PLASMA ENGINEERING IN METALLURGY AND INORGANIC MATERIALS TECHNOLOGY

N. N. RYKALIN
A. A. Baikov Institute of Metallurgy, Prospekt Lenina, 49 Moscow, B-334, USSR

Abstract—An account is presented of the work done in the USSR on the generation of thermal plasma, plasma melting, and plasma jet processes. The various methods of plasma generation are reviewed, such as arc plasma generators and high frequency (HF) plasma generators including HF-induction plasmatrons, HF-capacity plasmatrons and HF-flame plasmatrons. Plasma melting techniques covered include plasma-arc remelting and reduction melting. Plasma jet reactors, multi-jet reactors, and processes such as product extraction, dispersed material behaviour in plasma jets, production of disperse materials, reduction of metals, synthesis of metal compounds, and production of composite materials are briefly described.

INTRODUCTION
Thermal plasma engineering enables new inorganic materials, with pre-determined mechanical and chemical properties, shape and structure to be produced, such as metallic alloys, chemical metal compounds, ultra-disperse and spherical powders and refractory and composite materials. Thermal plasma processes can play an important role in extraction metallurgy, both in the effective utilisation of polymetal ores and concentrates, and in the processing of industrial wastes, particularly environmental pollutants.

The most promising application of thermal plasma engineering is in the production of materials with new specific properties, which cannot be synthesized by any other method.

The use of thermal plasmas, in a metallurgical installation, can essentially intensify many metallurgical processes, as chemical reactions occur in the gas phase, between the vaporised condensed phases, and the dissociated and activated vapours, and not on the surface. The kinetics of such reactions is therefore intensified, resulting in milliseconds being sufficient for completion of processes. The productivity of the installation per unit time, area and volume is remarkably improved if both the response time and volume are minimised.

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

The difficulties involved in realising plasma processes are primarily determined by an insufficient development of both the engineering and technological problems dealing with specific conditions arising in high-temperature rapid-rate processes. Among these are problems of jet diagnostics, powder mixing, quenching, condensation, high temperature filtering etc. A certain danger may also arise from non-critical attempts in applying thermal plasma to unsuitable objects and processes. It is therefore necessary, first of all, for metallurgists and chemical engineers to make a critical assessment of both the advantages and disadvantages in applying a particular plasma route.

Metallurgical and engineering plasma processes and devices (in plasma engineering the processes and equipment for their realisation are especially closely related) may be broadly classified, by the aggregate state of the material to be processed, into the following four groups: the processes involving the effect of plasma jets on a compact solid phase, on a compact liquid phase, on dispersed condensed material transformed to a certain degree into vapour and on gaseous phases (which in pure form is a typical plasmochemical process) (Table 1).

If one neglects the overlap of typical characteristics between these classes, and the complications arising from chemical reactions, during the process, this simplified classification may help to systematize the data and to assess the main advantages and shortcomings of each type of process.

A number of processes affecting a compact solid body has already been realised on an industrial scale: cutting of metallic and non-organic materials, welding and building-up, realizing predetermined surface properties by thermal or chemical means, processing and drilling of rocks, spraying on protective coatings (heat-resistant, wear-resistant and corrosion-resistant), producing composite materials by building-up matrix material on reinforcement fibres, producing refractory metal workpieces by spraying layers on the model subsequently smelting out. The hardware and engineering problems of these processes have to a certain extent been solved, and they are widely used in industrial material processing technology.

1. THERMAL PLASMA GENERATION
Thermal plasma jets for technological applications are generated in direct and alternating current arc plasmatrons, as well as in electrodeless high-frequency induction plasmatrons. Research is under way for developing plasmatrons operating at high (up to 100 bar) and low (down to 10^{-2} torr) pressures, as well as plasmatrons of the ultrahigh frequency, pulsed arc discharge and other types.

Arc plasmatrons have a high efficiency (60-90%) and provide high power of up to 2-5 MW. Their service life, however, is limited by electrode erosion and, when operating with reactive gases (oxygen, chlorine, air) does not exceed 100-200 hr. With electrodes that erode, such as graphite, the service life of arc plasmatrons used in the cracking of petroleum products, may reach several hundred hours.

At the Institute of Thermal Physics in Novosibirsk (Prof. M. F. Zhukov) several types of arc plasmatrons for
plasmatrons have been constructed. By joining several plasmatrons have been developed with a net efficiency exceeding 90%. At the Paton Institute of Electric welding (Kiev) a series of direct and alternating current arc plasmatrons have been constructed. By joining several plasmatrons in the reactor the total power may rise up to 2–3 MW and more.

High frequency induction plasmatrons have at present relatively small power (up to 1 MW) with efficiencies from 50 to 75% and their durability is limited only by the service life of power sources (up to 2–3 months). At the Baikov Institute of Metallurgy (Moscow) high frequency induction generators on a power level up to 300 kW have been examined. Powerful three-phase plasma generators have at present been examined.² Powerful three-phase plasmatrons have been developed with a net efficiency exceeding 90%. At the Paton Institute of Electric welding (Kiev) a series of direct and alternating current arc plasmatrons have been constructed. By joining several plasmatrons in the reactor the total power may rise up to 2–3 MW and more.

500–1000 kW have been examined.² Powerful three-phase plasmatrons have been developed with a net efficiency exceeding 90%. At the Paton Institute of Electric welding (Kiev) a series of direct and alternating current arc plasmatrons have been constructed. By joining several plasmatrons in the reactor the total power may rise up to 2–3 MW and more.

