THERMAL PLASMA TECHNOLOGY FOR PROCESSING OF REFRACTORY MATERIALS

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Abstract - A simple classification of thermal plasma reactors able to process re-
fractory materials is proposed. It is based upon the analysis of heat transfer bet-
ween the plasma flow and the particulate charge under processing. The main relevant
operating parameters which define each type of proposed plasma reactor are :
i) the residence time τ of the particles inside the plasma zone, ii) the diameter d
of the particulate feedstock, iii) the heat potential S available in the plasma
between the plasma temperature and the particle temperature, iiii) the temperature
T_o at the reactor wall.
In a second part, we report and discuss data on electrode erosion measurements. The
production of oxidizing plasmas for thermal processing of oxide raw materials sets
a difficult problem in the design and controlled operation of electrodes able to
withstand oxidizing media. Materials such as OFHC copper, zirconium and zirconium
oxide will be considered in that view.

INTRODUCTION

Thermal plasma technology is recognized to offer a high potential for processing of refracto-
ry materials. The scope of applications which has been proposed and developed is large. It
particularly covers :
- mineralurgy and ore beneficiation : (1), (2), (3)
- extractive metallurgy : (4), (1), (5), (6), (7), (8)
- synthesis of refractory compounds : (5), (9).

The feasibility of some processes has been demonstrated at the pilot scale but no application
has been yet successfully developed at the industrial scale. It is likely that such a situa-
tion will still prevail, as long as more severe external constraints will demand a more im-
portant effort of research in that domain. Energetic constraints - and the increasing utili-
zation of electricity in those countries where nuclear energy production will be developed -
constraints upon raw materials - development of new resources and of new routes for up -
grading and processing - can play in the next future the role of a catalyst to promote the
development of plasma technology up to a situation where its advantages and drawbacks will
be clearly established.
In the actual state of the art, the development of a plasma process shall be considered as
a difficult operation. Our purpose is to supply simple and valuable guide-lines for the se-
lection of a plasma process and the definition of a plasma reactor suitable for a required
application prior to its development.

DEFINITION OF THE SYSTEM

The system which is presently under consideration shall play two essential functions :
- produce the plasma through an electric discharge, the features and characteristics of
  which shall be sufficiently known and controlled.
- treat efficiently a given material for a required application. Such a thermal treatment
  is usually operated, if not in the discharge itself, in the plasma flow, in order to take
  advantage of the large heat potential which is available.

Steady state and continuous processing is achieved by direct introduction of the charge into
the plasma reactor. The material is heat affected during its residence time in the plasma
zone and undergoes physical and (or) chemical changes. The process is completed by the col-
lection of the products at the exit of the reactor.

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Among numerous phenomena which are involved during the interaction between the plasma and the refractory material, the most important for the efficiency and quality of the process are undoubtedly   heat, mass and momentum transfer between the plasma flow and the condensed phase.

The prediction of qualitative and, when possible, quantitative effects of the interaction requires a lot of information and data :
- for the discharge and the plasma : temperature and three dimensional velocity field,
- for the charge : temperature and velocity distribution in the reactor.

The temperature of the plasma shall be understood as the temperature of the neutral species, since for polyatomic gases of interest in thermal plasma processing, these species play a predominant role to convey heat to the reactive interface. But the role of ionic species and of some excited neutral species (whenever they are in equilibrium with the species present in the plasma) shall not be disregarded in the sense that they can supply a unique contribution to the chemical affection of the material, under specific conditions.

The electrical features of the system and electrode phenomena (for arc processes) are also of major importance because they directly influence the properties of the plasma and the behaviour of the charge under processing. Therefore this group of relevant parameters shall be considered with special attention.

By the end, the kinetics for reaction of the material shall be determined in order :
i) to identify those phenomena which are responsible for the progress of the overall reaction, ii) to select the optimal values of the operating parameters in order to increase the efficiency of the process.

The requirement for a better description of the system is incomplete if we do not add the knowledge of, i) the thermodynamic and transport properties of the plasma (heat conductivity, viscosity, coefficient for diffusion of species, radiative properties of emission and absorption), ii) its thermodynamic state (in particular its situation with respect to L.T.E.), iii) the physical properties of the condensed phase and the reaction products.

Total or partial knowledge of these reported phenomena, properties and physical data allows a microscopic and macroscopic description of the system, the selection of the parameters which are involved in the construction of the plasma furnace, and its consequent definition, which is detailed in table I.

Table I. Definition of the plasma furnace for processing of refractory materials

PLASMA FURNACE	Plasma generator	- type of discharge : R.F., d.c., a.c. single phase or three phase. - type of plasma production : gas/discharge interaction. - type of electrodes : thermoionic or cold (for arc systems). - choice of the plasma gas.
	Plasma reactor	- internal geometry. - nature of the wall (cold or hot).
	Introduction of the charge	- transportation to the entrance section. - mode of introduction. - characteristics of introduction. (location, velocity, orientation).
	Collection of the products	- gaseous - condensed - recuperation of sensible and chemical heat in the effluents.

