of the furnace geometry (bath depth and height of charge) and the configuration of the three plasma torches. It was found that melting times could theoretically be reduced from 210 min to 120 min by changing from vertical plasma torch operation to horizontal torch operation. This was explained by increased convection heating from the plasma gas to the molten pool with horizontal torches. Two further variations in furnace operation were similarly computed: (1) induction booster heating and (2) intermittent tapping of molten alloy from the furnace, and the configuration for minimum theoretical melting time (100 min) was found to be horizontal torches with intermittent tapping of melt from the furnace. This was confirmed experimentally and minimum energy requirement for a 10t remelt of scrap steel of 500 kW.h/ton was obtained.

The use of a laboratory closed-hearth, extended carbon arc plasma furnace for the reduction of many types of oxide ore fines has recently been patented by Segsworth and Alcock⁵⁰. The 'extended arc flash reactor' as it is known, shown in Figure 16, consists of a 20 cm diameter hearth formed within a high grade magnesia refractory lining. Three hollow graphite electrodes at 120° spacing supply up to 30 kW of 3 phase power to the furnace hearth. Gas injection through the hollow electrodes enables a much stabler arc to be established than in conventional carbon arcs, while not requiring such large volumes of gas as conventional plasma jets. The plasma arcs are stabilized with argon, nitrogen, or hydrogen gas supplies and arc lengths vary from between 80 mm and 150 mm according to gas composition.

Fine oxide materials are fed at rates of about 10 kg/h to the top of the exit gas (flash) column of the furnace by a

rotary feeder, which acts as a feed preheater. As the fines drop through the rising hot gas stream into the zone of diffuse plasma, considerable preheating and prereluction is possible. Metal and slag, resulting from the reduction of the ores, collect in the hearth below the plasma zone and are heated by radiation and convection from the diffuse plasma arcs. Batches of metal and slag are tapped from the hearth into cast-iron moulds. The extended arc flash reactor has been used for the reduction of many steel plant waste oxides, such as those from blast furnaces, basic oxygen furnaces, arc furnaces, and vacuum oxygen decarburization processes, to produce iron and saleable slags. Other particulate charges that can be treated in the flash reactor include fly ash, steel mill dust, flue dust, mill scale, and iron ore fines, such as ilmenite, hematite, magnetite, chromite, limonite, etc. Reducing agents such as low-grade coal, anthracite, coke, or sawdust can be mixed with the particulate charge. An example of the quality of products that can be made with the flash reactor is the treatment of 56 kg of flue dust/mill scale containing 50 per cent iron content, which was upgraded in 5 hours to produce 30 kg of Fe having the following analysis:

C 4.03%, Si 2.5%, S 0.029%, Mn 0.09%, P 0.06%,
Cu 0.05%

The use of this furnace for the reduction of other steel plant waste oxides and chromite fines is discussed more fully in the section on Plasma furnaces for the production of ferro-alloys.

Ingot-withdrawal furnaces

Ingot remelting furnaces using plasmas as the heat source are reported to be in operation in the USSR⁵¹, and the Ulvac Corporation in Japan have developed a 'plasma-beam' furnace that can attain purities in metals similar to those obtained with electron-beam remelting furnaces, but requiring less rigorous vacuum conditions.

The plasma-beam furnace consists essentially of a low-pressure, direct-current argon plasma, which is transferred for a hollow tungsten cathode to the workpiece, which is held in cold-hearth crucible. The higher surface area of the hollow cathode is necessary to provide sufficient electron emission from a primary cathode discharge, to maintain a stable plasma discharge between cathode and workpiece. Operating pressures of plasma beam furnaces are typically from 10^{-1} , to 10^{-3} torr in argon and therefore require less expensive vacuum pumping systems than electron beam furnaces (10^{-4} - 10^{-5} torr). The degassing of impurities from the molten metal in the plasma beam furnace is consequently not so effective as in the electron beam furnace.

Kinoshito *et al*⁵², in describing the use of the plasma-beam furnace for the melting of metals, assess the technical characteristics of the furnace as lying mid-way between those of the high-voltage, electron-beam furnace and the vacuum arc. The main advantages are summarized as being (1) controlled discharge between electrode and workpiece, which precludes the spontaneous discharges that are common in electron-beam furnaces (2) better control of components during melting, (3) better control of the distribution of input energy; and (4) temperature control of melt independent of ingot melting speed.

A comparison of impurity levels obtained by remelting titanium and zirconium sponges, molybdenum scrap, and

TABLE 2
COMPARISON OF ELECTRON BEAM, PLASMA BEAM,
AND VACUUM ARC⁵²

		O ₂ p.p.m.	H ₂ p.p.m.	C p.p.m.
Electron beam	Ti	300	12	210
	Zr	695	7.7	—
	Mo	30	0.4	—
	Ta	40	2.8	—
Plasma beam (high purity argon)	Ti	290	9	200
	Zr	682	10.4	—
	Mo	49	3.2	—
	Ta	103	2.5	—
Vacuum arc	Ti	1 400	36.0	380
	Zr	1 372	23.0	—
	Mo	72	1.8	—
	Ta	430	43	—

TABLE 3
COMPARISON OF ENERGY REQUIREMENTS FOR
BUTTON MELTING⁵²

Melting furnace, type	Energy requirement ratios			
	Titanium	Zirconium	Molybdenum	Tantalum
Argon arc (350 torr)	1.30	1.36	1.58	—
Plasma beam (5×10^{-3} torr)	1.00	1.00	1.00	1.00
Electron beam (2×10^{-5} torr)	0.76	—	1.80	1.42

tantalum powder in electron beam, plasma beam, and vacuum arc furnaces is shown in Table 2.

Thermal efficiencies of plasma beam furnaces of between 80 and 85 per cent have been obtained for button melting of refractory metals and Table 3 shows a comparison between the energy requirements for button melting by plasma beam with equivalent melting in electron beam and in direct-current argon arc furnaces.

One major limitation of the plasma beam furnace is that only metals that have a low volatility (i.e. the refractory metals) can be treated in the furnace. This means that

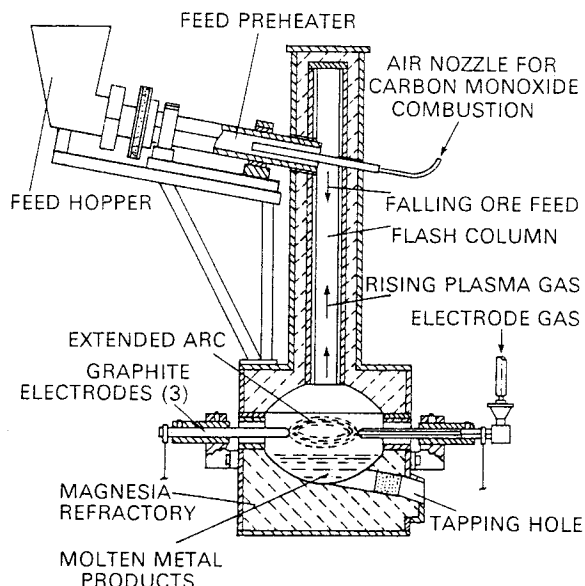


FIGURE 16 The extended arc flash reactor (after Segsworth and Alcock⁵⁰).

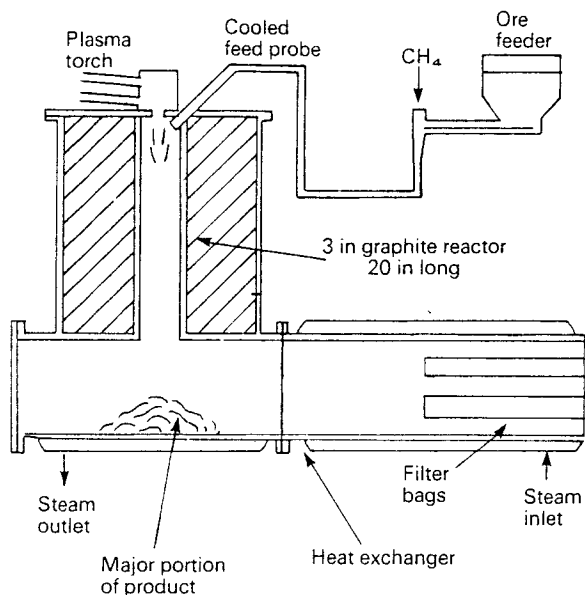


FIGURE 17 The 50 kW American Cyanamid falling-film plasma reactor (after Chase and Skriven⁵³).

removal of volatile metals from refractory metal alloys cannot be achieved in a plasma beam furnace, presumably because of contamination of the hollow cathode by the condensed metal vapour.

Falling film plasma furnaces

Two types of falling film furnaces have been developed for use with direct-current plasma jets.

Tubular-falling-film furnace

Chase and Skriven⁵³ patented a laboratory, falling-film plasma furnace for the beneficiation of titaniferous ore

finer. The furnace shown in Figure 17⁵⁴, consists of a thermally-insulated, hot-wall alumina reactor tube, supported with a water-cooled metal jacket. A direct-current plasma torch is mounted at the top of the reactor tube and feed material is injected to the plasma flame via a water-cooled probe. The titaniferous ore fines melt and form a liquid film on the alumina and the molten ore flows down the reactor wall as a falling film. By controlling the residence time of the falling film in the reactor by varying the operating parameters such as plasma gas feed, ore feedrate, plasma power, and slag content of the ore, Chase and Skriven⁵⁴ were able to reduce ilmenite ore fines (containing 69 per cent TiO₂ and 30.5 per cent Fe₂O₃) with methane to a beneficiated product containing 97.5 per cent TiO₂. Chase and Skriven⁵⁵ also report the use of this falling film plasma furnace for the production of phosphorus from tricalcium phosphate ore fines by methane reduction.

Energy requirements for this laboratory plasma furnace were considered to be reasonable considering the scale of operation (30 kW), being 8400 kW.h/ton TiO₂ (97.5 per cent purity) and 53 MW.h/ton phosphorus, (theoretical 15.4 MW.h/ton).