### Table 1. Metallurgy and inorganic chemical engineering thermal plasma processes

<table>
<thead>
<tr>
<th>Plasma interaction with:</th>
<th>I. Compact solid phase</th>
<th>II. Compact liquid phase</th>
<th>III. Dispersed condensed phase in carrying gas jet</th>
<th>IV. Gas phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processes</td>
<td>Welding</td>
<td>Melting</td>
<td>Metals reduction</td>
<td>Gas heating</td>
</tr>
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<td></td>
<td>Cutting</td>
<td>Refining</td>
<td>Synthesis of compounds</td>
<td></td>
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<td></td>
<td>Building-up</td>
<td>Alloving</td>
<td>Ore benification</td>
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<tr>
<td></td>
<td>(Spraying on substrate)</td>
<td>Reduction smelting</td>
<td>Powders processing</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Crystals production</td>
<td>Spraying</td>
<td></td>
</tr>
<tr>
<td>Machinery</td>
<td>Burners</td>
<td>Plasma furnaces</td>
<td>Plasma jet</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cutters</td>
<td></td>
<td>Reactors</td>
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</table>

1. **Arc plasma generators**

Among the electric arc plasma generators the most widely used are the *linear* types (Fig. 1). Cathodes are made of tungsten rods alloyed with thorium, yttrium or lanthanum and zirconium, generally in a water-cooled copper housing. The cathode service life ranges from twenty to several hundred hours depending on operation conditions. The service life of a copper ring-formed or tubular anode (intensively water-cooled) for currents up to 10 kA when operating with high enthalph gases reaches 100–150 hr. The magnetic field for the rotation of the arc anode spot is provided by a water-cooled solenoid mounted on the anode housing. The arc and solenoid are power-supplied, as a rule, in series from the same source. Argon, nitrogen, air, hydrogen, natural gas and their mixtures are used as the plasma forming gas. Depending on the type of gas, the efficiency varies within 60–85%. The average mass flow gas temperature for hydrogen on the plasmatron outlet is up to 3700°K, for other gases—up to 4500–12,000°K.

The tendency to increase jet temperature and flow rate by diminishing the channel diameter and increasing the length of linear plasmatron, results in current shunting to the tube body and can lead to the formation of a fluctuating (cascade) arc. The maximum current of the furnace plasmatron is limited not only by the service life of the cathode but also by the so-called current of stationary stability, i.e. the current value at which the arc can burn for a long time without forming a cascade. A fluctuating arc leads to destruction of the linear plasmatron assembly and has hindered further development of high power plasma furnaces. One way to decrease the possibility of forming a cascade arc is by arc current modulation. The fluctuating arc does not occur if the arc burning time is lower than a certain value. The so-called current of dynamic stability can considerably exceed the value of stationary stability current.³

Some developments of arc plasma generators are promising:

(a) A generator with interelectrode inserts in the sectioned channel and distributed gas supply (Fig. 2);²
(b) A generator with tubular electrodes and distributed gas inflow for heating up nitrogen, air and natural gas; with this type arc power is increased considerably by raising the voltage (Fig. 3);³
(c) A three-phase generator with 3 or 6 tungsten rod or tubular electrodes (Fig. 4)⁴ for heating hydrogen and inert gases. This type has a rather good service life at power levels up to 100 kW.

### Figure 1. Arc plasma generator—linear type.² (1) electrodes, (2) arc, (3) breakdown of low temperature gas, (4) electromagnetic coils, (5) vortex chamber, (6) thermo-cathode.
Fig. 3. Arc plasma generator with distributed gas injection.4 (1, 2) electrodes; (8) current-conductive washer; (9) collector for gas input.

Fig. 4. Three-phase arc plasma generators.3 (1) plasmatron body, (2) isolation insertion, (3) electrode holder, (4) electrodes, (5) current input, (6) nozzle chamber.

evaporation of tungsten and is in agreement with Langmuir's law.

The low-pressure plasma is essentially on a nonequilibrium state. The electron temperature measured by a probe method amounts to $40 \times 10^3 - 100 \times 10^4 \text{K}$. The temperature of the neutral species does not exceed $1500-3000 \text{K}$. This rather high electron temperature plays an important role in transferring energy from the discharge to the heated body.

For further development of arc plasma generators, it is very important to investigate the electrode phenomena in d.c. and a.c. arcs, in order to increase the heating efficiency and the electrodes' service life. Increasing the power of plasmatrons is an urgent problem, especially for big metallurgical and chemical installations. However, several plasmatrons of smaller unit power may be arranged in the same reactor. In this case, it is necessary to have several independent power supply sources and control units. The power supply scheme is much simpler with a.c. plasma generators.

Thyristors with automatic arc current stabilisation are now mostly used as power supply sources for d.c. plasma generators with parameters 1000 V/1000 A; more powerful sources are available up to 7 MVA. For small plasma generators silicon-diode power supply sources are rated at 350 V/600 A.

2. High frequency plasma generators

The main practical advantage of electrodeless HF plasma generators lies in that the service life of plasma installation is limited only by life time of electro-vacuum parts of a transformer and of an electromagnetic energy source—approx. 2-3 x 10^4 hr.

Energy generators and transformers providing the necessary constant anode voltage (usually 10-12 kV), assembled on thyristors or semi-conductor diodes, have high efficiency (99%) and are practically unlimited in power. The HF generators of electromagnetic energy circuits also use electro-vacuum parts: high power
industrial generators have high anode losses, up to 20–40%, thus sharply reducing the HF system efficiency which does not exceed 40–60%. Two ways of diminishing the anode losses to between 5–8% are being developed. These are (a) operating the generator under overload conditions and (b) using special generator lamps with magnetic focussing. HF industrial generator efficiency may increase by these means up to 70–85%.

Energy generated by a high frequency electromagnetic field is used for gas heating in different types of HF plasmatrons: induction, capacity, flame and combined (Fig. 6).

**HFI-induction plasmatrons** have been developed the most. Their power in pilot plants has reached 200–300 kW; in laboratories 500–1000 kW units are being tested. The minimum power necessary for self-sustained induction discharge is determined by the gas, pressure and frequency of electromagnetic field. As the frequency is reduced from the MHz range to the hundreds of KHz range, the power increases from less than 10 kV to hundreds of kW, and then rises hyperbolically on further frequency reduction. Difficulties in supplying the power for discharges on standard industrial frequencies (50–60 Hz) are explained by this very phenomenon. To reduce the minimum power for sustaining an induction discharge, it is necessary to increase the plasma conductivity by lowering the pressure or by adding ionizing mixtures.

