Pure & Appl. Chem., Vol.52, pp.1801-1815.
Pergamon Press Ltd. 1980. Printed in Great Britain.
©IUPAC

THERMAL PLASMA IN EXTRACTIVE METALLURGY

N.N. Rykalin

A.A. Baikov Metallurgy Institute, USSR Academy of Sciences, prospekt Lenina 49, Moscow, USSR

Abstract - Thermal plasma applied to metallurgical processes produces the materials with new properties; simplifies the production cycle and equipment; falls in line with prospective energy consuming system (electrical energy and hydrogen). Plasma processes have been carried out for complex raw materials decomposition (Zirconium) and for beneficiation of ores and slags. Plasma reduction of tungsten and cobalt from oxides, molybdenite dissociation and iron reduction and ferrovanadium production have been developed on semi-industrial sclale. Plasma heating of industrial gases is promising for nuclear metallurgy. Arc and high frequency plasma generators, plasma jet reactors for processing gases and disperse materials and plasma melting furnaces are being built for extractive metallurgy.

INTRODUCTION

The mostly prospective field of thermal plasma industrial application is the production of metal and ceramic materials with new properties - chemical, physical, mechanical - determined by specificity of plasma processes - quick heating, high temperature and high rate of reaction in plasma of a given composition and sharp quenching (spherical, ultra-disperse, surface active and pure powders, metastable nitrogen containing alloys, pure monocrystals) (1).

Obvious and scientifically proved advantages of thermal plasma jet and furnace processes are: significant reactions speeding in gases and in gas carried disperse materials: pronounced intensification, continuity and high output of processes; the possibility of carrying out few-stage and even one-stage processes simplifying the production cycle; compactness of the central plasmatron-reactor unit; lower capital investment and reduced product cost; improvement of labour and environment conditions; possibility of automatic regulation and control of process; service staff reduction. These advantages determine the technical and economical efficiency of substituting the conventional technological routes by plasma routes based on electrical energy.

Rising scarcity of fossil fuels and transportation difficulties tend to work out wider use of electrical energy and hydrogen for metallurgical processes. High economy of deficient fuels - coke, natural gas and oil - is becoming conceivable and even their full exclusion from energy balance may turn prospective. As expected in 25-50 years' time the gradual substitution of thermal energy from hydrocarbon fuels with electrical energy generated in coal or nuclear power stations - as well as by hydrogen energy - favours the use of thermal plasma for pyrometallurgical processes.

THERMAL PLASMA ENGINEERING PROBLEMS

The possibility of realizing thermal plasma processes depends on the development of the appropriate equipment, i.e. the plasma generators, furnaces and reactors. The general requirements of process engineers are: sufficient power, the possibility of utilizing active gases, such as hydrogen, oxygen, chlorine, methane etc. and a long service life.

Thermal plasma generators. Thermal plasma jets for technological application are generated in direct and alternating current arc discharges as well as in electrodeless high-frequency discharge. Main requirements for industrial plasma generators - plasmatrons - are: power, efficiency and continuous service life. By 1979 arc plasmatrons have been built for power up to 3-5 MW (Westinghouse, USA; Institute of Thermal Physics, USSR) with efficiency 60-90%. Their service life, however, is limited by electrode erosion and, when operating with active gases (oxygen, chlorine, air) does not exceed 100-200 hr. With electrodes that erode and recover (e.g. graphite in hydrocarbon plasma) the service life of arc plasmatrons may reach several hyndred hours. High frequency (HF) (0.5-15 MHz) plasmatrons for power up to 1 MW

(TAFA, USA Institute of High Frequency Currents, USSR) have efficiency 50-75% and high frequency generator service life up to 2000 h. The development of 10-20 MW arc plasmatrons with longer service life operating with chemically active gases and 5-10 MW HF plasma generators with frequency down to 1-10 kHz and efficiency up to 80-90% may be expected.

In arc plasmatrons the discharge is burning between rod or tubular electrodes and is stabilized by the flow of a plasma forming gas. Some types of arc plasmatron constructions have been developed with different shapes of electrodes and guiding nozzles - Fig. 1. The arc discharge is fed by direct or alternating current from 100 A up to 10 kA on voltage level from 50 up to 1000 V. To decrease tubular electrodes wear the arc is being rotated by magnetic field with frequency up to 1 kHz. For operation with agressive gases electrodes are protected by argon shield. Attempts to reduce electrode wear and to prolong their service life are being exerted by eminent scientists - M.Zhukov (USSR), Guile (Great Britain), M.Fey, E.Pfender (USA) (2-8).

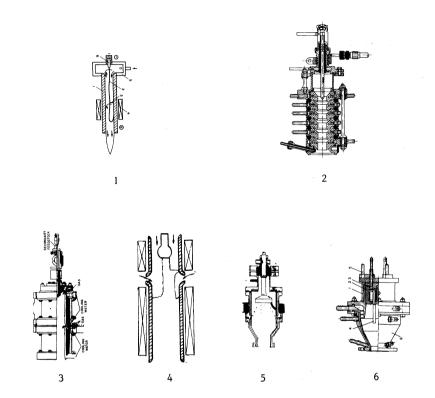


Fig. 1. Arc plasma generators. 1 - linear plasmatron with a rod electrode (2); 2 - linear plasmatron with a sectioned chamber (3); 3 - plasmatron with tubular electrodes (4); 4 - three-phase tubular plasmatron (5); 5 - coaxial plasmatron (6); 6 - volume plasmatron (7).

Arc plasma generators operating at high (up to 100 bar) and low (up to 10^{-2} torr) pressure (with a hollow cathode) as well as the pulse arc plasmatrons (with current modulation) have been developed (9). The new ideas and variety of design concepts are being put forward. For plasma technology it becomes necessary to develop arc plasma generators on 10-20 MW power level.

In high frequency plasmatrons: induction (HFI), capacity (HFC), flame (HFF) and combined - the gas discharge is sustained by the energy of high frequency electromagnetic field - Fig. 2. HF-plasma jets are not contaminated by products of electrode erosion and are essentially pure. The service life of electrodeless HF plasma appliances amounts to $2-3 \times 10^3 h$ and is limited by life time of electro-vacuum tubes of an electromagnetic energy generator. HF-induction plasmatrons on power level 0.5-1 MW with frequency about 0.5 MHz may operate both with quartz and metallic discharge chambers on various plasma forming gases including oxygen, chlorine and vapours of reactive substances (10-13).