A more sophisticated type of falling film plasma furnace for the reduction of iron oxides is described by MacRae *et al* in a recent American patent⁵⁶. This furnace differs from the falling film furnace used by Chase and Skriven in that the falling film of molten iron oxide ore flows down the inside wall of the anode tube. (see Figure 18). A d.c. plasma is stabilized between a tungsten cathode and the anode tube, in a vortex flow of plasma gas, and iron oxide fines are pneumatically transported to the anode section of the plasma torch. The ore fines melt on contact with the hot plasma gas and form a falling liquid film in the anode tube. The liquid film is thus in the current carrying path of the

TABLE 4
INTERRELATIONS BETWEEN TRANSPORT PHENOMENA AND VARIOUS PLASMA METALLURGICAL PROCESSES

Transport phenomena Metallurgical processes	Heat transfer (gas to solid)	Momentum transfer (gas to solid)	Mass transfer (solid to gas)	Unimolecular reaction (solid to gas)	Mass transfer (gas to solid)	Bimolecular reaction (solid and gas)	Bimolecular reaction (solid and solid)	Trimolecular reaction (gas and two solids)	Trimolecular reaction (three solids)
Cutting, welding, melting	x								
Spheroidization, plasma spraying	x	x							
Particle evaporation Bulk evaporation	x x	x	x x						
Particle pyrolysis Bulk pyrolysis	x x	x	x x	x x					
Gas-solid reduction (particle) Gas-solid reduction (bulk)	x x	x	x		x x	x x			
Solid-solid reduction (particle) Solid-solid reduction (bulk)	x x	x	x				x x		
Gas-solid-solid reduction (particle) Gas-solid-solid reduction (bulk) Solid-solid-solid reduction (bulk)	x x x	x	x		x x	x x	x x	(x) (x)	x

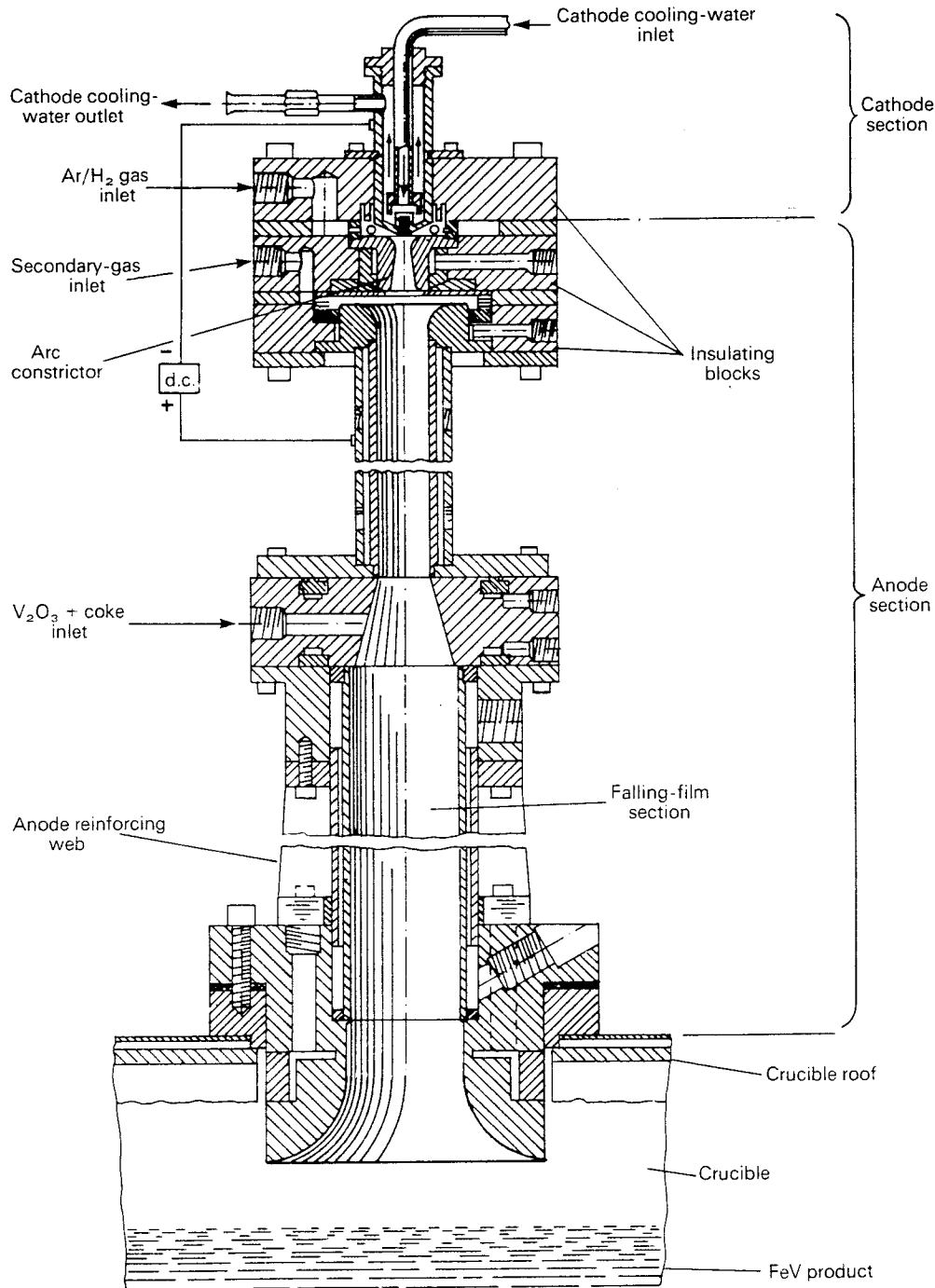


FIGURE 18 The Bethlehem Steel 1 MW falling-film plasma furnace (after MacRae et al⁵⁶).

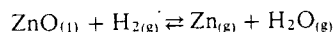
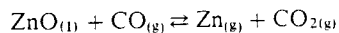
plasma furnace and will undergo resistive heating in addition to radiation and convection heating. Energy requirements for reduction of iron ore concentrates with mixtures of hydrogen and methane at 100 kW power level are reported to be 3300 kW.h/ton of high purity iron produced and no slagging additions were necessary to maintain a good flowing melt. MacRae *et al*⁵⁷ also report the use of this falling film plasma furnace for the production of ferrovanadium, where coke fines were used as the reducing agent. This work is described later under ferroalloys.

Cyclone furnaces

An analogue of the falling film plasma furnace is the cyclone plasma furnace in which the bulk processing of ores is possible with minimum loss of particles in the plasma gas stream. Cyclone furnaces, fired with pulverized-coal flames have been operated at pilot level for slag-fuming operations for some years. Blanks and Ward⁵⁸ describe the development of a cyclone furnace for the removal of zinc from lead blast furnace slags. They were able to reduce the zinc content of the head slags from 17.6 per cent to approximately 2 per cent by firing the

cyclone furnace with pulverized coal at a coal/slag ratio of 0.30.

Zinc oxide was reduced by hydrogen and carbon monoxide from the incomplete combustion of coal according to the equations:



and the metallic zinc volatilized from the slag and re-oxidized to ZnO fume, which is recovered from the process gas filtration.

The use of a cyclone furnace in conjunction with a rotating reactor for fumed silica production has been patented⁵⁹. This combination of rotating furnace and cyclone furnace which was fired by a 200 kW, direct-current, ethanol-stabilized plasma, was developed in order to overcome the problems of loss of particles of molten silica from the rotating furnace. Molten silica particles that were not trapped in the rotating silica melt but carried through the first stage furnace in the plasma gases, could be separated from the gases in the cyclone reactor and were deposited as a layer of molten silica, which could be further reduced to silicon monoxide by the reducing plasma gas. In general, plasma firing of cyclone furnaces could permit the processing of highly endothermic reductions or vaporizations, especially for systems in which the melt is free flowing and a good vortex flow of melt on the cyclone wall can be induced, which will provide prolonged contact times for the reduction or vaporization to proceed to completion.

THE USE OF PLASMA FURNACES IN METALLURGY

Table 4 shows the interrelations between transport phenomena and various metallurgical processes. The first column lists, in order of increasing complexity, metallurgical processes that have been carried out with plasma jets and plasma furnaces. The other columns show some of the physical and chemical transport phenomena that are involved in each metallurgical process. For example, cutting and welding involve only heat transfer from the plasma gas to the solid, whereas gas-solid-solid reductions involve almost all the transport phenomena. The following discussion of the application of plasma furnaces to metallurgy uses Table 4 as a framework.

Heat transfer

Processes involving only heat transfer from the plasma gas to the solid include cutting, welding and bulk melting.

Cutting and welding

The cutting and welding of metals and alloys by use of direct-current plasma jets were recently reviewed by Rykalin⁶⁰. Two modes of cutting are possible: that based on a non-transferred arc the nozzle of the plasma jet being used as the anode, and that in which the workpiece is used as the anode and the plasma is transferred between the cathode and the workpiece. By use of high gas velocities (up to 1000 m/s), very high cutting speeds have been obtained for metals such as stainless steel [300 cm/min for 6.35 mm (¼ in) sheet], aluminium [750 cm/min for 6.35 mm (¼ in) sheet], and carbon steel [500 cm/min for 6.35 mm (¼ in) sheet]. Substantial depths of cutting can be

achieved if plasma jets of high-enthalpy argon and hydrogen are used, where the cutting of 12 cm thicknesses of aluminium, as well as 10 cm thicknesses of stainless steel, copper, and magnesium, is possible⁶¹. Some recognized advantages of cutting with plasma jets are that the quality of the cutting is the same as that produced by the oxygen cutting of mild steel, and that metals such as aluminium, chromium and magnesium can be cut without the formation of refractory oxides on the surface of the cut.