Electrodynamics of HFI-discharges is governed by the laws of induction heating of conductive materials. However gas dynamic phenomena in HFI-discharge are rather complicated and can only be qualitatively evaluated. That is why engineering methods to calculate gas flow HFI-discharges, have yet to be developed. HFI-plasmatrons can operate with quartz or metallic discharge chambers for different plasma forming gases. The most promising is the operation on chemically active gases: oxygen, chlorine hydrogen and vapours of reactive substances.

**HFC-capacity-plasmatrons** have no wearing parts, as the electrodes are placed outside the discharge chamber. Capacity coupling of an HFC-discharge with the electrodes voltage leads to the formation of a phase shift between the electrode and discharge current. The electrodynamic conditions of HCF discharge are worse- ned by a phase shift and so the efficiency of the discharge electrodynamic conditions of HCF discharge are worse- ned by a phase shift and so the efficiency of the discharge.

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**HFF-flame plasmatrons** are essentially a combined type, as the electrode discharge current is grounded through the distributed capacity. The efficiency of the system is near to 50%. Even lower minimum power is necessary to maintain the HFF-discharge. The presence of an erodable electrode limits the choice of a plasma forming gas, though at a power level of up to 10 kW, erosion of this electrode is unessential.

Plasmatrons with combined energy supply: HF + direct current; HF + alternating current; HF + LF (low frequency) are not yet fully developed, but many present a certain interest.

In the field of HF plasma industrial engineering the following problems have to be solved: increasing the efficiency of the anode circuit up to 90–95%; increasing the power of HF-plasmatrons up to 3–5 MW; developing combined energy supply plasmatrons. On theoretical side of HF-discharges it is important to develop engineering methods to calculate HF-plasmatrons taking into account dynamics of a plasma gas flow, especially in turbulent conditions. Attention should also be paid to development of tubeless generation of HF-electromagnetic oscillations.

### 2. Plasma Melting

The processes concerned with the effect of thermal plasma on compact molten material, the melting of metals and ceramics, the alloying and refining remelting of metals and alloys, the reduction smelting of metals and the growing of metallic and ceramic crystals, are carried out in plasma furnaces. Processes in industrial use at the present are: the continuous remelting of bars or rods (electrodes) in the water-cooled crystalliser, the intermittent melting of materials in a ceramic crucible, and combined methods, e.g. induction plasma melting of metals and alloys.

#### 1. Plasma furnaces

A number of types of plasma furnaces for laboratory and industrial applications have been developed.

**Industrial plasma furnaces** for semi-continuous operation have been developed at the Paton Electric Welding Institute (Kiev)—Table 2. From 3 to 6 d.c. or a.c. plasmatrons are radially arranged (Fig. 7). The furnaces are designed for remelting of axially located ingots. These furnaces are used for refining of precision and heat-resistant alloys, high-temperature metals, ball bearing steels, high tensile special steels as well as for nitrogen alloying of metals (Fig. 8).

Furnaces with three-phase power supply have been developed by Electrotherme (Belgium). The furnaces are designed for the refining of niobium, tantalum, bolybdenum, titanium and other metals as well as of heat-resistant alloys based on nickel and cobalt.

#### Table 2. Paton electric welding institute plasma furnaces

<table>
<thead>
<tr>
<th>Furnace type</th>
<th>Y-461</th>
<th>Y-467</th>
<th>Y-600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total power, kW</td>
<td>160</td>
<td>360</td>
<td>1800</td>
</tr>
<tr>
<td>Number of plasmatrons</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Maximum weight of ingot, kg</td>
<td>30</td>
<td>460</td>
<td>5000</td>
</tr>
<tr>
<td>Maximum diameter of ingot, mm</td>
<td>100</td>
<td>250</td>
<td>630</td>
</tr>
<tr>
<td>Extrusion rate of ingot, mm/min</td>
<td>1.5–15</td>
<td>1.5–15</td>
<td>2–20</td>
</tr>
</tbody>
</table>
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Fig. 7. Radial type arc plasma furnace. (1) metal to be melted; (2) plasmatrons; (3) ingot; (4) energy source.

Fig. 8. Arc plasma furnace V-467—Table 1.

High and low pressure furnaces with axial plasmatron for melting horizontal rods (Fig. 9), as well as a furnace with radial plasmatrons for laboratory melting of bulk charge into ingots have been developed at the Baikov Institute of metallurgy (IMET) (Moscow)—Table 3. These furnaces are designed for nitriding metals and alloys, for remelting high temperature and active alloys as well as for processing bulk materials and industrial wastes.

Low pressure plasma furnaces with a hollow cathode for melting high-temperature, active metals and special alloys into crystallisers have been developed by Ulvac (Japan) (Fig. 10). An industrial furnace with six arc plasmatrons and a total power of 2.4 MW has been built for melting titanium sponge. The charge is melted in a water-cooled tray from whence the liquid metal flows into a crystalliser of circular or rectangular cross-section. The tray and the crystalliser are heated by individual plasma arcs. Ingots up to 3t can be produced in this furnace.

The axial plasma furnace for batch work with a ceramic crucible was developed by Linde (USA) (Fig. 11). This furnace for melting charge materials has a ceramic lining, one or several d.c. plasmatrons and a bottom electrode.

Fig. 9. Axial type arc plasma furnace for continuous melting operation. (1) metal to be melted; (2) plasmatron; (3) ingot; (4) energy source.

Fig. 10. Low pressure arc plasma furnace with hollow cathode.