<u>Plasma jet reactors</u> are very tightly linked with plasmatrons - arc or HF. Plasmatron and reactor usually form a unified constructive system where problems of plasma jet interaction

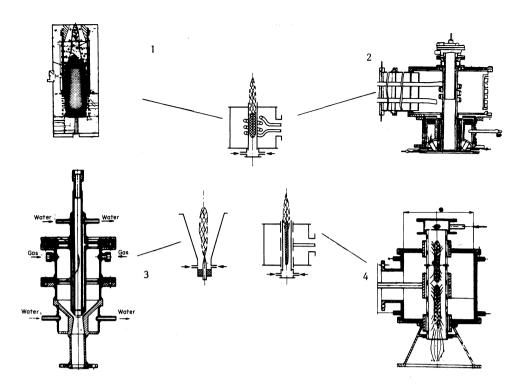


Fig.2. HF-plasmatrons. 1 - HF-induction plasmatron (USA) (10); 2 HF-induction plasmatron (USSR) (10); 3 - HF-torch plasmatron (12); 4 - HF-capacity plasmatron (11).

With dispersed matter carrying gas flow, proper development of reaction zone, effective quenching action, products take-out, by-products take-off and off-heat recycling are solved by electrodynamic and gasodynamic means. Plasmatron-reactor system has to realize - especially for heterogeneous reactions in thermal plasmas: maximum efficiency of heating and vapourizing dispersed components; completeness of prescribed chemical reaction; products quenching and take-out and easy regulation of process parameters.

Technical applicability of plasma jet process and equipment is evaluated by completeness of raw material processing and by energy consumption per unit of product. Direct flow cylindrical reactors with water or gas-cooled metal walls joined with a single plasmatron are mostly used for jet plasma process - Fig.3. The starting material is introduced by the transporting gas flow (dispersed raw material) or by pressure (liquids, vapours and gases). The quenching, i.e. rapid chilling of the reaction products is usually realized by cold gas jets. Fluidized bed reactors are designed for processes where rather coarse-dispersed products are required (15).

Multi-jet reactors with two conflicting plasma jets are used for processing polydispersed raw materials (16). The reactor with three arc plasma jet mixing chamber provides a rather uniform temperature distribution (2).

In falling film plasma reactor the dispersed material is injected tangentially to the anodereactor tube, it is being melted on tube inner walls forming a film which is reacting with plasma heated reducing gas - Fig. 4 (14).

Expanded conical arc plasma increases the residence time of particles in high temperature zone up to 200 ms (18).

A large scale three phase arc plasmatron-reactor has been developed by Tafa-Ionarc (USA) on power level up to 1 MW for powder processing in a plasma jet (17).

The types of plasma furnaces for reducing melting and for refining and alloying remelting are similar to traditional types of arc and electron beam furnaces - Fig.5. Rather original are: rotating plasma furnaces with horizontal or inclined axis (France, Belgium) or with vertical axis (Great Britain) for melting refractory ceramics and for fuming. Arc plasmatrons of linear type or with hollow cathode, single or in groups - are separate interchangeable parts of a plasma melting furnace (19-23).

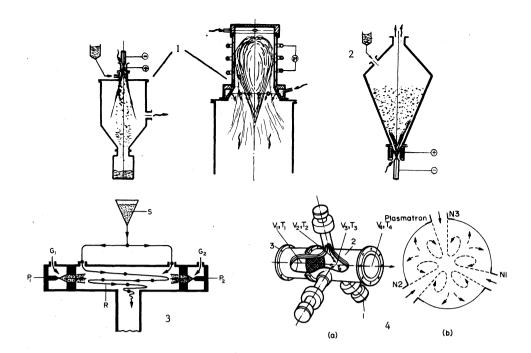


Fig.3. Plasma-jet reactors 1 - direct flow; 2 - with fountain layer (15); 3 - with conflicting plasma jets (16); 4 multi-jet (2).

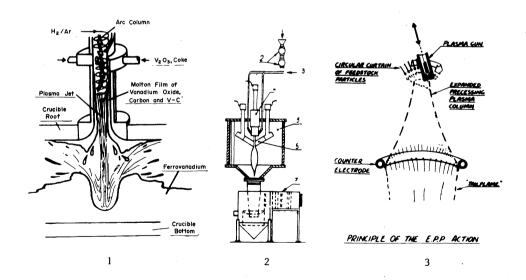


Fig.4. Plasma reactors 1 - falling film (14); 2 - three electrode arc (17); 3 - expanded conical arc (18).

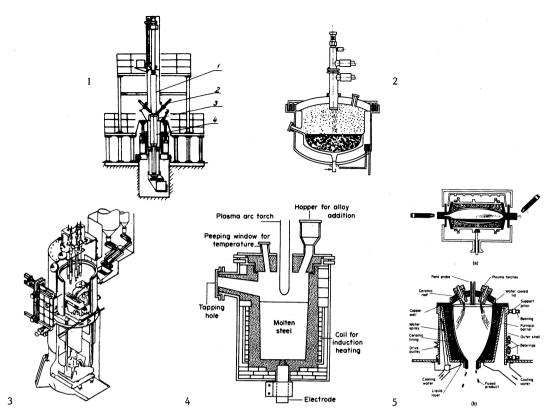


Fig. 5. Plasma furnaces. 1 - with a crystallizer (19); 2 - with a ceramic crucible (20); 3 - with a hollow cathode (21); 4 - plasma-induction furnace; 5 - with rotating ceramic crucible (23).

DECOMPOSITION OF METALLURGICAL RAW MATERIALS

Modern metallurgy and chemical technology tends to utilize raw materials completely and to develop processes without wastes, eliminating environmental pollution. By present level of engineering development the problem of processing and utilizing solid, liquid and gaseous wastes is being solved, as a rule, by multi-stage routes raising the cost of production, complicating equipment, increasing capital expenditure and bringing in inevitable losses of valuable components in numerous apparatus. Combined with such prospective processes as hydro- and chlorous metallurgy thermal plasma makes it possible to decompose and separate complex raw materials on early stages of their treatment, facilitating essentially further processing.

The process of zircon decomposition in arc plasma producing 400 tons per year has been developed and realized on industrial scale by Tafa-Ionarc (USA) in 1973. In the arc plasmatron-reactor with central tungsten cathode and three graphite anodes argon is heated up to 3750°C (Fig.4). Pure zirconium sand (100-200 μm), being heated above 1775°C in the argon plasma jet is dissociated forming a mixture of the phase enriched with zirconium oxide (less than 0.5% of SiO_2) and the phase containing mainly silicon dioxide, which are fixed by quenching in a cold gas jet. Silicon oxide is removed from zirconia rich phase by leaching in caustic, crystals contain 98% of zirconium dioxide in particles of 0.1-0.2 μm . At 300 kW of argonplasma power the energy consumption was 2.5 kWh/kg of raw material (17).

