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Plasma reactors for process metallurgy applications

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Thermal plasma technology is now an established alternative to be considered for upgrading existing metallurgical processes, for the treatment of new raw materials, particularly waste by—products, and for the production of new materials. Industrial thermal plasma heaters, furnaces and reactors have been developed for many process metallurgical applications. Commercial installations now include the production of ferroalloys by the reduction of oxide ores, the melting and refining of carbon steel and specialty metals, and the recycle and recovery of metals from industrial wastes.

The recently published volume by the Iron and Steel Society of the AIME, "Plasma Technology in Metallurgical Processing", and the Advanced Technology Symposium "Plasma 2000" held in October 1985 have alerted a wide audience of process metallurgists to the availability of this technology (1). This paper attempts to provide a starting point for the selection and design of a plasma reactor for a specific application. Plasma technology has evolved over the past twenty years from being a space age "glamour—tech" technology to become a modern metallurgial tool to be used for process development.

BACKGROUND

In 1867, large quantities of electric power were made available for continuous use by the invention of the electric generator. The practical application of thermal plasmas was introduced in 1878 by W. Siemens with the development of a D. C. furnace for the bulk melting of metals (2). This furnace consisted of a vertical graphite cathode with the arc transferred to the melt in contact with a water—cooled bottom anode. This "classical" Siemens configuration is presently of significant commercial importance in electric furnace steelmaking and in the production of ferroalloys as developed by ASEA using a hollow graphite cathode (3).

Another Siemens DC furnace used horizontal electrodes with a hollow anode for the passage of neutral or reducing gases into the furnace. This configuration is not unlike the A. C. extended arc flash reactor (EAFR) being developed by Howden—Tibur Metals (4). Siemens also introduced the use of water—cooled copper cathodes. In 1897, Moisson used a horizontal electrode furnace for metals processing in which the charge was heated by radiation from the furnace walls and from the arc itself. In this "independent" or "non—transferred" arc furnace (i.e., the arc was not transferred to the melt), Moisson prepared base metals and carbides of chromium, manganese, molybdenum, tungsten, uranium, vanadium, zirconium, titanium, silicon and aluminum from the oxides (5). His research also included the study of amorphous carbon and graphite and attempts to make artificial diamonds.

Thermal plasma as a modern metallurgist's tool has evolved over the past twenty years. This present era was initiated by the commercial availability of relatively low power, 5 — 40 kW, plasma jet torches used for cutting, welding and powder spraying (6). These relatively small and inexpensive units encouraged laboratory studies on the technical feasibility of carrying out metallurgical reactions in plasmas. Arc heaters from 500 kW to 35 MW were being used for aerospace material testing. High power levels were required for eventual process scale—up to commercial production rates.

Technically the "classical" Siemens furnace had graphite electrodes and a free—burning arc, similar to present conventional electric arc steelmaking furnaces. In comparison, the modern plasma devices have water—cooled electrodes of copper or tungsten and graphite, and an arc whose size, position and motion may be controlled by imposed aerodynamic, magnetic and mechanical forces.

A major distinguishing feature between the "classical" and "modern" devices is the influence the gas phase has on plasma reactor design. The critical conditions and capabilities for which thermal plasma reactors are designed include the high temperatures, high heat fluxes, atmosphere controls, rapid—quenching, fine particle processing, and, possibly, the plasma state. For these factors and for the process requirement of minimizing the total energy requirement, the type of gas (inert/reducing/oxidizing), and the gas flow rate strongly influence the reactor design.

For the design of plasma reactors, the relative importance of the plasma state or "plasma effects" should be discussed. At temperatures above 2000 — 3000 °C, excited gas species exist, i.e., ionized, nascent and radical gases. In the early 1960's, the uniqueness of the plasma state was emphasized to encourage the transfer of plasma technology to industrial applications. It was fashionable to promote plasma technology in expectation that unique reaction conditions would exist — resulting in increased reaction rates, novel chemical products and perhaps, plasma—specific phenomena.

Emphasis on the plasma state had a major effect on early plasma reactor design, especially for the processing of particulate raw materials. Existing plasma heaters were modified or new designs developed which were configured so that the raw material would "pass through the arc" to maximize any "plasma effects". At present, there are no commercial metallurgical processes that are based on any chemical "plasma effects" in either the gas or condensed phase. The advantages of plasma reactors in metallurgy are due to other factors. As compared to conventional ferroalloy processing the advantages are decreased electrode consumption, less critical selection of ore feed, wide selection of carbon reductants, wide range of slag compositions, improved process control, continuous feeding operation and decreased noise levels (7).