Fig. 11. Arc plasma furnace with ceramic crucible for batch melting operation.
Table 3. IMET laboratory plasma furnaces

<table>
<thead>
<tr>
<th>No. Layout</th>
<th>Number of plasmatrons (mm)</th>
<th>Diameter of ingot (mm)</th>
<th>Plasma-forming gas</th>
<th>Gas consumption (cbm/hr)</th>
<th>Operating pressure in melting space</th>
<th>Power (kW)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Axial</td>
<td>1—3</td>
<td>60-100</td>
<td>argon, mixture of argon and nitrogen and hydrogen</td>
<td>2–4</td>
<td>(1–3) bar</td>
<td>30</td>
<td>30–40</td>
</tr>
<tr>
<td>2. Axial</td>
<td>1</td>
<td>60–100</td>
<td>argon, helium, nitrogen, hydrogen</td>
<td>10^{-2}–10^{-1}</td>
<td>10^{-2}–10 torr</td>
<td>100</td>
<td>30–70</td>
</tr>
<tr>
<td>3. Radial</td>
<td>4</td>
<td>100</td>
<td>argon, argon–nitrogen, ammonia</td>
<td>2–4</td>
<td>1–2 bar</td>
<td>50</td>
<td>30–50</td>
</tr>
</tbody>
</table>

Note: The efficiency was measured on water-cooled copper anode.

(Anode). This type is especially promising for metal refining, melting steel and special alloys and for producing big-size high-quality castings. Furnaces for batch work having a capacity of up to 10t have also been built in USSR, GDR.

A plasma induction furnace, with the induction heating being combined with plasma arc heating (Fig. 12) has been developed by Daido Steel (Japan). A plasma arc using some 35% out of total power of 100–500 kW increases considerably the output of the furnace, and intensifies the refining action of slags. These furnaces are used for melting stainless steels, non-ferrous metals and special alloys.

2. Plasma-arc remelting

This substantially improves the quality of metal. Unlike vacuum-arc and electron-beam remelting, the losses of highly vaporizable components (manganese, molybdenum, magnesium etc.) by the plasma process are very low. Plasma arc remelting makes it possible to refine alloys with readily oxidizable and chemically active components—titanium, aluminium. The most widely used gases are argon, argon–hydrogen (for iron–nickel and nickel alloys) and argon–nitrogen (for alloying from the gas phase).

In a plasma furnace the liquid metal bath is affected by activated gas particles of the plasma jet. Therefore, the equilibrium concentrations of reagents in this case will differ from the equilibrium concentrations with the non-activated gas. Investigation of the interaction between liquid metal and nitrogen containing plasma has shown the possibility of alloying metal by nitrogen from the gaseous phase. The plasma alloying enables one to obtain higher concentrations of nitrogen in the ingot and a rather uniform distribution of the nitride phase, both of which are unattainable by other methods. The Paton Electric Welding Institute (Kiev) has developed the industrial technology of producing more nitrided grades of stainless steel. The way is thus open for producing new alloys with an increased nitrogen content, e.g. alloys of b.c.c. metals with internal alloying impurities. Plasma-arc remelting enables one to control the alloying phase content within the prescribed limits and is now an established industrial method for obtaining such compositions.

A plasma-arc method of growing large monocrystals of refractory metals, up to 50 mm in diameter and weighing more than 10 kg, has been developed in the Baikov Institute of metallurgy (Prof. E. M. Savitsky) and realized in industry. Tungsten monocrystals produced with plasma melting are characterized by a high purity (Fig. 13): high technological plasticity, resistance to recrystallization and creep, and anisotropy of emissive properties reaching 30–70%.

3. Reduction melting

A plasma melting process can be combined with metal reduction by gaseous or solid reducers: hydrogen, ammonia, natural gas, petroleum cracking products and carbon. The furnaces for reduction melting have to be
provided with appliances for the formation of the ingot and the removal of condensed and gaseous reaction products from the furnace.

Hydrogen plasma reduction melting with deep deoxidation, which has made it possible to discard the subsequent deoxidation process by producing soft magnetic alloys (50% Fe and 50% Ni) altogether,17 was carried out at the Paton Institute (Kiev). Reduction melting of a material containing 80% metallic iron was performed at Baikov Institute of metallurgy (Moscow) in a radial plasma furnace. Ammonia admixture to plasma forming argon acted as a reducer. After melting a 100% high purity iron ingot was obtained.

Refractory materials (oxides, nitrides) are melted in Belgium, France and Great Britain in plasma furnaces with rotating ceramic crucible.14,15 These furnaces have a horizontally or vertically located crucible of heat-resistant refractory material. The inner cavity of the crucible has a barrel shape and is heated by arc plasma column (Fig. 14). The charged material is melted by convective and radiative heat from the plasma arc column. Oxidising, reducing and vapourizing processes can be carried out in these furnaces under batch or continuous operating conditions.

3. PLASMA JET PROCESSES

Chemical and metallurgical processes progressing under the effect of thermal plasma jets on the condensed phase of the dispersed material, such as the reduction of metals from simple compounds, the direct and oxidising-reducing synthesis of metal compounds, the processing and decomposition of raw materials, are realised in plasma jet reactors.

1. Plasma jet reactors

Chemical and metallurgical plasma jet processes are carried out as a rule on dispersed particles of condensed materials. The introduction of dispersed material into the high temperature jet zone and its extraction from the wake of hot gases stream represent complex engineering problems, in view of the high temperatures and rates of gas flow. Complete processing of the starting material and a maximum fixation of the product must be achieved.

In research and development of plasma processes, simple direct flow cylindrical reactors with water or gas-cooled metal walls and with a single plasmatron are mostly used (Fig. 15). The reactor diameter at the jet inlet lies generally within 2–10 jet diameters. The starting material is introduced into the jet by the transporting gas (dispersed raw material) or by overpressure (liquid and vapour materials). Cooling gas is sometimes blown in through the reactor walls for terminating the high temperature reaction and fixing the condensed phase product.

The disadvantages of simple cylindrical reactors are as follows. The dispersed raw material, deposits on the outlet nozzle of the plasma generator and on the reactor walls. The optimum conditions that will eliminate or minimize these disadvantages for introducing the material into the jet that will eliminate or minimize these disadvantages are to be determined for each reactor type by special investigations. The deposit formation on the reactor walls can be dealt with in different ways; by increasing the reactor diameter by raising the temperature of its inner wall, by blowing on the walls with ballast gas, and by imposing ultrasonic vibrations.