In plasma-welding applications, the transferred-arc mode of operation is usually practised. The plasma jet moves along the joint to be welded while providing a shield of inert gas for the joint. If necessary, additional metal can be introduced into the weld by simultaneous melting of a metal rod, which can either be introduced into the arc as in tungsten-inert gas (TIG) welding, or it can be the electrode itself as in metal-inert gas (MIG) welding. The two types of plasma welding torches are shown in Figures 19⁶² and 20⁶³, together with typical temperature-distribution curves (Figure 20⁶³). The plasma is only a few millimetres in length, and the maximum gas temperatures in the region of contact with the weld are between 8000 and 9000 K. Plasma gas flows of up to 1000 m/s are used, and arc powers of 1.5 to 2.0 kW are typical. Only a small proportion of this power is transferred to the metal by convection, conduction, and radiation, the main heating effect being the voltage drop across the anode (workpiece) sheath.

Considerable development of cathode materials for specialized welding and cutting applications has been carried out. Weatherby and Anderson⁶⁴ report the successful use of a zirconium cathode for cutting high-temperature metals, and Aconsky and Doyle⁶⁵ developed a cathode of niobium-cerium alloy, which they used for purifying and welding niobium and niobium-based alloys.

Bulk melting

In addition to the applications of plasma furnaces for remelting scrap steel and purifying reactive metals, discussed earlier, plasma remelting furnaces have been used⁵¹ for the remelting of osmium, iridium, and ruthenium at power levels up to 1.8 MW and for the production of pure titanium from titanium sponge⁶⁶. The work on titanium sponge, carried out in a 65 kW plasma furnace at 20 to 40 kPa yielded titanium of commercial purity after only one remelt.

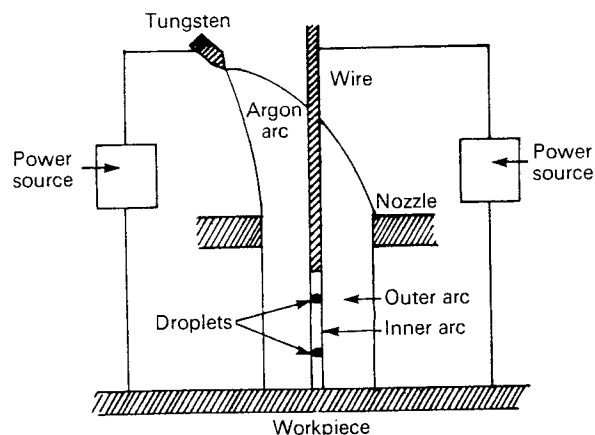


FIGURE 19 Metal-inert gas (M.I.G.) plasma welding scheme (after Ton⁵⁹).

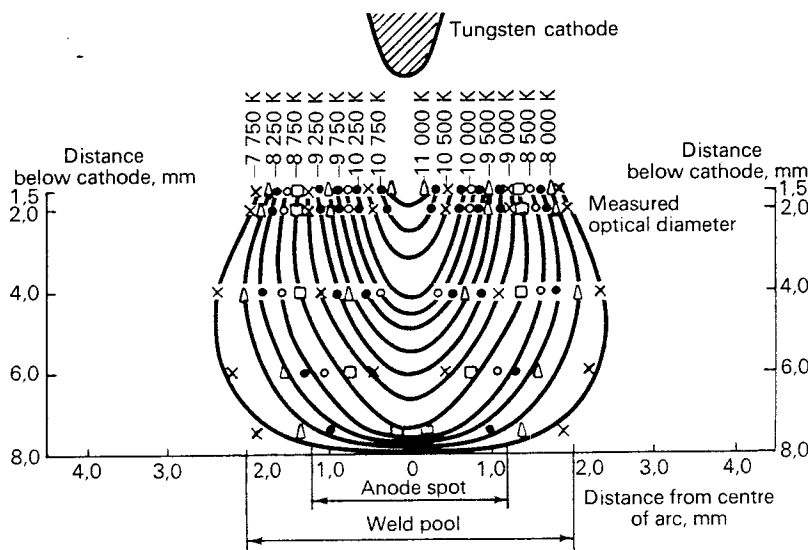


FIGURE 20 Tungsten-inert gas (T.I.G.) plasma welding scheme (after Swift-Hook⁶⁰).

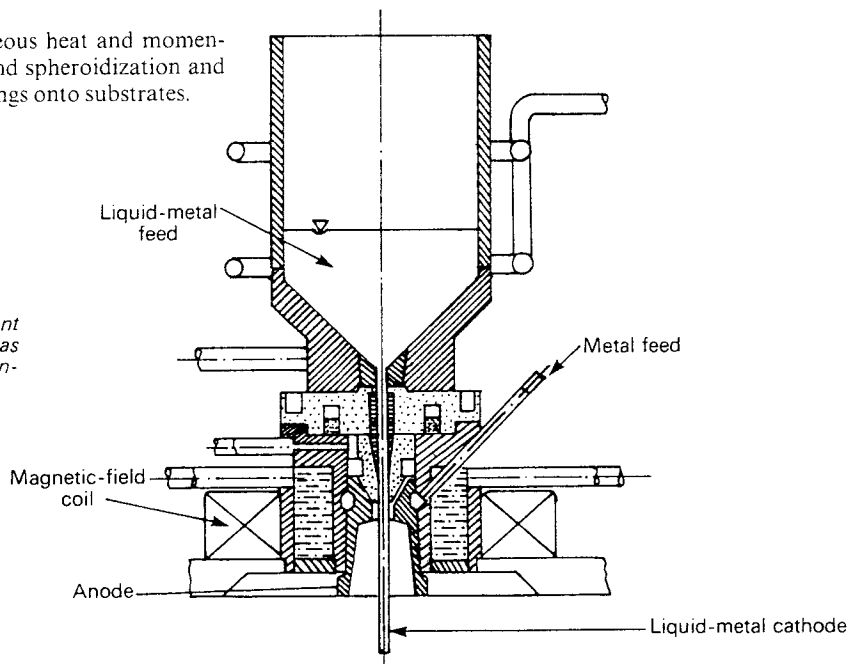
The melting and alloying of base metals in the novel plasma furnace shown in Figure 21 have been reported by Bach and Erdmann-Jesnitzer⁶⁷. They developed a plasma furnace having a stream of molten metal (i.e., lead or aluminium) as the cathode. Lead-copper and lead-iron alloys were prepared by injection of powdered copper or iron into the plasma jet, which was stabilized round the flowing molten-lead cathode. The lead-copper alloys so prepared were reported to be more resistant to corrosion by boiling sulphur than were conventionally produced lead-copper alloys. By the injection of powdered iron into the molten-lead cathode device, a previously unknown lead-iron alloy was prepared. A similar technique was used for the making of lead-aluminium alloys, a flowing molten-aluminium cathode being used⁶⁸.

The use of a vertical rotating plasma furnace for melting glasses and refractories⁴⁰, described earlier, falls within this class of process.

Heat and momentum transfer

Processes that include simultaneous heat and momentum transfer are particle melting and spheroidization and plasma spraying of protective coatings onto substrates.

FIGURE 21 A 30 kW direct-current plasma furnace using molten metal as the cathode (after Bach and Erdmann-Jesnitzer⁶⁴).



Melting and spheroidization of particles

The injection of solid particles into plasma jets results in melting of the particle and some degree of evaporation, depending on the physical properties of the solid, its residence time in the plasma, and the heat-transfer rate from the plasma to the particle. Waldie⁶⁹, in reviewing the field of particle dynamics in plasma jets and r.f. plasmas, reported that maximum particle velocities of up to 500 m/s in plasma jets had been measured, but that the majority of particles attained velocities of between 75 and 125 m/s. Typical residence times for melting, non-evaporative processes in plasma jets was thought to be up to about 10 m/s (for alumina particles 250 μm in size).

The melting of discrete particles in a plasma jet usually results in the formation of spheroidal particles by contraction under the influence of surface-tension forces in the molten droplet. The spheroidal shape is retained by the solid particle after it has cooled, and this process has become known as spheroidization.

The spheroidization of solids in plasma torches began on a laboratory scale in 1961, when Hedger and Hall⁷⁰ made some preliminary observations about the spheroidization of chromium, molybdenum, tantalum, and tungsten powders in a 25 kW r.f. plasma torch. Since then, this field has grown, and spheroidization in plasma torches is now carried out on an industrial scale. Magnetite grit (125 μm) is spheroidized by being injected into the tail of an alternating-current air heater²³ of 600 kW. Good, uniform spheroids are formed, requiring 2000 kW.h of electrical power per ton and this process is believed to be in operation on a commercial scale in the photocopying industry. Landt *et al*⁷¹ have patented a process for the spheroidization of ferrosilicon having a silicon content of between 18 and 20 per cent: ferrosilicon particles 40 μm in size were injected into the tail of a 25 kW argon-hydrogen plasma jet. The resulting spheroids, which were tested as a heavy-medium separator, had more resistance to corrosion than had conventional ferrosilicon spheroids made with a chemical flame, or by steam quenching. Ionarc-Tafa have developed a process for the separating of silica from zirconia in zircon sand that is based on a fusion treatment in an expanded-plasma furnace³². In this process zircon sand (20 to 200 μm in size) is fed to the low-pressure region of an expanded argon plasma stabilized between a cathode and three carbon anodes. The zircon particles undergo a diffusion separation in the molten state, and, on cooling, leave a core of zirconia crystallites of 0.1 to 0.2 μm in diameter, surrounded by an annulus of silica. The silica is leached from the zirconia with mild aqueous sodium hydroxide, leaving a porous zirconia particle that is used in fused-glass ceramics. The economics of this process for the extraction of zirconia from zircon sand are encouraging enough to warrant the planning of a plant having a capacity of 5 000 t/a and based on two 350 kW plasma furnaces⁷².

Plasma spraying

Plasma spraying is a well-established facet of surface-treatment technology that is also developing in South Africa⁷³. Plasma spraying of metal and refractory powder involves the transfer of heat and momentum from the plasma jet to the injected solid particles, which, after impact with a substrate, produce a tightly bonded, non-porous coating as they cool. The variables influencing the character of the coating and the economics of the coating process are complex, and several authors have reviewed this field^{74,75}.