A preliminary and important conclusion results from the previous analysis. The universal plasma furnace allowing to carry out processes as different as, reduction of metallic oxides, melting and fuming of refractories, cracking of hydrocarbons does not exist. Each element of the system shall be carefully designed and studied for each required application according to the available data.

HEAT TRANSFER TO THE CHARGE

A necessary condition for processing, is that heat transferred to the charge is more than E_t, which is the thermodynamic requirement for treatment, whenever the nature of the process and the complex situation which is prevailing in the system. The predominant role of heat transfer is still emphasized by the fact that, as it has been demonstrated by several authors, (Refs. 10 and 11), the overall kinetics of reaction can be controlled by heat transfer in the case of liquid particles reacting in the plasma flow.

Therefore, analysis of heat transfer between the plasma flow and the charge represents a valuable contribution to a better knowledge of the process, towards a further improvement of its efficiency.

Let us consider the direct introduction of a particulate feedstock into the plasma. This a practical common situation in many plasma systems. Heat is exchanged between the condensed phase and the plasma flow through different phenomena :

- conduction, which is predominant at low relative velocity between the particles and the plasma flow.
- convection, which provides a large contribution when the plasma-particle relative velocity is large enough.
- radiation, heating up of fine particles through radiation from the plasma is usually of minor importance compared to the other phenomena. But each individual particle exchanges also heat by radiation with the wall of the reactor and the other particles present in the reactor.

Heterogeneous plasma reactors are very dilute systems because of the short residence time of the particles in the plasma. (12) has shown that the magnitude of the radiative inter-action between a particle and the surrounding particles (at the same temperature) can be neglected provided that the inequation /1/ is valid :

$$n_o \; \Pi \; R \; \frac{D_p^2}{4} << 1 \qquad\qquad /1/$$

with : n_o : particles concentration
    R : radius of the cylindrical vessel
    D_p : diameter of the particles.

In the example illustrated, n_o = 7 particles.cm^{-3}, R = 20 cm, D_p = $2x10^{-2}$ cm. Therefore, in such a situation, the net radiation flux to be considered is essentially the radiative interaction between the wall and a particle.

Let q(M) be the net local power transferred to the particulate charge by unit of mass at point M.

During time t, the energy supplied is :

$$E = \int_o^t q(M)dt \qquad\qquad /2/$$

q(M) is expressed as the net local flux transferred to the unit of mass at point M in the plasma

$$E = \frac{S}{\rho V} \int_o^t \left[h(T_p - T_s) + \sigma \epsilon (T_o^4 - T_s^4) \right] dt \qquad\qquad /3/$$

h is the heat transfer conductance by conduction and convection,
S/V is the surface over volume ratio for the charge,
ρ is the density of the charge,
T_p, T_s, T_o are the respective temperatures of the plasma at point M, of the surface of the
    particle (considered as isothermal in its volume), and of the wall of the reactor
    (considered as isothermal),
ϵ is the emittance of the particle.

In equation /3/ we assume that the geometry of the charge and its density remain constant along the reactor, for the sake of simplicity.

Expression /3/ is developed for unidimensional spherical particles. In this case, S/V = 6/d (d is the diameter of the particles) and the transfer conductance h can be expressed in terms of the local parameter for heat exchange Nu.

$$h = \frac{NuK}{d} \quad \text{and} \quad Nu = f(Re, Pr), \qquad\qquad (13)$$

The total energy received during time t by unit of mass for spherical particles is then :

$$E = \frac{6}{\rho d} \int_o^t \left[\frac{NuK}{d} (T_p - T_s) + \sigma \epsilon (T_o^4 - T_s^4) \right] dt \qquad\qquad /4/$$

Let τ be the residence time of a given particle in the plasma zone. A necessary condition for treatment is that :

$$E(\tau) \geqslant E_t \qquad\qquad /5/$$

where E_t is the thermodynamic specific energy consumption requirement for the process (sensible heat plus enthalpy for reaction or physical heat affection).

In order to satisfy inequation /5/, equation /4/ shows evidence of the role of 5 parameters : d, Nu, $K(T_p - T_s)$, T_o, τ. These parameters are not independant, so that each combination among them shall not be considered. Furthermore some directions are contradictory : for instance, most often it is not possible to increase simultaneously Nu and τ. Physical limitations can also exist : introduction of very fine particles (d $\leqslant$ 10 μm) into the plasma is recognized as a difficult operation.

According to these requirements, we keep as a final selection the following parameters, which, via equation /4/ play an essential role for thermal processing of the material :

τ : residence time of the particles,
d : diameter of the particles,
$K(T_p - T_s) = \int_{T_s}^{T_p} K(T) \, dT = S$, heat potential of the plasma,
T_o : temperature of the reactor wall.

Identification of plasma reactors
The proposed following classification is based upon the choice of selected values of the 4
operating parameters τ, d, S, T_o, which directly influence heat transfer to the particulate
charge and efficiency of the process.