The quenching, i.e. rapid chilling of the reaction products for small scale processes, is usually realized by cold gas jets, on the cooling surface of a rotating metal drum.

Reactors in which the dispersed raw material is brought in directly to the zone of electric discharge have not yet gained wide application, though a number of interesting suggestions have been put forward. One of them is a reactor involving a fountain layer with high frequency discharge torch (Fig. 16).16 Another one is a magneto-hydrodynamic spatial discharge reactor (Fig. 17). The plasma jet formed by a conventional arc generator acts as a cathode for a more powerful spatial discharge in the zone of the solenoid magnetic field. The powder to be processed is brought into the same space. The particles residence time in the high temperature zone is essentially increased due to the comparatively low gas flow rate and drift due to the tangential component of the velocity. Since the concentration of raw material in the space is relatively low, the discharge remains stable, and variations of its parameters do not exceed 10%. With the bottom arrangement of the plasma generator the material residence time in the high temperature zone is still longer.2

High frequency and flame (ultra high-frequency) plasma generators are usually combined with the direct flow reactors, the raw material being introduced into the discharge area or below the discharge. An exception is the high frequency torch discharge with the fountain layer reactors.

Fig. 14. Arc plasma furnaces with rotating ceramic crucible. (a) horizontal or inclined axis.14 (b) vertical axis.15.
2. Multi-jet reactors

The reactor with two conflicting plasma jets is used for processing polydispersed raw materials (Fig. 18). The finely dispersed material formed in the process is carried out of the reactor, while the large unprocessed particles of the raw material oscillate in the high temperature turbulent wake of the opposite directed gas jets; the larger the particle the longer it stays in the high temperature zone.
The reactor with the three-arc mixing chamber shown in Fig. 19 provides a rather uniform temperature distribution across the section of 0.85 dia, at a distance of about two diameters from chamber outlet. Usually the plasma generators are placed normally to the chamber axis, but installation at an angle of 60° to the axis facilitates the axial injection of raw material.

Installations are available in which several plasmatrons are symmetrically arranged on a conical head attached to the cylindrical portion of the reactor. The material is supplied to the top of the cone, closer to the plasma jets, so that fraction of processed raw material is being increased.

Reactor with several plasmatrons fixed tangentially (Fig. 20) ensures a uniform temperature distribution across the sections of the reactor, although the heat losses through the walls are rather high.

**Product extraction.** If the product is formed in molten state and accumulated on a liquid bath its removal from the apparatus can be carried out either periodically or continuously. It is also rather easy to withdraw large-size friable powders. Rather complex problems arise with ultra-dispersed powders tending to stick together, or with pyrophoric powders. Such powders require highly effective filters, thereby increasing considerably their size. Special maintenance is required. Stringent requirements are imposed on reactor sealing; when producing highly active powders that are easily oxidized in the air; the extraction of such powders can be accomplished by intermediate lock chambers. Self-ignition of the powder in the air can be eliminated by introducing passivating additions or by thermal annealing in the reduction atmosphere.

**Dispersed material behaviour in plasma jets**

Interaction between the disperse material and the heated gas jets, as well as gas jets mixing phenomena, are investigated in order to develop optimal reactor designs for various plasma processes. Efficiency of chemico-metallurgical plasma processes as well as product quality are primarily determined by heating up and transforming the raw material (fusion, evaporation, chemical reactions), by condensation of the vapours formed, and by coagulation of the condensed product particles.

Material is held in the reactor zone for rather brief residence times. The complexity of experiments makes it impossible so far to obtain full information on the material behaviour, for the range of temperatures and rates for the state of substance in which we are interested. Certain results have been obtained on the heating up and the motion of rather large particles (over 100—150 mkm) in a plasma jet. Pictures of the jet were taken through a rotating perforated disk using high-speed filming and photometry at different wave lengths. Laser diagnostics of the bi-phase jet is very promising too.

**Mathematical modelling** of the disperse material behaviour in the plasma jet brings rather encouraging results. Undoubtedly, a complete model taking into account all known phenomena in the particle loaded jet would have been too complicated for calculation and analysis. Therefore several simplified models have been suggested.

A rather complete model worked out by Yu. V. Tsvetkov and S. A. Panfilov considers heating up, phase transformations (melting, evaporation) and acceleration of spherical particles less than 50 mkm diameter, which are uniformly distributed across a jet-section having no radial gradients of velocity and temperature.

This model enables one to analyse the kinetics of gas jet and particle velocity, to evaluate the degree of material evaporation and to choose the process parameters and the length of the direct-flow reactor Fig. 21. Length of the complete evaporation path of the tungsten trioxide particles of different diameter in a hydrogen—argon jet rises with initial jet temperature and with particle diameter, Fig. 22. Calculated and experimental data for the degree of reduction of tungsten oxide WO₃ in a hydrogen—argon jet, and in an argon jet with carbon particles rises with initial jet temperature—Fig. 23.
The discrepancy between the calculated and experimental results is observed at low average mass temperatures of gas jet because of jet temperature non-uniformity. This model is at present being extended to take into account the gradients of temperature and gas velocity across the jet section.