Mühlberger⁷⁶ described a plasma spraying system that can achieve coatings having a theoretical density of more than 90 per cent, using a direct-current plasma jet of which the exit-gas velocity is mach 3. Deposition rates for metals of up to $6 \times 10^5 \mu\text{m}^3/\text{h}$ are possible when the system operates at up to 90 kW, and the deposition of oxides is usually at half this rate.

Plasma spraying is carried out commercially in Switzerland with 200 kW water-stabilized direct-current plasma jets⁷⁷. Steel is sprayed onto aluminium brake discs, alumina is sprayed onto aluminium flooring panels, and copper is sprayed onto aluminium busbars. However, the commercial use of the plasma spraying process is unlikely to develop rapidly, since plasma spraying must compete with the flame spraying and detonation spraying. For certain applications (such as the spraying of refractory metals or ceramic oxides in powder form and easily oxidizable materials such as plastics), plasma spraying with inert gases of high enthalpy is economically attractive.

Heat transfer and mass transfer

Refractory oxides and ceramic materials subjected to argon plasma jets for longer than approximately 10^{-2} secs undergo melting and some degree of evaporative mass transfer. In a free-flight plasma system, such as in expanded plasma furnaces, momentum transfer from the plasma gas to the particle will also occur and this puts an upper limit on the residence time of the particle in the plasma. In a rotating plasma furnace no such upper limit on residence time usually exists and the rate of evaporative mass transfer from the rotating melt will be limited only by the surface area of melt available for evaporation and the rate of transfer of the necessary heat of vaporisation from the plasma gas to the melt (see Table 3).

Sheer *et al*³⁴ vaporized various refractory oxides in a direct-current 50 kW argon plasma using the fluid-convection type of cathode, described earlier. Table 5 below shows the energy requirements and product characteristics for the various oxides treated.

TABLE 5
EVAPORATION OF OXIDES IN THE FLUID
CONVECTION CATHODE³⁴

Oxide	Vaporization (%)	kW.h		Surface area of product (m^2/g)
		kg product		
SiO_2	75	11		150 to 336
MgO	40 to 62	22 to 37		63.5
ZnO	47 to 62	22 to 37		—
Sb_2O_3	—	22		152

The fumed silica so produced was reported to be little different from commercial fumed silicas, being slightly off-white because the initial sand was coloured, but was white if hydrogen was used as the carrier gas. Thickening effects of the fumed silica as a 2 per cent additive in epoxy and polyester resins varied with the mode of operation of the plasma torch, but were in general comparable to commercial fumed silica. Some differences in the physical characteristics of the plasma fumed silica were observed by Sheer *et al*³⁴, such as a broader particle size distribution, a low percentage of occurrence of oversize particles, and a lesser tendency towards reticulation as compared to commercial fumed silica. This direct vaporization process has distinct advantages over other plasma routes to fumed silica such as methane or carbon reductions of silica sand, in that no carbonaceous species such as carbon black, and silicon carbide can contaminate the product, which is important for some applications.

Bonet *et al*²² investigated the evaporation of pure zirconia, lime-stabilized zirconia and yttria-stabilized zirconia in a plasma-fluidized bed. The fluidized bed was fired with a 100 kW three phase nitrogen plasma. In the case of pure zirconia treatment, size ranges of zirconia between 200 μ and 800 μ were used and considerable submicron zirconia powder was produced. However, it was not clear if the product was the result of condensation of vaporized species or the result of thermal shock of the zirconia particles at their primary grain boundaries. The product from the pure zirconia runs was reported to be jagged in appearance, whereas in the runs carried out on stabilized zirconia the products were spheroidized. This was considered to support the thermal shock mechanism of micron-sized particle formation in the case of pure zirconia. However, Bonet *et al*²² were of the opinion that a

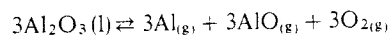
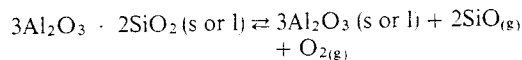
TABLE 6
FUMING OF TIN SLAGS IN VERTICALLY-ROTATING FURNACE⁴¹

Method of operation	Original tin content of slag %	Final tin content of slag %	Slag feed-rate kg/h	MWh	MWh
				ton slag	ton tin
Co-current, insulated	22.46	2.56	—	—	100
Co-current, insulated	3.42	0.6	9.30	4.50	160
Counter current insulated	3.42	0.72	8.16	6.00	222
Co-current, uninsulated	3.42	0.95	8.10	5.9	240

mixed mechanism of fine particle formation was more reasonable and up to 26 per cent conversion to fine particles was measured. For the experiments on stabilized zirconia, 10 per cent lime and 10 per cent yttria-stabilized zirconia (by mass) were used and good spheroidized products were formed with little or no vaporization for the yttria-stabilized zirconia. A slight evaporation of the lime-stabilized zirconia was observed, which was accompanied by a destabilization of the condensate with some formation of monoclinic zirconia from the original cubic solid solution.

Kessler *et al*⁷⁸, investigating the evaporation mechanism of the Al₂O₃-SiO₂ system by means of a radio-frequency nitrogen plasma, demonstrated that aluminosilicates do not evaporate congruently, but lose silicon monoxide preferentially, leaving corundum as a residue. Compressed pellets of mullite (78.4% Al₂O₃, 20.9% SiO₂) and mixtures of pure alumina and silica were supported at the base of a 2.4 GHz plasma torch and exposed to a nitrogen plasma for periods up to 50 minutes. By measuring the spectral emission from the plasma gas with a 1.5 m diffraction spectrograph, Kessler *et al*⁷⁸ were able to identify the chemical species evaporating from the samples. They identified three distinct phases of evaporation for the Al₂O₃-SiO₂ system: (1) evaporation of silicon-oxygen species, (2) evaporation of aluminium oxides, and (3) maximum evaporation of aluminium species.

Evaporation of aluminium and aluminium oxides was preceded by evaporation of silicon monoxide in all samples of Al₂O₃-SiO₂ (from 10 per cent Al₂O₃ to 90 per cent Al₂O₃) and for mullite. Kessler *et al*⁷⁸ postulated the following mechanism for mullite evaporation in nitrogen:



This mechanism predicts that the evaporation rate should decrease in an oxidizing atmosphere and increase in a reducing atmosphere. Higher evaporation rates of mullite under reducing conditions were confirmed experimentally.

Barrett *et al*⁴¹ investigated the fuming of low-grade tin slags in a vertically rotating plasma furnace (see Figure 14) as an alternative to the conventional sulphide fuming process. The furnace was fired with two 30 kW direct current plasma jets, and granulated tin slags, containing 3.4 per cent tin, were fed to the rotating furnace at rates of up to 17 kg/h. The furnace was lined with zirconia or alumina to prevent excessive heat losses, and a layer of molten tin slag was built up on the refractory lining. The flow of the molten slag through the furnace was controlled by its speed of rotation. Barrett *et al* were able to

evaporate 82 per cent of contained tin from the layer of molten slag as it passed through the furnace. Experiments were carried out with a cold skull of tin slag as furnace liner instead of a refractory liner and also with co-current and counter-current fuming. The energy consumptions and fuming rates for the different operating conditions are summarized in Table 6.

By thermodynamic equilibrium calculations, Barrett *et al*⁴¹ were able to postulate a tin evaporation mechanism involving the species SnO, Sn₂O₂, Sn₃O₃, and Sn₄O₄, the partial pressures of which were maximum for an equimolar mixture of stannic oxide (SnO₂) and hydrogen. The use of higher equimolar hydrogen ratios was found to repress the evaporation of tin species. Trials were also reported on a 150 kW prototype furnace that could run at slag feed rates of up to 54 kg/h and reduce the energy consumption to 2.730 kW.h/ton slag.

Heat transfer, mass transfer and reaction Pyrolysis (unimolecular decomposition)

Huska and Clump⁷⁹ investigated the decomposition of molybdenum disulphide in an r.f. plasma. Working with a 5 kW argon plasma and molybdenite particles 74 μm in size, they obtained conversions to molybdenum metal of up to 70 per cent at a molybdenite feed-rate of 0.07 g/h and decreased conversions at higher feed-rates. Charles *et al*⁸⁰ obtained conversions of molybdenite to molybdenum metal of between 60 and 70 per cent in an r.f. plasma, and were able to run their system at powder feed-rates of up to 400 g/h. Munz and Gauvin⁸¹ investigated the decomposition kinetics of molybdenite in an r.f. plasma and developed two decomposition models, one for solid-phase and the other for liquid-phase decomposition. They concluded that, in solid-phase decomposition (for molybdenite particles larger than 20 μm), the reaction was largely controlled by diffusion of sulphur from the shrinking core through the product layer. A relation between conversion and time was developed such that

$$T/\tau = 1 - 3(1-x)^{2/3} + 2(1-x).$$

where x is the fractional conversion to metal.

T is the reaction time, and

τ is the time for complete decomposition

For molybdenite particles smaller than 20 μm, the liquid-phase decomposition was considered to be more important than the solid-phase decomposition and to be controlled by heat transfer from the plasma gas to the reacting particle, which, in turn, was influenced by the mass transfer of sulphur vapour from the liquid droplet.

The decomposition of many single and mixed oxides have been investigated by use of r.f. plasma devices. Borgianni *et al*⁸² obtained low conversions (less than 60 per cent) to metals when Al₂O₃, CuO, NiO, and TiO₂ powders were injected into an argon plasma. Charles

*et al*⁸⁰ achieved up to 50 per cent decomposition of rhodonite and ilmenite into the respective single oxides. In the rhodonite experiments, solids rich in MnO were deposited in the cooler, downstream regions of the plasma reactor whereas SiO₂-rich solids collected in the plasma zone. A similar separation was observed for ilmenite with TiO₂-rich deposits in the plasma zone and FeO-rich deposits downstream.