In NPL (Great Britain) experiments on d.c. transferred arc heater have been carried out. Zirconium sand was fed into the plasma air jet with throughput of 240 kg/h and dissociated (up to 96%) into zirconium and silicon oxides mixture with energy consumtion 2-2.5 kWh/kg of feedstock (24).

Decomposition of complex oxides - rhodonite (Mn0. \sin_2), ilmenite (Fe0. \sin_2) into the respective single oxides has been achieved in HF argon plasma. Single oxides tended to separate Mn0 and Fe0 rich oxides deposited in cooler reactor zones, \sin_2 and \sin_2 rich - collected in high temperature plasma zone (Birmingham University, Great Britain).

N. N. RYKALIN

Beneficiation of <u>ilmenite</u> and <u>leucoxene</u> has been achieved by methane plasma reduction in falling film reactor. Leucoxene containing 77% TiO₂ could be upgraded to a slag with 97.5% TiO₂ at an energy expenditure 8400 kWh per ton of TiO₂. Up to 40% of iron content of the ore could be separated magnetically as metallic iron, and the remainder easily leached out (25).

Low grade nickel serpentine ores (0.75% Ni) have been thermally upgraded in an argon arc plasma to a magnetic spinel with 2.3% Ni (Meubus, Université de Québec à Chicoutimi, Canada).

The process has been developed for direct production of silumin by carbothermic reduction of alumosilicates and also for producing alloy from lean ores and aluminous slags; subsequently aluminium may be extracted by sublimation and decomposition of monochlorides (26).

<u>Slags beneficiation.</u> A number of processes of metals selective recovery with simultaneous separation of metallurgical enriched slags have been developed. Test melting at $1500-1600^{\circ}\text{C}$ of vanadium-iron converter slags ($\sim 16\% \text{ V}_2\text{O}_5$ and $40\% \text{ FeO} + \text{Fe}_2\text{O}_3$) in a hydrogen arc plasma furnace with bottom electrode (39) has shown the possibility of selective iron reduction and slag enrichment up to V_2O_5 content of 30%.

Experiments have established the possibility of plasma processing <u>titanium-iron concentrates</u> with iron selective reduction. Plasma process slags have had higher titanium dioxide content than slags produced by conventional process (27). Fractional separation of oxides is also possible by plasma dissociation of these concentrates (28).

Odeillo laboratory (France) has developed a plasma process of <u>fuming tungsten trioxide</u> tungsten concentrates melt with addition of various fluxes (29). Such process may replace complex hydrometallurgical route of concentrates decomposition and cut down labour expenditure.

Tin oxide has been fumed from low-grade tin slags (3.4% tin) in vertically rotating 150 kW plasma furnace at a throughput of 50 kg of slag per hour and energy requirement of 2730 kWh per ton of slag. Spent slag contained 0.5% of tin (NPL, Great Britain).

For effective development of upgrading process the proper choice of basic chemical reaction type - dissociation, selective oxydation or reduction, chlorination - is very important. Processing of finely dispersed nickel sulfide in neutral, reducing and oxidizing plasma jets - by same throughput and temperature - has produced the conversion rates of 36, 55 and 66% respectively. Processing of slags, containing 9% Zn in oxidizing and reducing plasma jets has fumed zinc up to 0.5 and 0.2% (30).

Plasma jet processes are applicable for complex treatment of ores and valuable production wastes such as e.g.phosphates, silicon-aluminium and titanium ores, ilmenite, titano-magnetites, pyrite ores, wastes of refractory and rare metals, metallurgy dust wastes and slags.

METALS RECOVERY

Prospectiveness of thermal plasma processes for metal reduction has been proved by numerous investigations on laboratory and semi-industrial levels. The most prospective route is to use thermal plasma for reducing of metal oxides and chlorides which are semi-products of final stages of the metallurgical production. At present these processes, e.g. hydrogen reduction of tungsten oxides are characterized by low productive, non-continuous and multistage routes, high reagents consumption, difficult automation. Dispersity, shape and other properties of the powder products are difficult to control, that leads to unstable product quality. These shortcomings may be eliminated by thermal plasma process with solid carbon, raw or converted natural gas or hydrogen as reducers. Depending on the process organisation and requirements metals may be obtained both in compact form and as powders of various dispersity.

Reduction in a thermal plasma jet along with the essential intensification of the process, makes it possible to control powder dispersity and shape both by jet parameters (power, temperature, partial pressure of metal vapours, jet velocity) and by the quenching type and intensity. It is possible to obtain ultra-disperse powders with dimensions near the critical nucleus.

The main limitations of plasma-jet processes are: a short residence time of raw material staying in high temperature zone (0.1-10 ms); higher energy consumption due to the water cooling of the plasmatron-reactor parts and to the heat loss with waste gases. The development of plasma heating in the fountain layer units, where the residence time in high temperature zone is much longer, is still on the laboratory level. That's why more attention is now given to the development of plasma processes in melts, either making up a liquid falling film layer around the discharge, or forming a pool heated up by plasma jets or arc by Joule effect of electric current. The melt in the high temperature zone is moving slower than disperse particles in the jet. Residence time of the melt in the high temperature

reaction zone can be controlled by the selection of the process parameters.

Disperse raw material being directly injected into discharge zone may disrupt its stability and lower the thermal efficiency. Energy consumption of plasma process may be lower than for traditional technology due to increased out-put and equipment miniaturization.

Refractory metals. The plasma route for the production of refractory and rare metal powders has good industrial prospective due to the comparatively small scale of production and to the cumbersome traditional technology. Plasma-jet technology is rather prospective for reduction of compounds with low enough sublimation temperatures, when substance transfer into gaseous phase is possible during its short residence time in high temperature jet zone. Such materials are: oxides and ammonia salts of W, Mo, Re and some halogen compounds. Metallic powder with particles size < 0.1 μm could be produced by hydrogen reduction of oxides or ammonia salts of W and Mo in 100 kW arc plasma jet with energy consumption 5-6 (for W) and 5-11 (for Mo) kWh/kg. Sintering of these powders at 1450-1500°C provides compact metal density close to theoretical values (31).

Reduction of tunsten oxide in hydrogen arc plasma linear plasmatron (300 kW) and a direct-flow reactor has been developed on semi-industrial scale (IMET, VNIITS, VNIIETO, USSR). By rapid cooling (quenching) metallic tungsten powder with the globular particulates and a specific surface of $10-12~\text{m}^2/\text{g}$ - Fig.6.a.) was produced. Stabilization of the process conditions provided relatively monodisperse powder (40-50 nm). By slow cooling (mild quenching) high purity tungsten powder (0.02% $^{\circ}0_2$) was obtained with particulate dimensions ($^{\circ}1$ $^{\circ}1$ $^{\circ}1$ $^{\circ}1$ close to commercial fine powders.