In general, in designing plasma reactors, the primary factors to be considered are heat and mass transfer limitations, such as heat transfer to discrete particles, solid/liquid/gas contact, the mixing of reactant gases, the nucleation, condensation and quenching of products, and the controlled stirring of melts to facilitate refining reactions. In this respect the design of plasma reactors follows the classical chemical engineering considerations of thermodynamics, reaction kinetics and heat, mass and momentum transfer, as applied to high temperature metallurgical systems.

'PLASMA EFFECTS' IN PROCESS METALLURGY

The "Fusion Torch" concept of Eastlund and Gough (8), proposed in 1969, is an extreme example of "plasma effects" in metallurgy. Ore was to be reduced by injection into an ultra—high temperature plasma causing vaporization and ionization of the solid. The ionic gaseous species then would be separated, for example, by electromagnetic means to collect the meal.

A fusion concept has not been demonstrated; dramatic claims for the potential capabilities to be achieved by the plasma state and by citing temperatures of 50,000 °C, distract from the usefulness of available thermal plasma devices.

Plasma effects in metallurgy have been observed in the enhanced absorption of gases by molten metals. Plasma devices can produce high concentrations of reactive gas species, such as atomic (nascent) nitrogen and hydrogen, especially at the arc root attachment area at the melt surface. The nitrogen solubility saturation level in molten iron and ferroalloys has been increased over 100 times by this method. The effects of total pressure, nitrogen and hydrogen partial pressures above the melt, and sulfur and oxygen concentrations in the melt have been studied (9, 10). The development of chromium—alloyed steels with nitrogen substituted for nickel has been extensively studied in the USSR (11).

For the reduction of iron oxide melts heated by transferred arcs the efficiency of hydrogen reductant utilization has been as high as 70% in comparison to the thermodynamic equilibrium value of about 40% (12). This increase is attributed to reduction by atomic hydrogen; curve filling of rate data has supported a reaction mechanism derived by assuming atomic hydrogen as the reductant (13, 14). The product iron should fall below the surface of the iron oxide melt and the reverse reoxidation process should be prevented. Scale–up to higher power levels has not been reported.

In studies by Gilles (15) on iron ore reduction with hydrogen using a D. C. spray–type torch, an "internal metallization" effect was observed. Small spheres of metallic iron surrounded by iron oxide were observed in the plasma–treated particles. Walsh and Hudson (16) noted the same effect under non–plasma conditions when ore particles were dropped through cracked natural gas at 1600°C. Heat transfer studies by both Gilles and Walsh gave residence times that were more than sufficient to achieve surface and bulk melting of the iron oxide particles. As explained by Walsh, "internal metallization" is a result of surface reduction of molten iron oxides followed by coalescence of the iron due to surface tension effects. "Internal metallization" was observed by Tylko using the EPP (expanded precessive plasma) and SSP (Sustained Shockwave Plasma) furnaces; these effects should be attributed to the "Walsh/Hudson" phenomena rather than to a plasma specific effect (17).

The study of plasma–melt interfacial reactions (18, 19) should be encouraged. Refining reactions (gas, liquid, solid) could benefit from localized high energy inputs for increasing the local bulk melt temperature and providing for the endothermic heat of reactions, and even possibly from plasma effects due to excited gas species.

The average and peak temperatures in thermal plasma reactors can far exceed temperatures in conventional reactors. Unusual physical and chemical phenomena can be expected to occur at these high temperatures. Attributing new and unexpected phenomena to an undefined "plasma effect" though should be avoided. Conventional interpretations, based on phase transformations, melt phase behavior, high temperature gas properties, etc., will be much more useful for reactor scale–up and optimization.

DEVELOPMENT OF PRESENT PLASMA METALLURGICAL REACTORS

Plasma reactors are being developed for metallurgical applications of varying complexity – heating, melting, refining and extraction. According to the arc mode these reactors are either transferred or non–transferred. Processed materials include bulk scrap, scrap chips/shreddings, particulate reverts, ore fines and melts. The products include melts, plasma castings, and metal condensates.

Conventional high temperature metallurgical reactors include shaft furnaces, rotary kilns, fluidized beds, cyclones, oxygen converters, ladle refiners, electric arc furnaces. Still under development are coal/oxygen combustion reactor systems to replace coke, to provide additional energy and to intensify the reaction conditions.

The patent literature describes thermal plasma systems in combination with all of these conventional metallurgical reactors, including the coal/oxygen reactors. The only presently commercial operating plasma reactors are based on either shaft furnace or electric arc furnace technology.

Shaft blast furnaces have evolved from a cold to a hot blast and now include a plasma blast operation. Rejuvenation of the iron blast furnace by electric superheating of the blast air was proposed by Cordier in 1962 (20). Ferromanganese blast furnaces have been retrofitted with plasma blast heaters to allow flexibility in the choice of electricity or coke as the energy source (21). The Westinghouse cupola uses a similar plasma blast concept with intensified hearth reaction conditions (22). The SKF plasma furnace technology uses a shaft furnace with hearth injection of particulates with a plasma blast (23). These shaft furnaces all use non–transferred arc devices which have high gas flow rates.