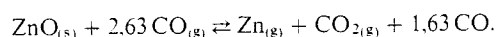
The upgrading of low-grade nickel ores formed the subject of an investigation by Meubus⁸³ in which serpentine ore having a nickel content of 0.25 per cent was thermally upgraded in an argon plasma to a magnetic spinel having a nickel content of 2.3 per cent.

Since the work done by Krukoniš *et al*⁸⁴ on plasma pyrolysis of high-volatile, low-ash coals to yield acetylene, in which up to 35 per cent of the total carbon was converted to acetylene, several attempts have been made to pyrolyse other coals in plasma furnaces. The most recent investigation carried out by Chakravarty *et al*⁸⁵ on Assam coal (46.6 per cent volatile matter) indicated that, with a simple direct-current plasma-jet reactor using argon, a conversion of up to 13.5 per cent of the total carbon to acetylene was possible. It was reported that the presence of higher levels of ash in Assam coal was not detrimental to the formation of acetylene, but highly coking coals were found unsuitable for treatment.

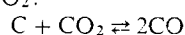
In all of these studies, experiments used a free-flight particle reaction system (see Table 4), in which the residence time of the solids is limited by momentum transfer from plasma to solid. Little use has been made of plasma furnaces in which the bulk treatment of solids is possible, independent of their residence time.

Gas-solid reactions

Many gas-solid reactions have been investigated in both free-flight particle plasma reactors and in bulk treatment plasma furnaces. Among the most common types of reaction systems investigated are oxidations and reductions. As indicated in Table 4, these reaction systems involve most of the transport phenomena together with bimolecular reaction ($A + B \rightleftharpoons C + D$). Thursfield and Davies⁸⁶ investigated the roasting of FeS to Fe₂O₃. They injected FeS particles, 50 μm in size, into a 20 kW oxygen r.f. plasma and obtained up to 200 g of Fe₂O₃ per hour at 95 per cent conversion. These results, while indicating that the roasting of sulphides in an oxygen plasma is chemically feasible, were not economically attractive at the low sulphide feed rates used (i.e. equivalent to 100 kW.h/kg Fe₂O₃). Harvey and Fey⁸⁷ describe a plasma process for the recovery of zinc from zinc roast. Zinc oxide particles were injected into the trail region of a carbon monoxide three-phase, arc heater where the reduction of zinc oxide occurs according to the following equilibrium reaction:

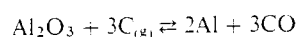


Assuming an overall thermal efficiency of 60 per cent Harvey and Fey estimate an energy requirement for zinc production at 1700 K of 2650 kW.h/ton Zn. The zinc vapour leaving the reaction chamber is quenched by injection of carbon particles, which absorb energy from the gas mixture by undergoing the following reaction with CO₂:

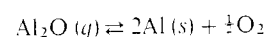
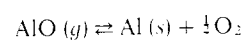
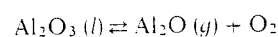


Complete removal of the CO₂ by this method is preferable, so that the carbon monoxide can be recycled after the separation from the zinc condensate. The main advantages that this plasma reduction process offers over conventional retort and blast furnaces and smelters are: shorter residence times owing to rapid heat transfer, elimination of burden preparation, elimination of elaborate zinc condensation techniques.

Rains and Kadlec⁸⁸, investigating the reduction of Al₂O₃ with various reducing agents, obtained up to 30 per cent conversions of Al₂O₃ to aluminium with hydrogen as reducing agent, when injecting 6 g/min Al₂O₃ to a 5 kW r.f. plasma. As the Al₂O₃ feedrate was increased to 36 g/min, the conversion to aluminium decreased to near zero. With carbon monoxide or methane as reducing agent, increased aluminium yields were obtained, which were thought to be caused by carbon reduction of Al₂O₃ in the vapour phase by the overall reaction:

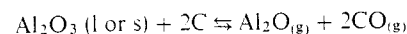


A tentative reduction mechanism was outlined by Rains and Kadlec⁸⁸ which involved the formation of the aluminium suboxides Al₂O and AlO and aluminium metal as follows:



The products from the argon and argon-carbon monoxide treatments of Al₂O₃ were determined to be aluminium metal and α- and γ-Al₂O₃, while the product from the argon-methane treatments were aluminium, aluminium carbide, Al₄C₃, and the oxides. Rains and Kadlec⁸⁸ reported that no solid sub-oxides or aluminium oxycarbides were found in the products.

Everest *et al*⁸⁹, investigating the carbothermic reduction of Al₂O₃ in a 30 kW rotating plasma furnace (see Figure 12), were able to identify aluminium metal, γ-Al₂O₃ and trace amounts of the oxycarbides, Al₂OC and Al₄O₄C, when the exit gases from the plasma furnace were quenched with argon. Quenching the exit gases with air resulted in the formation of a mixture of ultrafine particles of γ- and δ-Al₂O₃ having surface areas up to 130 m²/g. Maximum alumina evaporation rates of up to 1.9 kg/h were possible, at 13000 kW.h ton of Al₂O₃. Everest *et al*⁸⁹ considered that the major aluminium species present in the evaporation products was the suboxide Al₂O, formed by the reaction



From the work carried out on vaporization of alumina and aluminosilicates in plasma systems, it would appear that the major evaporating aluminium suboxide species in a non-reducing atmosphere is the suboxide AlO (Kessler *et al*⁷⁸, Rains and Kadlec⁸⁸) but that the species Al₂O is predominant in the evaporation of alumina under reducing conditions. (Everest *et al*⁸⁹).

The gas-phase reduction of silica in plasma furnaces, as

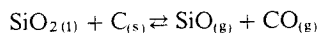
TABLE 7
SUMMARY OF FUMED SILICA PRODUCTION IN PLASMA FURNACES

Plasma device	Power level	Reductant used	Quench gas	Rate of production kg/h	kW.h	Surface area m ² /g	Reference no.
	kW				kg F.S.		
RF (argon)	24	—	N ₂ , air, steam	0.25	96	260	Barnes & Barby ⁹⁰
Rotating RF (argon)	30	Carbon	Air	—	—	—	Bush & Sterling ⁹¹
Rotating DC (argon)	30	H ₂ , N ₂ , NH ₃	Air, O ₂	1.8	14	130-160	Everest et al. ⁹²
DC argon	50	none	Air	4.55	11	150-340	Sheer et al. ³⁴
Rotating DC (ethanol)	200	Methane	Steam	15	13	160-250	Schnell et al. ¹⁴

an alternative route for producing high surface area, fumed or pyrogenic silicas, has been investigated by many research groups. The existing commercial route to fumed silica is a multi-stage process involving the production of silicon tetrachloride by chlorination of silicon metal or silicon carbide, which are themselves produced by carbothermic reduction of silica sand. Inherent in the process is the necessity to remove 4 moles of hydrogen chloride per 1 mole of silica from the process gas stream and to degas traces of hydrogen chloride from the product surface, both of which increase production costs and pollution problems. Sheer and Korman¹ originally demonstrated that silica sand could be directly reduced in a high-intensity arc to give a high surface area silica fume on reoxidation. Many attempts have since been made to develop a successful plasma system in which fumed silica could be produced, by either direct vaporization or chemical reduction (gas and solid reductant) of silica sand.

Developments in the direct vaporization of silica were briefly described earlier. Sheer *et al.*³⁴ were able to vaporize silica sand in a fluid-convection cathode plasma reactor at energy requirements of 11 000 kW.h/ton silica. A process for the vaporization of silica sand by means of an RF plasma torch operating on argon/oxygen mixtures has been patented⁹⁰. Silica particles (200 mesh) were fed into the plasma at rates up to 0.25 kg/h and a silica fume of surface area 260 m²/g could be prepared by quenching the evaporated species with air. When hydrogen was used as quench gas instead of air, a surface-activated silica with hydrophilic properties was formed. The requirements for the formation of a hydrophilic-activated silica were that free hydrogen should be present in the quench region during the condensation of the silicon dioxide primary particles. This condition could be achieved by the inclusion of hydrogen or hydrogen-containing compounds with the plasma gas, so that their dissociation to free hydrogen could occur. When the silicon dioxide condensation took place in the presence of a hydrogen compound with a hydrophobic group (such as a straight-chain alcohol or a chlorosilane) and this compound was injected into the quench region at low enough temperature, decomposition of the hydrogen compound did not occur and the activated silica so formed had hydrophobic properties.

Bush and Sterling⁹¹ extended this work on the production of activated silica in a radio-frequency plasma torch, by use of carbon as a reducing agent. They developed a rotating RF plasma furnace into which mixtures of sand and carbon, in the form of paste or rods, were fed. Operating with an argon plasma and speeds of furnace rotation of up to 1000 rev/min Bush and Sterling were able to maintain a semi-plastic ring of molten silica around the plasma, held in place by centrifugal force. As the silica was consumed according to the following reaction:



the silica melt was replenished by new feed material. The silicon monoxide was oxidized with air at the furnace exit to form an activated silica. A summary of the results of development work on the production of fumed silica by vaporization and reduction of sand in plasma furnaces, is shown in Table 7. The chemical reduction of silica with gaseous reductants to produce silicon monoxide was first investigated by Everest *et al.*⁹². By means of a horizontal rotating furnace fired by a 30 kW direct current plasma jet, they were able to reduce up to 1.8 kg/h of silica using mixtures of hydrogen, nitrogen and ammonia as reducing gases. By simultaneous quenching and oxidation of the silicon monoxide vapour at the furnace exit with mixtures of air and oxygen, Everest *et al.* were able to prepare an activated silica of specific surface area of 130-160 m²/g, the thickening properties of which, when measured as the viscosity of a 1 per cent w/w dispersion of silica in tritolyol phosphate, were considerably superior to the commercial product. Energy consumptions of the furnace at maximum reduction rates were given as 14 000 kW.h/ton silica. The use of the rotating plasma furnace for production of fumed silica was further developed by Schnell *et al.*¹⁴, who reduced silica sand with methane. The design and operation of the furnace are discussed earlier in this article. Production rates of 15 kg/h of fumed silica were attained at an energy requirement of 13 000 kW.h/ton silica. The thermal efficiency of the uninsulated furnace drum was approximately 65 per cent. The properties of the fumed silica produced in this pilot plant process compared to a commercial fumed silica are summarized below in Table 8.