Ultra-disperse tungsten powders are processed by usual methods of metal-ceramic production. Short time annealing refines tungsten plasma powders and it becomes possible by sintering at 1500°C to produce compact tungsten with density near to theoretical. For the ultra-disperse molybdenum (deoxidation of Mo is rather difficult) sintering at 1400°C is sufficient (32).

Ultra-disperse tungsten powders may be used for production of hard alloys on the tungsten carbide base. Micro-structure homogeneity is quite indispensible for high quality of such alloys. Small and uniform grain size of the carbide phase increases hardness and consequently the alloy wear resistance. Particulates of plasma tungsten form nearly spherical agglomerates $(0.3-0.6~\mu\text{m})$ consisting of several deformed particulates with a clear separation boundary. This is the result of coagulation process; agglomerates however are unstable and decomposed easily. Carbidization by solid phase synthesis forms still finer particulates with a narrow particle size distribution $0.2-0.3~\mu\text{m}$, which is nearly optimum - Fig.6,b.

The cobalt-tungsten carbide alloy based on plasma tungsten powder (Fig.6,c) in comparison with the standard alloy is distinguished by uniform grain distribution and by complete lack of large recrystallized grains of tungsten carbides. The size of carbide grains for the standard alloy stays in the 1-2 μm range and for experimental alloy less than 1 μm , that is below the sensitivity level of the X-ray spectrum microprobe. Improved structure essentially increases hardness and wear resistance of cutting tools manufactured of a hard alloy based on plasma tungsten powder.

However, the high dispersity of plasma tungsten powders causes some production troubles due to their inflammability, as a result of elevated reactive ability of surface layers with metastable crystal structure possessing excess energy. X-ray investigations of plasma tungsten powders have revealed up to 40% metastable β -W phases. Its quality, affected by conditions of the product precipitation correlated with higher activity of the plasma powder (33). It is possible to prevent formation of β -W phase by providing appropriate conditions of reactor process.

The plasma gas composition essentially affects the reduction process. In hydrogen plasma processes are intensified as compared with other plasma atmospheres, e.g. argon. High hydrogen conductivity increases essentially heat transfer from plasma to disperse particles and low viscosity and density leads to longer acceleration time of particles and their residence time in high temperature zone.

1808

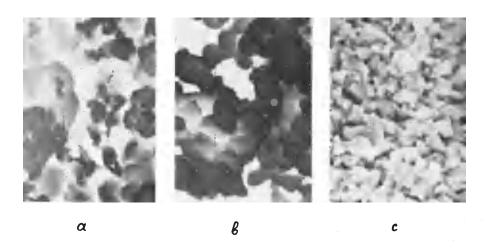


Fig.6. Tungsten powder reduced in a plasma jet (a), tungsten carbide powder (b) and WC+CO alloy structure (c).

According to thermodynamic calculations optimum reducing effect of hydrogen lies at temperature about 2000 K, its upper temperature level being limited by thermodynamic stability of the reduction product - water vapour, i.e. 4000 K. Introduction of carbon containing gases, e.g. reformed natural gas, or carbon black will broaden hydrogen reduction temperature ranges and provide conditions for powder passivation and formation of tungsten-carbon mixtures and tungsten carbides.

Interaction of a chemically active plasma jet with the disperse material is limited by heat - and mass transfer and affected by the degree of homogenization, i.e. by condensed phase vapourization - Yu.V.Tsvetkov (34). This model does not take account of possible effect of free electrons appearing by pronounced plasma non-equilibrium, nevertheless it allows to predict the reduction process results and its optimization. Computer modelling of this process, describing heating and evaporation of particles in gas jet, chemical reactions and condensation and coagulation of particles makes it possible to choose the parameters of process control, raw material input, size of particles and type of their injection into the jet and to establish their influence on reduction degree and on product dispersity (35).

Ultra-dispersed molybdenum powders are obtained by plasma hydrogen reduction route in direct flow reactors. Coarsely dispersed powders (particulate size exceeding 0,5 mm) of W and Mo can be obtained from their oxide coumpounds in fluidized bed reactors.

A plasma process based on the direct dissociation of molybdenite (MoS₂) to molybdenum and sulphur is being developed by Noranda (Canada). First results obtained by Munz and Gauvin (36) on a Laboratory scale induction plasma were encouraging. Further experiments were carried out on a three-electrode arc reactor at Odeillo Laboratory (France) and on a three plasma anode 100 kW d.c. arc reactor at the National Physical Laboratory (Great Britain). While 94% molybdenum was obtained, the results did not meet the process objectives for the production of 99.5% purity molybdenum with a sulphur content less than 0.15% at a specific energy consumption of 10 kWh/kg Mo. The process presently under study at Noranda uses a transferred arc reactor in which the initial flotation concentrate of molybdenite is fed using nitrogen as the plasma gas. The anode consists of the molten metal bath while elemental sulfur is condensed separately in a heat exchanger. Details of the flowsheet and the economics of the process are given by Kubanek et al. (37).

Nickel and cobalt oxides have been carbon reduced in the plasma furnace with a crystallizer (TSETSM, USSR) (38). Experimental results have shown that by plasma reduction melting rather pure metal is obtained containing few impurities, especially sulphur, which is being removed through gas phase without using lime slags. The process is characterized by high reaction rate and stability and also by favourable labour conditions. By optimum ratio of carbon to oxygen (~ 0.52) in the oxide + carbon shift one stage reduction melting provides for content of these elements in the ingot metal less than 0.1%. At present this process is being developed on an experimental production scale.

IRON REDUCTION

For plasma iron reduction various methods have been tested: method of blow-through by reducing gas jet (40,41), prereduction by the gas upstream jet with final reduction on the surface of the molten pool by intense arc radiation (flash-reactor) (39). These methods could be applied also for recovery of other metals, i.e. Cu, Ni, Cr, Mn, V and for treatment of complex ores.

Single-stage process of producing pure iron ingot (0.01% C) from oxide by hydrogen-methane plasma reduction is being developed by Bethleham Steel (USA). This process may substitute the blast furnace converter steel production route and direct iron reduction with subsequent electric furnace melting route. Magnetite and nematite concentrates and hot rolling wastes have been melted and prereduced in a combined plasmatron-falling film reactor and fully reduced under the slag in the ceramic crucible by plasma jet heating. The energy consumption of the experimental unit of 1 MW power and 280 kg/h productivity (750 ton/year) has been as low as 3.75 kWh/kg iron when $\mathrm{CH}_{\mathrm{A}}/\mathrm{H}_2 = 1/2$ (42).