Simplified models have been developed: a model of heating up of moving particles in the isothermal jet of gas, a model of heating up of moving particles in a jet with parameters changing along its length, a model of condensation and coagulation of particulates in an isothermal jet. Assuming that the velocity \( V_g \) and temperature \( T_g \) of a gas jet in the course of its interaction with particles remain constant, which is reasonable for the high-enthalpy gases and taking the Nusselt criterion in order of 2, then for the small diameter particulates (<50 mkm) it is possible to express the dependence of particle velocity \( V_p \), cm/sec and temperature \( T_p \), °C on time \( t \) in explicit form (Nikolaev)

\[
T_p = T_e - (T_e - T_0) \exp\left(-\frac{t}{t'}\right); \quad \text{Bi} \ll 1
\]

\[
V_p = V_g \left[1 - \exp\left(-\frac{-t}{t''}\right)\right]; \quad \text{Re} < 1
\]

\[
V_p = \frac{V_g t}{t'' + t}; \quad \text{Re} > 2
\]

\[
t' = \frac{C_p \gamma_d d}{6 \alpha}, \quad t'' = \frac{d^2 \gamma_v}{18 V g}, \quad t''' = \frac{4 d \gamma_v}{3 \psi \gamma_v}
\]

Here: \( d \)—particle diameter, cm; \( \alpha \)—heat exchange coefficient, cal/cm²·sec·deg; \( \gamma_v \)—density of jet gas, g/cm³; \( V \)—gas kinematic viscosity, cm²/sec; \( \psi \)—drag coefficient.

These expressions can be used, e.g. for evaluating the time of heating particles up to the melting temperature and length of heating path.

4. Production of disperse materials

Disperse metallic and non-metallic materials are used in manufacturing powder metallurgy products and porous parts (filters), to strengthen metals and alloys, to produce special ceramics and plastics, components for electronic appliances and also directly as abrasives, catalysts, propellant components and pigments. When manufacturing powder materials in plasma jets, the dispersity and shape of powder particles, their purity and surface physico-chemical properties are controlled by the jet parameters (power, temperature, flow rate, gas partial pressure) and the tempering intensity. As the reactions proceed within the plasma jet and its wake, the processed materials have no contact with the reactor walls, so the reaction products are not contaminated by the lining material. Therefore, a jet of low-temperature plasma, and, especially, that of high-frequency induction plasma, makes it possible to obtain high-purity powders (ultradispersed, spheroidized, composite etc.) based on metals, alloys, oxides, nitrides, carbides, borides, hydrides and complex compounds.

Spherical particulates of pre-determined size are produced by plasma heating: from wire or bars butt-melted by plasma arc (Fig. 24) or by supplying standard or granular powders to the plasma jet (Fig. 15). The process has been realised in both versions on installations rated up to 100 kW.

Particles of tungsten, molybdenum, nickel and other metals and high-temperature oxides from 0.1 up to 2 mm, with an output up to 15 kg/hr are produced by wire or rod melting. By powder surface melting particulates are obtained of high-temperature metals and their alloys, titanium and chromium carbides, tungsten, aluminium and zirconium oxides measuring from 1 mkm up to 1 mm with an output of the spherical fraction of over 90% (Fig. 25). This process is realized in electric arc plasmators with a...
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Fig. 23. Coefficient of WO₃ reduction α in jets of argon and hydrogen (a), argon and carbon (b), hydrogen (c) depending on initial temperature Tₑ of gas jet: — measured experimentally; --- calculated. d₁, d₄ — particle diameter of WO₃ and carbon, mm.

Fig. 24. Installation scheme for spherical powders production by plasma spraying. (1) plasma generator, (2) reactor body, (3) rod to be sprayed, (4) power supply source.

Fig. 25. Tungsten spherical particulates 0.1–0.2 mm (area 750–300 mkm).

sectioned anode, and in argon plasma jets with admixtures of hydrogen or hydrocarbon gases (when spheroidising carbides). The decarboxamination of carbides is slowed down by adding hydrocarbons to the plasma-forming or transporting gas and by adding some soot to the starting carbide powder.

Spherical powders of various oxides (e.g. of silicon, magnesium, zirconium and aluminium) are produced in argon + oxygen high frequency plasma jets with discharge power up to 40 kW with particle size up to 400 mkm and the output of spherical fractions approaching 100% (Fig. 26).

A HF-discharge is used with a cooler central zone. This type of discharge enables one to introduce rather easily the initial powder into the plasma jet. Powder plasma treatment rounds up the particulates and refined them from contaminations. For example, by spheroidization of the aluminium oxide powder the content of other oxides (Na, Fe, Mg) is diminished.

The refining effect of plasma powder processing, simultaneously spheroidizing particulates, helps to create new porous materials for various purposes (filters, cathodes, electrodes) to operate at very high temperatures. Spherical particulates of aluminium oxide, 60–100 mkm, are used to produce new types of cathodes powerful vacuum tubes. Spherical refractory powders, obtained in plasma, provided a means for developing new refractory products.

**Ultra refractory materials**

Plasma processes make it possible to produce on a ceramic base, i.e. on oxides, carbides, nitrides etc., structural (insulation and electrode) materials for MHD-generators which are heat resistant and stable to thermal shocks and which can withstand, in active media, temperatures greater than 2000°C for hundreds of hours. Existing refractories are not very suitable for use as structural or electric materials, because of their brittleness.

Creating materials on such a base requires, first of all, an increase in their plasticity. This can be accomplished by imparting to the material a certain internal structure, for example, one made up of spheroidized particulates fused by plastic binders. At the Institute of High Temperatures (Moscow) structural ceramics based on stabilized zirconium dioxide have been obtained with plasma technology. Thermal plasma makes it possible to conduct the whole process of producing highly refractory materials, with enhanced plasticity, from
synthesis. Standard macro-dispersed powders, mainly metallic, are evaporated in the plasma jet and the condensed vapours rapidly cooled (quenched) at rates of \(10^5\) to \(10^7\) deg/sec by cold gas jets. This way aerosol condensate powders with a non-equilibrium crystalline structure formed. Therefore, ultradispersed powders obtained in the plasma jet are characterized by enhanced chemical activity, that cannot be explained by their high specific surface only. These powders are effective in direct processes of chemical synthesis, and as catalysts and raw materials for high rate processes.

Closed circuit technological plasma processes, on power level up to 200 kW, for producing aluminium, iron and manganese ultradisperse powders, based on the evaporation-condensation route have been developed.

5. Reduction of metals

The use of plasma jets up to now has been mainly confined to the reduction of pure metal compounds, using solid carbon, converted natural gas or hydrogen as reducers. Simple metal oxides and halogenides are used primarily as the starting raw material.