Two further examples of solid-gas reactions, that were studied in a falling-film plasma reactor, are the reduction of tricalcium phosphate ore with methane⁵⁵ and the beneficiation of ilmenite by methane reduction of iron oxide⁵⁴. In the reduction of tricalcium phosphate with methane, 200 μm particles of phosphate were injected into the tail of a direct-current plasma jet of hydrogen (30 per cent) and argon (70 per cent) mounted at the top of a vertical

TABLE 8
COMPARISON OF COMMERCIAL AND PLASMA FUMED SILICA¹⁴

Property	Commercial process	200 kW plasma process ¹⁴
Bulk density (g/l)	60	20
Surface area (m ² /g)	170 to 300	190 to 300
SiO content (%)	—	0.1
Carbon content (%)	—	0.1
Silane content (=SiH/100Å ²)	—	0.09
Silanol content (=SiOH/100Å ²)	3.5	7.5
Viscosity (CP) 3% Disp. in DOP	156	162
Yield point of dispersion (dyn/cm ²)	30	78

alumina column, methane gas was used as the carrier gas for the phosphate particles and was controlled at the stoichiometric amount of 13 per cent for the following overall reaction:



The theoretical energy for this reaction is approximately 15 400 kW.h/ton of phosphorus, as compared with some 13 200 kW.h/ton for the silicothermic reduction, but the reaction between calcium phosphate and methane should proceed at 1400 K instead of 1650 K. In practice Chase *et al*⁵⁵ were able to reduce up to 80 per cent of the phosphorus in the tricalcium phosphate at feed rates of up to 1.20 kg/h, requiring 52 000 kW.h/ton phosphorus or 7000 kW.h/ton tricalcium phosphate.

Chase *et al*⁵⁴ were also able to beneficiate ilmenite and leucoxene ores by use of their falling-film plasma reactor. Leucoxene, having a titania content of 77 per cent, and ilmenite (65 per cent titania) were both successfully beneficiated by injecting the ores, in turn, to the tail of an argon/hydrogen direct-current plasma. Power levels of up to 50 kW were used and the ore particles were transported to the reactor in a stream of methane. For both ores, methane was found to be a better reducing agent than hydrogen on its own and the reduction of iron ore in the ilmenite and leucoxene facilitated the leaching of iron from the treated ore. Final titania and iron oxide contents of the ores after one plasma treatment and a leaching with 6 N hydrochloric acid were 91.8 per cent TiO₂, and 6.6 per cent Fe₂O₃ for leucoxene and 90.6 per cent TiO₂ and 8.75 per cent Fe₂O₃ for ilmenite. These results were obtained by operation of the falling-film reactor in the slagging mode, i.e. with a layer of melt falling down the furnace wall and collecting as a bulk melt. Operation of the furnace in the particulate mode (i.e. no bulk slagging) resulted in a final leached product containing less than 90 per cent titania. The best performance of the furnace was achieved for 32 kW d.c. power, at an ore feed rate of 0.87 kg/h, in which the titania content was upgraded to 97.5 per cent at a net power requirement of 8 330 kW.h/ton TiO₂.

Bonet⁴², in reporting research on reduction of ilmenite in solar furnaces and plasma furnaces, suggests that the thermal treatment of ilmenite in a neutral controlled atmosphere (air and nitrogen) results in a transformation of the initial phase into pseudobrookite and ilmenite solid solutions. Treatment with a reducing gas results in selective reduction of the iron content of ilmenite.

Gas-solid-solid reactions

When this type of metallurgical process takes place in a plasma furnace, it usually involves the reaction of two solids (oxide and carbon), the heat of reaction being supplied by the plasma gas. The process is normally carried out in bulk flow furnaces to improve inter-solid contact or by the use of prefabricated pellets.

The pioneering work of Sheer and Korman¹ covered the carbothermic reductions of many metal oxides including the oxides of beryllium, aluminium, magnesium, calcium, barium, manganese, titanium, zircon, silicon, and boron⁹³. Prefabricated anodes of oxide and graphite were fed to a free-burning carbon arc (see Figure 1). Holmgren *et al*⁶ also investigated the reductions of mixed oxides such as rhodonite for which up to 10 kg of rhodonite per hour was

fed to the plasma in the form of the anode and required a vaporization energy of 5500 kW.h/t. Conversions to recoverable products were approximately 50 per cent.

The carbothermic reduction of oxides has been effected by the exposure of prefabricated pellets of oxide and carbon to the tail of a direct-current plasma jet⁹⁴⁻⁹⁷. In these investigations a wide range of reactions was studied, including the carbothermic reductions⁹⁴ of Fe₂O₃, SiO₂, Al₂O₃, MgO, and B₂O₃, the carbothermic and hydrogen reductions⁹⁵ of Nb₂O₅, Al₂O₃, and Fe₂O₃, the carbonization of zircon sand⁹⁶, and the formation from Nb₂O₅, of niobium carbide⁹⁷. A more recent development in this field is the preparation of superconducting metal carbides, such as NbC, TaC, and MoC, by carbonization of the oxides in the tail of a direct-current argon plasma⁹⁸.

The use of continuous bulk-flow plasma furnaces for reduction of oxide ores with solid reductants, such as coke or coal fines, has recently come to the forefront of plasma ore processing with the successful development of pilot scale plasma furnaces capable of operating at up to 1 Megawatt and at high thermal efficiency. Most of the applications for these furnaces are concerned with the production of iron or ferroalloys and they will be discussed separately in the following section.

PLASMA FURNACES FOR THE PRODUCTION OF FERRO-ALLOYS

Several investigations have been conducted into the possible use of plasma furnaces for the production of iron and ferro-alloys.

Reduction of iron oxide

Gilles and Clump⁹⁹ investigated the hydrogen reduction of iron oxide in a 25 kW direct-current plasma jet reactor. The plasma jet was operated with either pure hydrogen or a 3-to-1 mixture of argon and hydrogen. Two different size ranges of Carol Lake hematite concentrates were used: 44 to 53 μm and 63 to 74 μm. The iron ore was conveyed in an argon stream to the nozzle of the plasma jet, where the oxide was reduced in flight. Products were quenched on a water-cooled copper plate some 20 cm downstream from the exit nozzle of the plasma jet. The reaction system was totally enclosed in a stainless-steel duct that was cooled with hot water to prevent condensation of the product water.

Using ore particles of 44 to 53 μm, Gilles and Clump⁹⁹ were able to reduce 70 per cent of the iron oxide feed at feed rates of 60 g/h when the plasma reactor was run on pure hydrogen. They concluded that the reduction of iron oxide was controlled by heat transfer and that the mechanism of free-flight reduction varied with the rate of heat transfer. For low heat-transfer rates (with an argon-hydrogen plasma), the reduction started on the outside of the particle and layers of iron of decreasing oxidation states were formed. At high heat-transfer rates for pure hydrogen plasmas, the product iron was distributed within the particle in a continuous wustite phase, probably resulting from a liquid-gas reaction. This work demonstrated the feasibility of reducing iron oxide with hydrogen in a plasma reactor but the energy requirements were approximately 100 times greater than those required theoretically.

Greenewald and Groteke¹⁰⁰ developed a reduced-pressure plasma furnace for the batch reduction of metal oxides, in which the oxide batch is heated by a single-phase alternating-current plasma struck between graphite

electrodes. They claim to have achieved successful catalytic reductions of hematite when the furnace was operated at a pressure of 70 kPa and a melt temperature of approximately 1 100 K. They produced 50 kg batches of steel having a carbon content of 0.35 per cent.

Recently, Tait and Wall¹⁰¹ investigated the reduction of hematite in a 20 kW electrically augmented reactor using a methane-air flame. In this device, the combustion products from a conventional gas burner are passed to a direct-current plasma jet, where the temperature of the combustion products is increased electrically. The temperature of the methane-air flame can be increased in such a device from 2 300 K, for an air-to-methane stoichiometry of 1, to 3 500 K by the addition of 300 per cent electrical energy to the chemical energy available from combustion. Tait and Wall¹⁰¹ injected pre-roasted Carol Lake concentrate (passing 200 mesh in size) into the tail of the augmented flame at 0.6 kg/h at air-to-methane stoichiometric of between 1 and 0.67 and electrical-boost ratios of 0.2 to 3. At low electrical-boost ratios, most of the hematite recovered was unaltered, but, as the boost ratio was increased, more spheroidization of hematite occurred. Spheroidization was found to be a prerequisite for reduction, and reduction was greatest at low air-to-methane stoichiometric (i.e. with excess methane). The reduced product consisted of magnetite or wustite in magnetite. Metallic iron was present only in trace quantities.

Gold *et al*¹⁰², working at Bethlehem Steel Corporation, reported the successful reduction of hematite and magnetite concentrates to molten iron with methane and hydrogen in a direct-current plasma furnace at power levels up to 1 MW. Ore concentrates (45 per cent smaller than 37 μm) were injected into a direct-current plasma falling-film reactor (see Figure 18) together with a mixture of methane and hydrogen as reducing gases. Ore feed rates of up to 500 kg/h were used with reducing-gas flows of approximately 400 m³/h, the gas being a 2-to-1 mixture of H₂ to CH₄ (equivalent to an enthalpy of 70 MJ per kilogram of hydrogen). The iron ore was totally reduced to molten iron by the mixture of hydrogen and methane, and molten iron was collected in a magnesia crucible (having a diameter of 0.6 m) at a rate of 320 kg/h. The ore had a residence time of several minutes in the falling film. The crucible was emptied intermittently by tilting of the whole apparatus. The net power consumption for the reduction of the Carol Lake concentrate was 2 600 kW per ton of iron, and losses to the cooling water, etc., amounted to 400 kW.h.t. This gave a gross energy consumption of 3 000 kW.h/t per ton of iron, which, when compared with the theoretical minimum of 2 000 kW.h/t, meant a 66 per cent overall thermal efficiency. The analysis of the iron product from the Carol Lake hematite was as follows:

	%
Sulphur	0.005
Phosphorus	0.001
Carbon	0.006
Silicon	0.006
Copper	0.007

The use of ores having higher sulphur and phosphorus contents resulted in corresponding increases in sulphur and phosphorus in the iron product. This successful use by Gold *et al*¹⁰² of a 1 MW plasma pilot plant for the

production of iron at Bethlehem Steel Corporation is a turning point in the metallurgical application of plasma technology, since it demonstrated the feasibility of continuous ore reductions at economic energy requirements.