Reduction of iron ores by gases heated in an arc discharge has been investigated at Tulachermet, (USSR). Bed shift reduction of ore-carbon and ore granules by the products of oxygen reforming of methane in an arc discharge with the stoichiometric proportion of hydrocarbons and oxidizing agents has been carried out. The natural gas consumption has been reduced almost to a half and the oxygen consumption – to one-third compared with their consumption by reducing gas conversion in conventional reforming burners, which operate steadily only with a certain excess of oxidizing agent. This saving in consumption of process gases may compensate the additional costs of electrical energy for reforming in an arc discharge. The total content of oxidizing agents ($H_2O + CO_2$) in the products of natural gas reforming in an arc discharge does not exceed 1-2%, which makes it possible to obtain, during simultaneous reduction of iron oxides and alloying elements, a sponge alloyed with chromium and nickel (NPO Tulachermet, USSR, 40,41).

Reduction of finely dispersed iron-ore concentrate with a methane-hydrogen mixture heated to 2500-3500°C in an arc gas heater is completed in hundredths of a second. It has been possible to obtain both practically pure ferrite and highly carburised iron, this being e termined by the ratio of oxydizers and reducers at the reactor inlet. By combined reduction of iron, chromium and nickel oxides a starting material for making stainless steels could be obtained. The lining formed on the furnace walls by adhering material being processed effectively protects the walls from aggressive action of oxydizing jets with temperature up to 3000°C and prevents contamination of smelting products by compounds of refractory lining.

Experiments in a converter-tupe furnace have shown that it was possible to bubble gases heated in an arc discharge through the molten oxides for reduction process. The following specific productivities were obtained in laboratory furnaces: bed process, 80 ton/m^3 per day; cyclone and converter processes, 60-100; jet process, 950. Thus highly concentrated energy fluxes enables to step up the specific productivity of apparatus used in metallurgical processes.

Optimized construction of plasma iron reduction furnace could be developed after testing on power levels > 1 MW, that is an actual task of near future. Some experience on refractory oxides melting in rotating plasma furnaces (horizontal, inclined, vertical) has been collected. Scaling up of these furnaces in power and size by high rotation rate is limited.

Steel production. Tetronics and Foster-Wheeler (Great Britain) have suggested plasma routes for steel production by carbothermic reduction of iron ore powder and bituminous coal (with addition of fine lime powder) in expanded conical arc plasma (Fig.4). Reduction occurs when the particle is flying through the plasma cone and is fully finished in the metal slag pool. Short time of metal-slag interaction diminishes the impurities content in metal. The plant has been proposed for 20 000 ton per year, based on two-plasma-reduction furnaces 30 MW, 15 ton/h each, operating continuously on 30 ton molds. This idea of mini-plant corresponds to some modern tendencies to organize small-scale metallurgical production which is of great interest for developing countries. The material and energy balance of the plant have been estimated: energy consumption, 2500 kWh, coal consumption; 440 kg/yon of steel ingot. The capital investment has been estimated as 30 million doll. Tentative production cost \$140/ton of steel ingot (18).

Ferroalloys. Fey and Harvey (Westinghouse, USA) proposed two-stage plasma reduction process of chromite ore ${\rm FeCr_30}_4$ for producing ferrochromium alloys: prereduction of FeO at 800°C by carbon monoxyde and hydrogen mixture from the main reduction furnace, separation of the metallic iron from the prereduced ore and final reduction of the upgraded chromite by methane at 1700°C in a 16 MW arc plasma generator (43). Hamblyn estimated energy requirements for carbo thermic reduction of chromite ore in a falling-film plasma furnace at 2770 and 2960 kWh

per ton of alloy (for reduction at 1700 and 1900° C respectively), as compared with 3400 kWh for submerged arc furnace reduction at 1500° C. Plasma furnace off-gas could be utilized for preheating of feed ore or for prereduction of iron oxide content. Experiments on a semi-industrial scale are under way (44).

Mc Rae (Bethleham Steel, USA) has produced ferrovanavium by carbothermic reduction of V_2O_5 oxide in falling-film arc reactor on 500 kW with iron scrap added into the melt (Fig.4). Vanadium oxide powder prereduced previously in hydrogen has been mixed with coke powder and brought into argon-hydrogen plasma. The reduction takes place in the falling film on inside walls of tubular anode-reactor. Residence time of particles in the melt may reach several minutes. In the ceramic crucible, oxides have been heated and fully reduced by plasma jet and iron scrap and aluminium for complete deoxidation have been added. At experimental melts ferrovanadium has been obtained containing 48-55% vanadium with energy consumption about 7.7 kWh/kg vanadium metallic vanadium output 90%, efficiency of plasma heater 80%. The cost of plasma reduced ferrovanadium is estimated at \$12.5/kg, the cathode service life; 100 h. In contrast to the demonstration unit for iron reduction the ferrovanadium reactor falls within industrial production scale (45).

Shaft reduction. By the shaft reduction the utilization of thermal energy and heated gas chemical potential is highly efficient. Opposite streams of acting substances make it possible to utilize the energy of waste gases for preheating and prereduction of solid shift. In spite of numerous patents there are only few examples of the practical use of plasma gas heating in shaft reduction processes.

Plasma shaft melting has been carried out with the arc plasma 90 kW generator to produce 17% Si silicomanganese. Shift of manganese concentrate, quarzite, coke, lime and iron chips has been loaded into the shaft furnace up to level 650-700 mm ligher than plasma generator, which was set on the lateral wall in the lower part of the furnace and operated with nitrogen gas (a heat source only). Temperature of the waste gases did not exceed 300°C. The recovery grades of Mn and Si in the alloy have been higher than the concentrations obtained by conventional ore melting thermal furnaces, concentration of phosphorous being 2 to 3 times lower (VNIIETO, USSR, 46).

INDUSTRIAL GAS HEATING

Plasma heating of industrial gases and activation of flames in arc and HF plasmatrons can provide considerable technical and economical advantages for intensifying of big-scale chemical and metallurgical processes. Most promising processes for plasma heating are: heating up gases to optimum reaction temperature, also gases preheated by nuclear reactor off-heat; conversion of methane by carbon oxides and metallurgical furnace off-gases; heating of sulphur containing off-gases of sulphide ore treatment; heating of air, nitrogen, oxygen etc.

The conversion of methane by carbon dioxide in argon arc plasma has been investigated on power level up to 100 kW (IREC, Canada). By single pass conversion 50% transformation of methane into reducing mixture of carbon oxide and hydrogen has been achieved. The possibility is considered of conversion in alternate current arc plasma generator with direct heating of $\text{CH}_4\text{-CO}_2$ mixture (without argon). From the economical point of view it is possible to reduce the lean natural gas on a power level 2MW (47).