- Reduction of refractory metals. The reduction of oxides and ammonium salts of tungsten and molybdenum, chlorides of the same metals as well as of titanium, zirconium and niobium has been investigated in arc and high frequency hydrogen–argon and hydrogen plasma jets on power level up to 200 kW.

Minimum initial gas temperatures and maximum particle size of the raw material for reducing tungsten and molybdenum in a hydrogen arc plasma jet into ultradispersed powders have been determined, and the properties of powders, and routes for their processing, have been studied\(^{27,29}\). The size of tungsten powder particulates varied within 0.05–1 mm, the oxygen content was 0.6% or greater depending on the dispersion (Fig. 27). Plasma processed tungsten powder can be used for the production of hard alloys of the tungsten-cobalt carbide type. When carbidising, the grain does not grow (Fig. 28) forming a uniform fine-grain alloy structure alloy. Similar tungsten powders can be obtained from haloid compounds by hydrogen reduction in a high frequency plasma jet.\(^{30}\) Some amount of metastable phase \(\beta\)-tungsten is present in the product, indicating the specific conditions of forming metallic particulates in a plasma jet.

Ultra-dispersed molybdenum powders are obtained by a similar route in direct-flow reactors. Coarsely dispersed powders (particulate size exceeding 0.5 mm) of these particulates spheroidization to finished product by a route similar to that of the monocystal growing.

-Ultradisperse- powders of metals and non-metallic materials with dimensions of 10–100 nm, and specific surface up to 200 m\(^2\)/g are obtained by condensation after evaporating initial powder or by concluding a high temperature chemical reaction of reduction, oxidation or

![Fig. 26. Spherical powders of zirconium dioxide (a) 30–40 mkm (365 × 365 mkm area) and carbides of tungsten (b) and titanium (c) 2–7 mkm (52 × 52 mkm area).](image1)

![Fig. 27. Tungsten powder reduced in a hydrogen plasma jet from ammonium paratungstate 0.02–0.1 mkm (2.35 × 1.65 mkm area).](image2)
ally obtained in the form of powders, or coatings may be formed in the process of the synthesis, so that the reaction mixture contains both the synthesized elements and their complex compounds.

Plasma processes for obtaining metal oxides, in particular, those of titanium, aluminium, silicon and zirconium are the best investigated.

The pigment titanium dioxide modified by additives of aluminium oxide is obtained by burning titanium tetrachloride vapour with an admixture of aluminium trichloride in an atomic oxygen jet generated by a 160 kW high frequency discharge. The installation output may go up to 5.000 t per year with a power consumption about 1.93 kWh per 1 kg of pigment—Fig. 29.

With an increase in the temperature of the starting materials, the reaction rate grows considerably and the number of nuclei per unit time increases. Therefore, the degree of dispersity of titanium dioxide particulates (the content of particulates smaller than 1 mkm) rapidly increases and reaches 95–98% (Fig. 30). In the high frequency induction discharge zone, oxygen is heated up to 7000–8000 K and atomized. The average mass temperature of the atomic oxygen jet where the tetrachloride vapour is introduced, is controlled by the oxygen flow rate and the discharge power. The best results, from the point of view of titanium dioxide quality and the duration of continuous plant operation, have been obtained with average mass temperatures of 1600–1800°C.

The physico-chemical properties of titanium pigment dioxide conform with the production requirement: the dispersity is 97.3, the tinting strength—1800 units, the luminosity—over 95. The concentration of chlorine in the exhaust gases amounts to 80–90%. The exhaust gas is used for blowing up the inner walls of the reactor, and for regeneration of gas filters and is recirculated for ore chlorination. The route makes recycling of chlorine

Fig. 28. (a) Tungsten powder reduced in a hydrogen jet from tungsten trioxide 0.2–0.5 mkm (5 × 5 mkm area). (b) Tungsten carbide powders synthesized from plasma tungsten and carbon black powders 0.2–0.5 mkm (5 × 5 mkm area).

metals can be obtained from their oxide compounds in fluidized bed reactors.25

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 complexity of the traditional technology.

Reduction of other metals. Research on plasma reduction of non-ferrous and ferrous metals has been carried out. Reducing nickel and cobalt oxides by hard carbon in 100 kW argon plasma jet in a liquid metal bath, has been investigated as well as reduction of nickel oxides in a hydrogen jet.

Silicon powder was obtained from silicon tetrachloride in an argon hydrogen 10 kW high frequency jet.26 Reduction of iron by iron carbonyl decomposition in an argon jet has made it possible to obtain an average size of metal particles 0.3–0.7 mm (conventional process—about 2 mcm). The concentration of carbon in the plasma produced iron powder amounts to 0.1–1.0%.27

Reduction of iron from its oxides in a natural gas arc plasma jet has been investigated.28 The degree of reducibility varied from 25 to 100% depending on the dispersity of the starting raw material (0.84–0.015 mm, respectively). The product was trapped on a liquid metal bath without slag accumulation.

6. Synthesis of metal compounds

The plasma synthesis of metal compounds has an extensive product nomenclature. The products are gener-

Fig. 29. Installation scheme (a) and HF-generator-reactor (b) for titanium dioxide plasma production. (1) high frequency generator, (2) titanium chloride meter, (3) titanium chloride evaporator, (4) aluminium chloride meter, (5) aluminium chloride evaporator, (6) mixer, (7) discharge chamber, (8) quartz tube reactor, (9) metal reactor (10) collector, (11) hopper; (12) lock.
possible when processing titanium ores with high silica content.\textsuperscript{24}

Aluminium dioxide powder has been obtained by the direct oxidation of aluminium in a high frequency plasma jet.\textsuperscript{24} The Al\textsubscript{2}O\textsubscript{3} product contained primarily two fractions: 30–40 nm (metastable modifications: \(\Theta\), high temperature \(\gamma\) and \(\delta\)) and a larger one with particulate size 120 nm (\(\alpha\)-Al\textsubscript{2}O\textsubscript{3}); the relationship between these fractions being controllable by quenching conditions.