Pickles *et al*¹⁰³ report the use of a 30 kW extended arc flash reactor (described earlier) for the production of iron from steel-plant waste oxides, whereby various waste oxides were successfully reduced to molten iron by reduction with contained-carbon or additional carbonaceous material. Four main types of waste oxide were treated in the flash reactor

- blast furnace-basic oxygen furnace-mill scale mixture,
- electric arc furnace dust,
- vacuum oxygen decarburisation dust, and
- millscale and scarfing fines.

The BF-BoF-millscale mixture, containing 50 per cent iron, 12 per cent carbon, and 12 per cent moisture was successfully reduced to iron at an energy consumption of 6 550 kW.h/short ton (2 000 lbs) of iron, compared to the theoretical requirement of 2 350 kW.h/short ton. Although the waste oxides could be reduced without additional fluxes, highest metal recoveries (95 to 100 per cent) were obtained with the addition of lime and/or silica as fluxes. The melting point of the CaO-SiO₂-MgO slag formed from the waste oxides could be reduced to 1 620 to 1 670 K by silica addition, which increased metal recovery and low-sulphur metal could be made by fluxing with lime to obtain a slag melting at 1 850 K with a basicity index of 1.5.

Electric furnace baghouse dust, containing high concentrations of zinc, lead, and lime and low concentration of iron (17 per cent), yielded a high melting slag (67% CaO, 17% SiO₂, and 16% MgO; melting point approximately 2 500 K), which was successfully handled by addition of silica flux. Iron recovery from the electric furnace dust was 89 per cent, obtained by use of a mixture of anthracite and coke fines as reducing agent. Energy consumptions for this waste oxide were high, some 50 000 kW.h short ton metal, owing to the low iron content of the waste oxide. The zinc and lead oxides present in the baghouse dust were flashed from the particulate feed as it passed through the plasma furnace and resulted in low zinc and lead contents (Zn < 0.001, Pb < 0.001) in the final metal.

A V.O.D. dust containing 33 per cent Fe and 25 per cent Cr₂O₃ was reduced with a mixture of anthracite and coke fines in the flash reactor in the presence of fluorspar as flux, which enhanced slag fluidity and metallic yield. Iron recovery up to 66 per cent was obtained at energy requirements of 16 650 kW.h/short ton iron. The lowest energy consumptions were obtained for the reduction of millscale and scarfing fines, in which very little slag was present and no fluxing additions were necessary. Between 95 and 98 per cent recovery of iron was possible from the millscale and scarfing fines by reduction with anthracite fines at energy consumptions of between 3 040 and 7 200 kW.h/short ton iron. The main advantages of this extended-arc, closed-hearth plasma furnace are that

- (1) fine oxides can be preheated and pre-reduced before entry to the plasma zone,
- (2) the furnace performance is insensitive to variations in raw materials.

The benefits of plasma reduction furnaces, such as the Bethlehem Steel falling-film reactor and the extended arc-flash reactor, as direct reduction processes for steel-making arise from their ability to use finely divided iron-ore concentrates without pre-agglomeration and the

greater degree of controllability the furnace offers when compared to blast furnaces or electric arc furnaces. If successfully implemented on a large scale, plasma furnaces could remove the need for coke works, agglomeration plants, blast furnaces, and oxygen steel making operations in future steel-making technology. Work is currently being undertaken in Sweden¹⁰⁴, in collaboration with the Kawasaki Steel Corporation, on the evaluation of the reduction of iron ore in plasma furnaces as a viable direct steel-making route that would reduce investment costs and result in less environmental pollution. Foster Wheeler/Tetronics have demonstrated the feasibility of producing steel from iron ore and coal in the expanded, precessive plasma furnace, and are now constructing a 1.4 MW pilot plant for further development work³¹.

Ferrovandium

Akashi *et al*¹⁰⁵ reduced V_2O_5 with pitch coke in a direct-current argon plasma. The V_2O_5 and coke were pelletized, and the pellets were heated to 2500 K for up to 20 minutes. The plasma reduction yielded a mixture of vanadium oxycarbide (VC_xO_y) and metallic vanadium. The optimum ratio for the formation of vanadium was reported to be $V_2O_5/C = 1/4.75$.

Morel¹⁰⁶ has estimated that the plasma-magnesium reduction of V_2O_5 should be cheaper than the conventional process. Morel bases his calculations on the use of composite anodes consisting of a mixture of V_2O_5 and magnesium in a consumable-anode plasma reactor, and concludes that the raw materials and operating costs of such a process amount to 1 per cent of the local market price of pure vanadium in Poland.

MacRae *et al*⁵⁷ have demonstrated the feasibility of the continuous production of ferrovandium at 0.5 MW in the Bethlehem Steel falling-film plasma furnace. This development was done in two phases: firstly at 100 kW, and then at 500 kW. The target for energy requirement at 100 kW was initially set at 8 800 kW.h/t of vanadium and this was successfully accomplished in four stages of development, as indicated in Table 9.

TABLE 9
DEVELOPMENT OF THE ENERGY REQUIREMENT FOR THE BETHLEHEM STEEL FALLING-FILM PLASMA FURNACE⁵⁷

Runs at 100 kW

Run no.	Oxide	Reducing agent	Product	Energy per ton of V kW.h
1	V_2O_5	H_2 and CH_4	V metal	22 000
2	V_2O_5	Graphite	V metal	15 400
3	V_2O_3	Graphite	V metal	11 000
4	V_2O_3	Coke fines	V metal	5 500

TABLE 10
OPERATING CONDITIONS FOR THE 100 kW FERROVANADIUM PLASMA FURNACE⁵⁷

Feed rate for V_2O_3 , kg/h	36
Feed rate for coke fines, kg/h	11
Initial crucible iron, kg	2.5
Power to plasma, kW	124
Heater efficiency, %	80
Run time on feed, min	48
Post-reaction heat, min	26
Energy consumption, kW.h/t	5 500
Product composition, % V	75 to 88
Recovery of V metal, %	90

Table 10 shows the operating conditions for a typical ferrovandium run as reported by MacRae *et al*⁵⁷.

The second phase of the development of the Bethlehem Steel ferrovandium process was carried out at 500 kW, and consisted mainly of the development of the plasma reactor so that a high enough enthalpy level could be attained for easy melting of the solids in the falling film and for prevention of blockages in the feed ports. Initial tests carried out at enthalpies of 150 to 200 MJ per kilogram of hydrogen did not yield a molten product, but by progressive increase of the gas enthalpy to 260 MJ/kg and decrease of the size range of coke to 90 per cent smaller than 150 μm , a satisfactory ferrovandium was produced. The first good results were obtained at an energy requirement of 12 800 kW.h/t of vanadium, yielding a product of 50 per cent vanadium. Subsequent optimization led to final energy requirements as low as 7 700 kW.h/t of vanadium. (i.e., 3 240 kW.h/t of alloy) for a product analysing:

	%
Vanadium	42
Iron	53
Carbon	3.1
Suiphur	0.44
Phosphorus	0.02

The energy distribution for operation of the ferrovandium plasma furnace is shown in Table 11 for an extended run of 8 hours at 410 kW, producing 53 kg of vanadium per hour at a power requirement of 7 700 kW.h per ton of vanadium.

TABLE 11
ENERGY DISTRIBUTION FOR THE FERROVANADIUM PLASMA FURNACE⁵⁷

Energy input to electrodes, kW	410	} $\Sigma = 410$ kW
Energy utilization, kW		
(i) loss to cooling water	80	
(ii) reaction energy	117	
(iii) crucible loss	35	
(iv) heat for melting FeV	58	
(v) sensible heat for gas	120	

The plasma-produced ferrovandium was tested for its acceptability as an additive for steel alloys. The tests were conducted in a 50 kg induction furnace to yield steels having vanadium contents of 0.5 per cent, 0.01 per cent, and 0.05 per cent. The rate of solution of ferrovandium in the iron melt and the degree of vanadium utilization were both reported as being comparable with commercial ferrovandium products.

Reduction of chromite

A two-stage process for the methane reduction of Transvaal chromite by use of a 16 MW methane plasma generator has been proposed by Fey and Harvey¹⁰⁷. This process is based on the prereduction of FeO at 1 100 K by the carbon monoxide and hydrogen off-gases from the main reduction furnace separation of the metallic iron from the prerduced ore, and a final reduction of the upgraded chromite by methane reduction at 2000 K. Fey and Harvey¹⁰⁷ estimate that the theoretical energy requirements for such a process would be 2 000 kW.h per ton of alloy, and that the installation of a 16 MW plant producing 32 000 t of alloy annually would cost approximately 5 million U.S. dollars. The total operating costs are estimated to be \$180 per ton of alloy (i.e., R165 per ton of alloy).

Trials on chromite reduction with gaseous reducing

agents are known to have been carried out by both Westinghouse¹⁰⁸ and Bethlehem Steel⁵⁷, and in both instances the main product was high-carbon ferrochromium. The reducing agents used were either methane or mixtures of methane and hydrogen, but no experimental data or energy requirements for these plasma reductions are available.