In the last decade research has been going on in industrially developed countries on technical and economic expedience of nuclear, chemical and metallurgical plants, where both electric energy from nuclear reactor and its thermal energy would be used for technological processes. The modern high temperature nuclear reactors with helium cooling (HTGR) at 100-1000 MW thermal power may produce helium at $600-700^{\circ}$ C at the outlet. Experimental constructions are being developed for $800-1000^{\circ}$ C. Towards the end of the century it expected to get cooling helium at $1000-1200^{\circ}$ C in super-high temperature gas reactors (SHTGR) (48).

Active technological gases may be heated in heat exchangers up to temperature slightly lower (about 100°) than the temperature of helium cooling the nuclear reactor. Heated up even to 800-850°C by the nuclear reactor off-heat the technological gases may be directly used for many metallurgical processes: direct reduction of metallized iron oxide pellets by hydrogen (or other reducing gas) in a shaft furnace or in a fluidized bed reactor producing iron powder or sponge iron with subsequent remelting in electric furnaces; evaporation of technological aqueous solutions in some non-ferrous metallurgy processes; hydrogen reduction of nickel, cobalt, tungsten and molybdenum oxides for producing metal powders in fludized bed reactors or in rotating furnaces.

At higher temperature, 900-1000°C, it is expedient to heat up and to convert carbon containing reducing gases - such as natural gas, coke and blast-furnace off-gas, products of coal or liquid hydrocarbon gazification. Hot reducing gases may be used for ore direct reduction in shaft furnaces or for prereduction of iron concentrate for blast-furnace process with an

essential coke economy - Fig.7 (49).

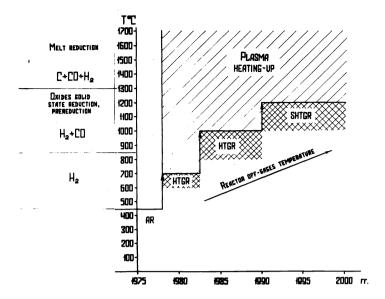


Fig.7. Prospective development of nuclear preheating and heating-up of reducing gases (49).

For many important ferrous and non-ferrous pyrometallurgical processes the necessary temperature level is not attained by the preheating of reducing gases with nuclear reactor off-heat especially with present day reactors. The electrical energy generated by the nuclear power station from the same reactor may heat the gases up to the necessary temperature level and also activate them. Reducing gases heated up to the blast-furnace process temperature; $1200-1300^{\circ}\text{C}$, and their full conversion may economize coke up to 30-40% and economize natural gas as well. In the direct iron reduction process the heating of reducing gas up to $1000-1100^{\circ}\text{C}$ essentially reduces the natural gas consumption up to $180~\text{m}^3/\text{ton}$ of sponge iron.

The necessary temperature for reduction gas may be obtained either by burning out of a part of gas or by plasma heating. The maximum temperature of oxy-hydrogen flame is 2800° K, in arc plasmatrons hydrogen may be heated up to 3500° K and other gases - up to still higher temperatures (5-12 10^{3} K). The heat transfer coefficient of a hydrogen plasma jet is approximately 5 times higher, than that of the oxy-hydrocarbon flame, the high temperature increases the fraction of thermally activated molecules and their chemical activity as well.

By heating gases up to 1500-1600°C and even higher temperature is possible to combine prereduction in a jet type plasma reactor with final reduction and refining under a slag layer in a plasma melting furnaces and with continuous casting. Such a process has the following advantages for steel production: simplified charge preparation using fine-disperse (even better) concentrates; excluding of oxidizing (steel-melting) stage; high intensity, continuity and possibility of automatization, possibility of obtaining by one-stage process standard quality metals, of alloy steels and of complex alloys and ferro-alloys. Plasma process of this type has been developed by Bethleham Steel (USA) (14).

Plasma nuclear metallurgical plants may be suggested (Fig.8):

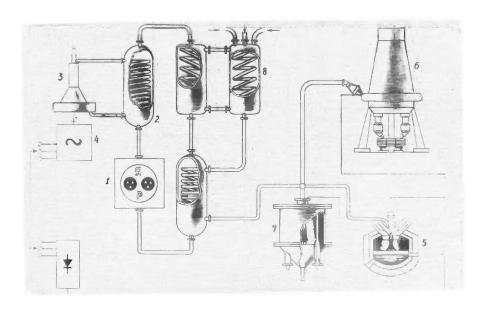


Fig.8. Nuclear-plasma metallurgical plant flowsheet (49). 1 - nuclear reactor; 2 - high temperature heat exchangers; 3 - turbine; 4 - generator; 5 - plasma electric furnace; 6 - blast furnace with plasma heated-up reducing gas; 7 - plasma reactor for producing metallic powders; 8 - heat exchanger for raw materials preheating.

- a) for ferrous metallurgy processing of standard iron ores and concentrates; of superconcentrates enriched with iron and of finely disperse iron slimes (wastes of non-ferrous metallurgy); plasma shaft direct reduction furnaces, for example, of 300 m³ volume and up to 100 MW power, the output of such furnaces is about the output of 1200-1500 m³ furnaces; direct reduction plasma reactors (10-50 MW); plasma furnaces for steel and ferroalloy melting; 10-15 MW.
- b) for non-ferrous metallurgy processing in plasma reduction furnaces of oxides of cobalt, nickel, tungsten, molybdenum and zinc; sulphide concentrates of molybdenum, nickel, copper chlorides of titanium and aluminium; alumina and materials containing alumina; for nickel reduction melting on power level up to 5 MW, for ferronickel 10 MW, for thermal melting of copper, nickel and alumina ores 10-50 MW.

Superheating and activation by the electric energy in gas discharge of reducing gases, preheated by off-heat of nuclear reactors, may economize valuable fossil fuels in metallurgy and also in chemical technology. These bi-scale (> 10 MW) prospective processes call for development of powerful and effective plasmatrons and for working out suitable metallurgical and chemical one-stage processes.

OUTLOOK FOR THERMAL PLASMA METALLURGY PROCESSES

In the USSR and abroad in the 60-70 ies research, experimental and commercial development work on application of thermal plasma for pyrometallurgy and high-temperature chemistry, have been carried out. In some industrially developed countries the energy crisis of the seventies, relatively high cost of electric energy and tendency for its saving, have not favoured a wide development of experimental work and commercial realization of plasma processes in industry, especially on a large scale. As the means for overcoming energy crisis are emerging, the wide use of new sources to generate abundant electric energy such as nuclear and thermal fusion energy, energy of low-grade fuels and of alternate energy type (solar, geothermal and others) looks more promising. Therefore, research, development and realization of plasma processes based on electric energy may be technically and economically well founded.

By means of plasma technology it is possible to produce both cast metal and metallic powders, including highly dispersed and spheroidal, and materials with a single-crystal and multi-layer structure, multi-component alloys, pseudo-alloys and composites (1).