Pure oxides of silicon, zirconium, vanadium are also produced by oxidation of chloride vapours in a plasma jet.\textsuperscript{24,25}

Silicon monoxide powder is produced in a high frequency argon jet at 15 kW from the stoichiometric mixture of silicon and silicon dioxide powders. The average mass temperature of the jet is about 7000°K, the argon consumption—30 l/min.\textsuperscript{35} The monoxide having the bulk weight of 0.05 g/cm\(^3\) in the process of plasma production is being refined from impurities: copper, iron, chromium, nickel.

Disperse silicon dioxide and zirconium oxide grinding powders, obtained by burning the chlorides in an oxygen plasma jet have enabled the efficiency of polishing processes of electric device parts to be raised by an order of magnitude. Condensate powders of complex barium-silicon oxide, spherical powders of special glass and powders of silicon monoxide are now used for producing parts of integrated circuits.

High temperature spinel MgAl\textsubscript{2}O\textsubscript{4} is synthesized in plasma jet from the stoichiometric mixture of aluminium and magnesium oxides. The product has smaller crystallites than the starting raw materials, which indicates that the material goes through a process of vapourization-condensation.\textsuperscript{36}

Nitrides of titanium and zirconium are obtained by direct synthesis in a nitrogen arc plasma jet. Ti or Zr powder (10–60 mkm) is introduced into a direct flow reactor. At a jet power 50 kW the powder throughput is up to 10 g/min, the nitrogen consumption—10 l/min.\textsuperscript{36,37}

Titanium nitrides of TiN\textsubscript{0.95} composition can also be obtained from titanium tetrachloride vapours in a nitrogen plasma jet on admixture of hydrogen. The process is carried out in an ultra high frequency 3 kW nitrogen plasma jet and a graphite direct flow reactor at a pressure of about 1.1 atm. In the same way titanium boronitrides are obtained by processing the mixture of vapours of boron and titanium.\textsuperscript{26,29} Carbides of these metals can be produced by decomposing chlorides of titanium and niobium in pure argon, or with admixtures of hydrogen or methane in a fluidized bed reactor on particles of graphite with a pulse plasma discharge (the pulse frequency is 9–10 Hz).\textsuperscript{40}

Synthesis of super-conductive compounds of A-IV structure (vanadium with silicon or germanium; niobium with aluminium or germanium) in 15 kW HF plasma is carried out with the hydrogen reduction of the mixture of chloride vapours. The chlorides are obtained by direct metal chlorination.\textsuperscript{33} This procedure may be recommended for the reducing synthesis of other metal compounds.

7. Composite materials

Plasma technology has opened up new ways to obtain super-strength and high modulus fibre reinforced composite materials.

By plasma arc spraying, metallic matrix material is deposited on high-modulus boron and silicon carbide fibres, as well as on high-strength steel and tungsten fine wires. Research on the effect of the argon plasma arc and of the sprayed metal drops on fibre properties made it possible to develop the technology of plasma spraying producing semi-finished strips of composite materials. The significant role of spraying dispersity has been shown. At present the composite strips of aluminium matrix alloys and boron fibres are produced on a semi industrial scale. The subsequent processing of the composite strips to obtain finished products comprises hot vacuum pressing, or rolling packets of the strips cross-wise to the fibres. To eliminate fibre crushing, fine-grained matrix materials which have a superplasticity effect are used. The subsequent thermal treatment of the product results in the matrix acquiring the necessary strength due to the cossering of the grain size or the phase structure.\textsuperscript{42}

CONCLUDING REMARKS

Research problems

In the USSR several institutes of the Academy of Sciences, industrial research centres as well as technical universities take part in research and development of metallurgical and technological plasma processes.

In the field of thermal plasma jet generator methods have been developed for calculating the characteristics of the arc and the induction discharges—power, temperature, jet velocity (Institute of Thermal Physics, Novosibirsk, Institute of Heat and Mass Transfer, Minsk). Methods of thermal plasma diagnostics—spectral, probing, microwave—were worked out and have been applied (Lebedev Physical Institute, Moscow, Kurchatov Atomic Energy Institute, Moscow).

The development of plasma process theory, in particular, physical hydrodynamics of nonsothermal jets, the kinetics and reaction mechanism in multi-phase systems at plasma temperatures is going on (Baikov Institute of Metallurgy, Moscow; and in Institute of Petrochemical Synthesis, Moscow).

There is an urgent need to investigate the complex mechanism of physico-chemical transformations of material in turbulent non-isothermal plasma jets and, especially in non-equilibrium plasmas. It is also necessary to collect experimental and calculated data on the
thermodynamic and transport properties of substances in a dissociated and partially ionized state (Institute of High Temperatures, Moscow).

Research of non-stationary, modulated and interacting plasma jets with superimposed electric and magnetic fields as well as of pulse, cascade, colliding and multi-jet plasmatrons operating in a.c., d.c. HF, UHF at elevated pressures, and in vacuo, shall enlarge appreciably the field of thermal plasma technological applications.

**Industrial applications**

Thermal plasma processing is in industrial use for producing special quality alloys, obtaining monocrystals, producing pure powders of specific structure, spherical and ultradispersed, carrying out direct synthesis of compounds and a synthesis combined with oxidising and reducing reactions. Plasman processes are rather suitable for processing of complex ores such as phosphate, silicon-aluminium and titanium ores and valuable industrial wastes ("man-made ores"), e.g. wastes of refractory and rare metals, cinder wastes, sulphur containing gaseous wastes of non-ferrous metallurgy. The possibility of varying both the temperature and the medium composition in the reaction zone of a thermal plasma presents powerful means for developing fundamentally new processes, as well as modernising the traditional routes in metallurgy and inorganic materials technology.

**Acknowledgements**—Author is grateful for the assistance given by his co-workers: Dr. A. V. Nikolaev and Dr. S. A. Panfilov in preparing this lecture.

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