Pickles *et al*¹⁰⁹ have successfully produced high carbon ferrochromium by reduction of low grade chromite ores with a variety of reducing agents in a 30 kW, extended-arc, flash reactor (described earlier). By premixing chromite fines (100 per cent less than 35 mesh) with reducing agents and introducing this mixture at rates of 10 kg/h into the top of flash column (see Figure 16) via a rotary preheater, Pickles *et al* could produce a high-carbon ferrochromium (C% between 6.46 and 8.80) containing high levels of silicon and low sulphur and phosphorus concentrations:

(Si% 1.76–15.50; S% 0.007–0.010; P% 0.005–0.064)

The plasma was stabilized in mixtures of argon, nitrogen and hydrogen (at flow rates between 0.5 and 2.25 M³/h) and anthracite, graphite, or coke fines were used as reducing agents. Metal recoveries of between 84 and 94 per cent were obtained at energy requirements of approximately 12 000 kW.h/ton alloy. By taking samples of the chromite particles at different levels in the flash column, Pickles *et al*¹⁰⁹ were able to follow the progress of the prereduction. They observed, by examination and analysis of the particles, that liquefaction of the chromite ore particles occurred as they passed from the flash column to the plasma zone. This liquefaction was followed by the formation of iron oxide droplets on the surface of the chromite when the furnace was operated on pure argon. When hydrogen or carbon monoxide was injected into the furnace, reduction of the iron oxide occurred. In the absence of hydrogen, no reduction of chromium oxide by carbon monoxide was found, but in the presence of hydrogen, Pickles *et al* found that the chromite was reduced to chromium, iron, and silicon, confirming that chromium oxide and silica can be reduced by hydrogen when iron is present to decrease the activity of the metal products.

THE FUTURE ROLE OF PLASMA FURNACES IN FERRO-ALLOY PRODUCTION

Investigations into the use of plasma furnaces for ferro-alloy production have been restricted mainly to the low-volume ferro-alloy ferrovanadium⁵⁷ and to a laboratory investigation of ferrochromium production¹⁰⁹. The ferrovanadium work established that it was possible to produce this particular ferro-alloy economically on a small-scale plasma furnace, and that the product was acceptable to the steel industry.

The ferrochromium work established that it is technically feasible to reduce low-grade chromite fines in a laboratory plasma furnace and produce a high-carbon ferrochromium, although the specific energy requirements were some three times that required in a conventional submerged arc furnace.

Theoretical considerations

If the theoretical energy requirements for the carbothermic reduction of chromite in a conventional submerged-arc furnace are used as a basis for comparison, an

estimate can be made of the theoretical energy requirements for the plasma reduction of chromite fines with coke. Such estimates are presented in Table 12 and allow for the differences in heat requirements resulting from the operation of the plasma furnace at temperatures higher than those used for submerged-arc furnaces. Extra heating is required for plasma gases and slag fusion, but a net decrease in overall heat requirements is obtained because of factors such as lower reaction energy, raw-materials heating (because less flux is present), and higher levels of heat recovery from the furnace off-gases. The estimated theoretical energy requirements for plasma reductions at 2 000 K and 2 200 K are 2 770 kW.h per ton of alloy and 2 960 kW.h per ton of alloy respectively. These estimates are not as low as those of Fey and Harvey (2 000 kW.h per ton of alloy)¹⁰⁷ since prereduction of the chromite ore is not included in the calculations.

TABLE 12

ESTIMATES OF THE THEORETICAL ENERGY REQUIREMENTS FOR THE PRODUCTION OF FERROCHROMIUM IN A PLASMA FURNACE

All estimates are given as kilowatt-hours per ton of alloy.

	Plasma furnace 2 000 K	Plasma furnace 2 200 K
Theoretical energy requirements ¹¹⁰ for submerged-arc furnace at 1 800 K	3 400	3 400
<i>Add:</i>		
(1) increased heat for slag fusion	200	200
(2) heating of plasma gases	470	530
Gross energy requirements	4 070	4 130
<i>Subtract:</i>		
(1) reduced heating of raw materials at lower additions of flux	585	350
(2) reduced heats of reactions at higher temperature	335	346
(3) heat recovery from CO*	150	188
(4) heat recovery from plasma gas*	230	287
Net energy requirements	2 770	2 960

*Raw materials preheated to 1 200 K.

Pickles *et al*¹⁰⁹ have established that prereduction of chromite particles by the hot gas stream leaving the plasma zone is feasible and hence net energy requirements could well be as low as the 2 000 kW.h/ton alloy estimated by Fey and Harvey¹⁰⁷.

Pilot-plant technical feasibility

The high temperature available in a plasma furnace should permit the reduction of chromite at temperatures at which it is molten, without the addition of fluxes, thus saving energy in melting the flux additions. Although more energy must be used in heating the chromite and reductant to the higher operating temperature, this disadvantage would be offset to a certain extent by the lower specific heats of reaction and the faster reaction rates. However, even if operation of plasma furnace with chromite without fluxes is technically possible, flux additions may nevertheless be necessary to improve phase separation between metal and slag and to improve the metal recovery by increasing the activity of Cr₂O₃ in the slag. Pickles *et al*¹⁰⁹ in fact operated their plasma furnace using

silica, alumina and fly-ash as fluxing additions. An alternative system for reduction of chromite in a plasma furnace would be to prereduce the chromite by a conventional, low-temperature, combustion-heated process, such as a rotary kiln and to use the prereduced chromite as the feedstock for the plasma furnace, thus using the high temperature enthalpy of the plasma most rationally.

Energy transfer in a plasma furnace is necessarily via a gaseous medium, usually a mixture of argon and hydrogen. The high cost of argon as a raw material would necessitate its collection, recompression and recycle to the plasma furnace, which would increase the capital investment required for setting up the plant. The operation of the plasma furnace on pure hydrogen would be preferable, enabling make-up hydrogen to be produced from the carbon monoxide furnace gas by shift reaction with steam, the surplus hydrogen and carbon monoxide being available for use as a fuel gas or as a feed to a catalytic conversion process.

The main technical advantages offered by a plasma furnace for carbothermic reduction of chromite are summarized as follows:

- lower specific energy requirements obtained by operation at higher temperatures, with reduced flux additions,
- higher reaction rates owing to higher operating temperature, which should lead to higher furnace productivity especially when operating on prereduced ores,
- direct use of particulate chromite and reductant without pre-agglomeration or burden preparation,
- better controllability of the plasma furnace operation, owing to the relative insensitivity of the plasma to variations in raw material characteristics,
- metallic water-cooled electrodes can be used instead of Söderberg electrodes,
- continuous operation of the plasma furnace should be possible owing to its better controllability, and a greater degree of automation could be developed, leading to a reduction in operating costs.

Economic feasibility

A complete analysis of the costs involved in the plasma production of ferrochromium from chromite fines as compared with the costs involved in the agglomeration of fines for use in submerged-arc furnaces is not possible at this stage of development. However, an indication can be given of various savings that the plasma route offers.

The theoretical specific energy requirement of between 2770 and 2960 kW.h per ton of alloy (shown in Table 12) means that, if a plasma furnace can be developed to operate at thermal efficiencies approaching those of a medium-sized submerged-arc furnace (20 MW) say 70 per cent, the actual energy requirements would be about 3960 to 4230 kW.h per ton of alloy. Lower specific energy requirements obtained by prereduction of the chromite by the furnace off-gases or by a separate prereduction step, would further reduce the actual energy requirements.

Savings could also be effected in regard to the agglomeration of fines and the transportation of agglomerates to the submerged-arc furnace. A plasma furnace could operate direct on fines, which could be transported pneumatically by the recycled plasma gas mixtures, thus considerably reducing the costs involved in the handling of raw materials. Costs could also be reduced in the fabrication of electrodes. The plasma furnace operates on water-cooled metal electrodes that can be replaced periodically as required.

Electrode life at 3.5 MW has been measured¹¹¹ as being up to 1000 h; thus, replacement should be necessary only once in every six weeks of operation.

The capital costs of plasma equipment of 1 MW and higher (furnaces and generating equipment) are usually estimated as being in the region of R200 000 per installed megawatt; thus, a 20 MW plasma installation would cost 4 million rands. However, capital costs rarely follow a linear relation with scale, and the actual costs per installed megawatt would probably decrease with increased power rating.

Estimates of the capital costs of three-phase plasma furnaces are shown in Table 13.

These cost estimates are based on cost data from Westinghouse¹⁰⁸ for plasma generators of 1 to 3.5 MW, and are scaled up by the usual 0.6 power rule for scaling. The costs are higher than those for submerged-arc furnaces at the lower power levels, but, at higher power ratings, could be lower than the current cost of submerged-arc furnaces. The costs of ancillary equipment, whether similar to or different from that for a submerged-arc furnace, would have to be added to the cost estimates given.

TABLE 13
ESTIMATED CAPITAL COSTS OF PLASMA FURNACES

Power rating MW	Capital cost R × 10 ⁶	Total installed cost* R × 10 ⁶	Total cost per installed megawatt R × 10 ⁶
1.0	0.1	0.2	0.2
3.5	0.5	1.0	0.3
16.0	1.35	2.7	0.17
30.0	2.0	4.0	0.13
50.0	2.7	5.4	0.11

*Installation cost taken as being 100 per cent of capital cost.

CONCLUSIONS

Plasma technology has become established in specific fields of application at power levels up to 10 MW, especially for metallurgical fusion and refining processes and for the production of fine powders and pigments. The introduction of bulk-melt handling furnaces such as rotating furnaces and falling-film furnaces, has made it possible for the residence times of reactants within the furnace to be increased to the extent that gaseous and solids reductions can be carried out to completion. Specific energy requirements for metallurgical reductions carried out in pilot-plant plasma furnaces (1 MW) compare favourably with energy requirements obtained in conventional metallurgical furnaces. The inherent advantages that the plasma furnace offers the process metallurgist, such as higher temperatures and reaction rates, higher furnace productivities, better furnace controllability owing to continuous operation on fine ores and reductants, without their agglomeration and briquetting, should result in the plasma furnace playing a useful role in future extractive metallurgical and refining processes.

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