Besides the tendency of an increase in the unit capacity of metallurgical plants there is a trend towards the building of so called "mini-plants". Engineering plants generally use 20 000-50 000 ton of metal a year and only the largest ones up to 100 000 ton. In a number

of cases it is economically expedient to meet this demand largely by the output of the plant's own metallurgical shop, making, for example, metallic powders for the production of metalceramic parts. Plasma technology may enable to design compact and easily managed plants with a high level of process mechanization and automation. A reduction in the dimensions and metal consumption of production process equipment and correspondingly in capital investment may also be expected from plasma techniques.

Low inertial plasma processes allow to organize production using off-peak (e.g. night) power station operating periods.

Plasma technology makes it possible to reduce damage to the environment around the metallurgical works. With the increase in plant specific productivity the water consumption and waste water discharge should decrease substantially. With hydrogen as the reducing agent, atmospheric pollution will also decrease.

Industrial realization of small-scale plasma processes, not requiring large capital investment, such as welding, cutting, surface coating, powder production, synthesis of oxides, carbides, nitrides is rather simple. Medium and big scale processes require the development of high-power equipment and experimental scaling up: heating and superheating of industrial gases, beneficiation and composition of complex ores, reduction of iron and some non-ferrous metals (aluminium, copper, nickel), titanium dioxide production, large ingots melting, refractory materials production.

Thermal plasma is no longer an object of laboratory research and experimental development, but becomes a real means of solving metallurgical problems. As an effective means of electrical energy conversion into the high temperature heat energy thermal plasma has to play an important role in the development of metallurgy and inorganic materials technology.

REFERENCES

- 1. N.N.Rykalin. Plasma engineering in metallurgy and inorganic materials technology. Pure & Appl.Chem., 48, 179-199 (1976).
- 2. M.F.Zhukov, V.Ya.Smolyakov, B.A.Uryukov. Elektrodugovye nagrevateli gaza (plasmatrony), Moskva, Nauka (1973).
- Elektrodugovye plasmotrony. M.F.Zhukov (ed.), Novosibirsk (1977). 3. A.S.Sahiev, G.P.Stel'mah, N.A.Chesnokov. Nekotorye osobennosti tehnologicheskih plasmatronov dlya obrabotki dispersnyh materialov. P<u>lasmennye protsessy v metallurgii i tehno-</u> logii neorganicheskih materialov. Moskva, Nauka (1973).
- 4. M.C.Fey, J.McDonald. Electrode erosion in electric arc heaters. A.I.Ch.E. Plasma Chemical Processing Symposium. August 1976.
- 5. M.C.Fey, C.B.Wolf, F.I.Harvey. Magnetic spheroidization using an alternating current arc heater. Ind.Eng.Chem.Process Des.Dev. 16, 108 (1977).
- 6. M.F.Zhukov, A.S.Koroteev, B.A.Uryukov. Prikladnaya dinamika termicheskoj plasmy. Novosibirsk, Nauka (1975).
- 7. A.A.Kiselev, F.G.Rutber. Trehfaznaya plasmotronnaya ustanovka. Generatory plasmennyh struj i sil'notochnye dugi, pp. 31-39. Leningrad, Nauka (1973).
- 8. Ch.Sheer, S.Korman. The high intensity arc in process chemistry. Arcs in inert atmos-
- pheres and vacuum, pp. 169-183. New York (1956).
 9. R.R.Akers, N.Griffing, R.K.Bul. Primenenie vodoohlazhdaemyh nerashoduemyh elektrodov dlya vakuumnoj plavki. Vakuumnaya metallurgiya, pp. 50-61. Moskva, Metallurgiya (1973); N.N.Rykalin, A.V.Nikolaev, A.P.Borzhov. Energy parameters of low pressure discharge with a hollow cathode. Physics of Welding Arc. London (1979).
- 10. P.H.Dundas, M.L.Thorpe. <u>Chemical Engineering Progress</u> 66, 66 (1970); N.N.Rykalin, S.V.Ogurtsov, I.D.Kulagin et al. <u>FHOM</u>, 1, 154 (1975).
- 11. J.Galliker. Plasma Erzengung mit Hochfrequenz. Bull. d'Information, Union Internationale d'Electrothermie, Paris, $\underline{11}$, 1 (1972). N.N.Rykalin, I.D.Kulagin, L.M.Sorokin, A.N.Gugnyak. FHOM 4, 2 (1975).
- 12. G.N.Kolpakov, V.L.Teplouhov, I.A.Tihomirov, K.N.Yugaj. Generirovanie plasmy v metallicheskom reaktore s ispol'zovaniem fakel'nogo HF razryada i issledovanie ego ustojchivosti. Generatory nizkotemperaturnoj plasmy, p.341. Moskva, Energiya (1969).
- H.U.Eckert. Induction plasma at low frequencies. AIAA 9, 1452 (1974).
 N.N.Rykalin, I.D.Kulagin, A.V.Nikolaev, L.M.Sorokin. FHOM 7, 155 (1977).
- 14. R.C.Gold, W.R.Sandell et al. Plasma reduction of iron oxide with hydrogen and natural gas at 100 kW and one megawatt. Internat.Round Table on Study and Applications of Transport Phenomena in Thermal Plasmas. Odeillo, 12-16, 9 (1975).
- 15. A.L.Mosse, V.V.Pechkovskij. Primenenie nizkotemperaturnoj plazmy v tehnologii neorganicheskih veschestv. Minsk, Nauka i tehnika (1973).
- 16. A.V.Nikolaev. Generatory nizkotemperaturnoj plazmy, p.572. Moskva, Energiya (1969).
- 17. P.H.Wilks. Plasma process for zirconium dioxide. Chem.Engng.Prog. 4 (1972). 18. J.K.Tylko. High temperature treatment of materials. Can.Pat. N 957733 (1974). Foster Wheeler (PTY) LTD/Tetronics LTD. Techn.Rep., Dec. 1976.