Electric arc furnaces based on plasma technology concepts have been commercialized for the melting/refining of refractory metals, high–alloy steels and carbon–steels, for the production of ferroalloys and for the recovery of metals from industrial by–products and wastes.

For specialty metals, furnace designs with plasma arc heaters, provide high intensity clean melting conditions with protective atomospheres, reduced pressures, and water–cooled self–contained crucibles (Daido Steel, Retech, Krupp, Nippon Steel, Freital/Voest–Alpine, USSR), (24). Carbon steels are being produced in D. C. plasma furnaces with graphite electrodes with capacities of about 30 tons (ASEA, IRSID), (25).

Ferroalloys (7) produced by ore reduction and/or remelting of ferroalloy fines include ferrochromium (ASEA/Mintek) using a hollow graphite electrode and ferromanganese (Voest–Alpine) using the Freital high current tungsten cathode system.

Platinum is being recovered from Al2O3 catalyst supports by fluxing and melting with separation of the platinum by solution in molten iron. The Texasgulf installation (26) has a Tetronics R & D plasma reactor that uses a tungsten cathode placed in the center of the furnace roof. A mechanical arrangement allows for the continuous positioning of the cathode horizontally above the melt and for sweeping the arc along the melt surface. The sweeping arc (10 – 15 rpm) decreases melt surface overheating, provides for uniform or selective heating of the reactants, and provides for uniform energy distribution throughout the bulk melt.

The development of these commercial plasma processes based on shaft and electric arc furnace reactors required substantial advances in plasma hardware design and operating know–how. This plasma technology is now available for transfer to other conventional metallurgical reactors.

CURRENT STATE OF PLASMA METALLURGICAL REACTOR DEVELOPMENT

Over the past twenty years some major trends in reactor design have been observed:

- The capability of handling fine solid particlulates as a reactor charge material has been established as a major advantage of plasma reactors. Depending on the specific reactor configuration the fine particles are melted by hot gas entrainment, injected into an arc melt attachment zone or swept by an arc on the melt surface.

- The critical plasma reactor design factors depend on the chemical processing steps and final product requirements rather than the specific means of treating the particles.

- A major advantage of transferred arc reactors is the low volume flow rates of the plasma working gases. Energy requirements for heating the gas are minimized. The cost of maintaining an inert (argon) gas environment is minimized. The thermodynamic conditions (gas partial pressures, temperatures) are controllable which is critical for processes involving metal volatilization and intermediate gaseous reactants. The capital and operating costs of downstream auxiliary equipment for gas handling, cooling and clean–up are minimized.

- Non–transferred plasma reactors and systems operate with high gas volumes. The reactor or system must be designed for recovery of the sensible and possible chemical energy in this gas. This is accomplished in the plasma shaft reactors by heat exchange through the countercurrent flow of hot gases and charge material (FeMn blast furnaces, Westinghouse cupola) and by utilization of the energy for municipal heating (SKF system).

- The promise of minimal reaction times has not been realized for plasma extractive metallurgical processes. A prevalent concept was that capital costs would be drastically decreased due to high reactor throughputs. Ultra–rapid reactions would result from high temperature processing and from the raw material "passing through the arc". Although substantial degrees of conversion can be achieved in the gas phase, other much slower process rate–limiting factors have determined the reactor design – such as, time for completion of the reaction in a bulk melt phase, liquid diffusion rates in slag refining reactions and heat transfer rates in the bulk melt. As a result, residence times and therefore plasma reactor throughput capacities are comparable to conventional reactors.

CONCLUSIONS

The past twenty years have resulted in the development of several plasma arc systems with reliable operating characteristics and commercially acceptable performance. Successful developments with these plasma systems have resulted in shaft furnace and electric arc furnaces reactors characterized by a plasma blast and by plasma–type electrodes, respectively.

In considering the application of plasma technology, every reaction system should be considered to be unique and therefore require a specific plasma reactor design. This design may be a plasma retrofit to an existing conventional metallurgical reactor or may be a unique plasma reactor configuration.

In the near future, the greatest opportunity for the application of plasma reactors at high power levels (>5 MW) is for the clean melting of specialty, high–alloy and carbon–steels. At medium power levels (1 – 5 MW), the processing of industrial by–products and of wastes for the recovery of metals, and production of a non–hazardous residue is of great industrial and commercial interest. At low power levels specialty metals melting, spray metal overlays, and powder production will increase in commerical importance.

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