- 19. V.I.Lakomskij, B.E.Paton. Plazmenno-dugovoj pereplav. Kiev (1974); Plazmenno-dugovoj pereplav. Paton Welding Institute. Prospectus (1976).
- 20. R.I.Kuloukh. Plasma furnace. New concept in metals melting. J.Metals, December (1962).
- Plasma Metallurgy. DDR prospektus, Freital. 21. K.Murase, T.Suzuki, T.Kijma, Takei H., V.Voneda. Production of titanium slab ingot in vacuum plasma electron beam furnace. IV-Vacuum Metallurgy Conf., Tokyo (1973).
- 22. S.Asada, I. Yegushi, T.Adashi. Industrial plasma induction furnaces. J.Japan Inst. Metals 34 (1970).
- 23. I.R.Travers, R.F.Flammand et al. Study and utilisation of high temperature plasma processes. Super high temperature materials Symp. Plasmochemistry, Kiel, September (1973). Rotating plasma furnace. Electrotherme, Brussels. F.H.Howie, I.G.Sayce. Plasma heating of refractory melts. Rev.Int.Hautes Temp. et Refract. 160 (1974).
- 24. I.G. Sayce. Plasma processes in extractive metallurgy. The Institution of Mining and Metallurgy, London, Oct. (1971). I.G.Sayce. Heat and mass transfer in thermal plasmas. IUPAC Round Table, Odeillo, France (1975).
- 25. USA patent 3856918.
- 26. N.A.Kaluzhskij, Yu.D.Ostanin, V.M.Kozlov et al. Rezultaty issledovanij po ispol'zovanivu plazmennogo nagreva v metallurgii alyuminiya i osnovnye trebovaniya k plazmotronam. 11 Vsesoyuznoe soveschanie po plazmohimicheskoj tehnologii i apparatostroeniyu pp. 77-79, 1, Moskva (1977).
- 27. R.Ishizuka, K.Akashi. The reduction of ilmenite ore in a direct current plasma arc. Intern.Round Table on Study and Applicat. of Transport Phenomena in Thermal Plasmas pp. 111-10. France, Odeillo (1975).
- 28. M.B.Ouiada, J.C.Bonet, M.Foex. Traitment thermique de minerals a base d'ilmenite dans un four a plasma. 3-eme Symp.Internat. de Chimie des Plasmas, t.III, p.53. Limoges (1977).
- 29. C.Bonet, P.Chaussade, D.Gold. Metallurgia extractive du tungstene dans un four a plasma. 3-eme Symp.Internat. de Chimie des Plasmas, t.III, p.57. Limoges (1977).
- 30. N.V.Alekseev, O.G.Pozdnyakov, S.N.Shorin et al. Obrabotka tsinkosoderzhaschih shlakov vysokotemperaturnymi potokami vosstanoviteľ nogo gaza. III Vsesoyuznoe soveschanie po plazmohimicheskoj tehnologii i apparatostroeniyu, pp.71-72, 1, Moskva (1977).
- 31. Yu, V. Tsvetkov, S.A. Panfilov, I.K. Tagirov, A.V. Savin. Doklady na II natsional'noj konferentsii po metallokeramicheskim konstruktsionnym izdeliyam, p.74. Sofia, NTS Mashinostroenie (1974).
- 32. A.V.Savin, S.A.Panfilov et al. FHOM 2, 141 (1974).
- 33. S.A.Panfilov, A.A.Oganyan, Yu, V.Tsvetkov, V.G.Glebovskij. FHOM 6, 66 (1977).
- 34. Yu.V.Tsvetkov. Issledovanie termodinamiki i kinetiki vosstanovleniya okislov tsvetnyh i redkih metallov v razlichnyh agregatnyh sostoyaniyah. Doktorskaya dissertatsiya, Moskva
 - Yu.V.Tsvetkov. Nekotorye voprosy plazmennoj metallurgii. I.P.Bardin i razvitie metallurgii v SSSR, pp.329-347. Moskva, Nauka (1976).
- A.I.Pustovoitenko, S.A.Panfilov, Yu.V.Tsvetkov. FHOM 2, 62 (1979).
- 36. R.J.Munz, W.H.Gauvin. The decomposition kinetics of molybdenite in an argon plasma. AIChE 21, 1132 (1975).
- 37. Kubanek, G.R., Gauvin, W.H., Irons, G.A. and Choi, H.K., The industrial application of plasmas to metallurgical processes, proceedings of the 4th International Symposium on Plasma Chemistry, Zurich, 27 August - September 1st 1979.
- 38. Yu.V.Tsvetkov, Zolotov B.V., S.A.Panfilov, B.L.Rozenberg. FHOM 6, 62 (1977).
- 39. A.I.Drugovskij, Yu,V.Tsvetkov et al. Issledovanie pirometallurgicheskogo peredela vanadijsoderzhaschego syr'ya s primenemien nizkotemperaturnoj plazmy. III Vsesoyuznoe soveschanie po plasmohimicheskoj tehnologii i apparatostroeniyu, pp.30-31, 1, Moskva, (1977).
- 40. N.N.Rykalin, A.I.Manohin et al. <u>Steel</u> 11, 574 (1977).
- 41. V.A. Frolov, V.M. Minkin, I.B. Frolova et al. Protsessy vosstanovleniya okislov zheleza, hroma i nikelya nagretymi v elektrodugovom razryade. Pryamoe poluchenie Fe i poroshkovaya
- metallurgiya pp.39-44, N 4. Moskva, Metallurgiya (1978). 42. C.A.Pickles et al. Investigation of a new technique for the treatment of steel plant waste oxides in an extended arc flash reactor. Advances in Extractive Metallurgy (1977). <u>Inst. of Min. and Metal</u>. pp.69-88. London (1977).
- 43. M.G.Fey, E.J.Harvey. Plasma heating devices in the electric energy economy. Metals Eng. Quart. May (1976).
- 44. S.M.L.Hamblyn. Nat.Inst. for Metallurgy Rep. N 1895, Apr. (1977).
- 45. D.R.Mac Rae et al. Ferrovanadium production by plasma carbothermic reduction of vanadium oxide. 34-th Electric Furnace Conf. St. Louis, Dec. (1976).
- 46. A.S.Mikulinskij, Yu,M.Vlasov, L.A.Mel'tsev. Trudy VNIIETO 8, 95-97. Moskva, Energiya (1976).
- 47. C.H.Leigh, E.A.Dancy. Etude de la reformation du gaz naturel par un arc plasma. IUPAC Thermal Plasma Round Table, Odeillo (1975).
- 48. A.A.Erohin. Plasmennodugovaya plavka metallov i splavov. Moskva, Nauka (1975).

- 49. N.N.Rykalin et al. Plasmennyj pereplav metallov. I.P.Bardin i razvitie metallurgii v SSSR. Moskva, Nauka (1976). N.N.Rykalin et al. Nekotorye voprosy fiziki i himii plazmennodugovogo pereplava.
- Konstruktsionnye i zharoprochnye materialy dlya novoj tehniki. Moskva, Nauka (1978).

 N.N.Rykalin. Termicheskaya plasma v metallurgii i tehnologii. Doklad na Vsemirnom elektrotehnicheskom kongresse WELC 1977 Moskva, June 1977.

 N.N.Rykalin et al. Perspektivy ispol'zovaniya atomnoj energii v metallurgii. Voprosy Atomnoj nauki i tehniki, ser. Atomno-vodorodnaya energetika pp. 25-39, vyp.1(4), Moskva (1978).