Residence time τ. The practical values to be considered depend as well on the conditions
of injection as on the flow and temperature fields in the plasma. The recent progress in de-
velopment of laser Doppler anemometry techniques allows a statistical determination of the
local velocity of the particles along their trajectories. Vardelle (14) has recently measu-
red axial velocities up to 300 m.s^{-1} for Al_2O_3 particles, 30 μm in diameter, injected into
an argon-hydrogen d.c. plasma jet. Typical residence time lies then in the range 10^{-3}-10^{-2}s.
At the opposite, liquid wall reactors fed by a particulate charge exhibit much higher resi-
dence times of the liquid material at the wall, in the range 10-10 ^{2}s.

Diameter of the particles d . Typical values range between about 100 μm (some tens of μm
in plasma spraying) up to some hundreds of μm in plasma spheroidization. In the liquid wall
reactors, we consider for the sake of simplicity that the diameter becomes infinite as soon
as the particles impinge on the wall. Equation /4/ is then no more valid, since it applies
to a particulate medium.

Heat potential S . The level of heat potential depends upon the nature of the plasma
(plasma gas, vapour species, gaseous products) and of the temperature difference between
the plasma and the condensed phase. It represents the amount of heat which can be transfer-
red by conduction.
For a direct treatment of particles inside the discharge, S is large, mainly because of the
large temperature gradient. Treatment inside the plasma, but outside the discharge is ope-
rated at lower value of S. The combined role of S and d is illustrated in figure 1, after
(13), where we have calculated the equilibrium temperature of a stationary ZrO_2 particle
inside an air plasma. In the heat balance, we take into account the role of conduction,
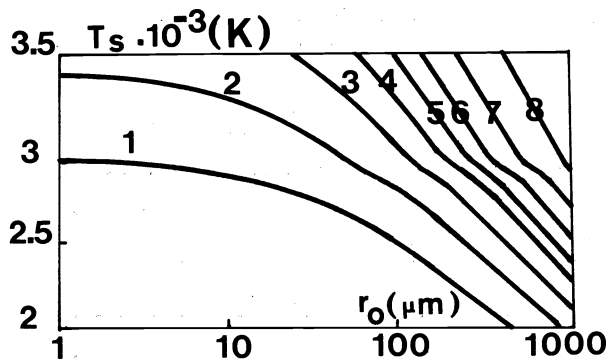radiation and convective evaporation, at low vapor concentration of the particle and low
Re (Re < 1).

Fig. 1. after (13). Theoretical equilibrium surface temperature of a ZrO_2
spherical particle suspended in an air plasma at low Re (Re < 1) versus
its radius, r_o, for different plasma temperatures T_p.
1 : T_p = 3000 K; 2 : T_p= 3500 K; 3 : T_p= 4000 K; 4 : T_p= 4500 K ;
5 : T_p = 5000 K; 6 : T_p= 5500 K; 7 : T_p= 6000 K; 8 : T_p= 6500 K ;
9 : T_p = 7000 K; 10 : T_p= 7500 K.

Temperature at the wall T_o. Mathieu (12) has shown that the radiative contribution of a hot
wall (T_o= 2000 K) upon heating of particles up to the melting point (2000 K) is not signi-
ficant at d = 300 μm. The curves 1 and 2 upon figure 2 illustrate the comparison of a hot
and cold wall. A liquid wall reactor exhibits by nature a high temperature wall, and hea-
ting up of particles can then be achieved efficiently by direct radiation from the wall,
provided that the temperature is higher than in the previous case (for instance T_o = 3000 K).
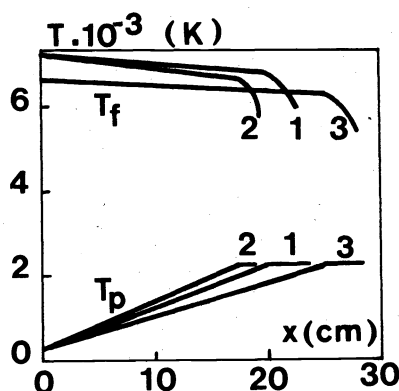
Fig. 2. after (12). Thermal behaviour of silico-aluminate particles when injected into a N_2 plasma flow under the following conditions : available power 80 kW ; initial particle velocity $6 m.s^{-1}$; particle diameter 300 μm; particles mass flowrate 30 $kg.h^{-1}$.
x is the axial coordinate along the plasma reactor, T_f is the enthalpic axial temperature of the plasma, T_p is the surface temperature of the particles.
1 : T_o= 300 K, Q = 12 STP $m^3 h^{-1}$; 2 : T_o= 2000 K, Q = 12 STP $m^3 h^{-1}$;
3 : T_o= 300 K, Q = 16 STP $m^3 h^{-1}$; with T_o temperature at the wall,
Q plasma flowrate.

We indicate in table 2 the values of the parameters which have been discussed and identify in the last row the type of plasma reactor (a,b_1,b_2,c) which is associated to these conditions.

Table 2. Identification of the plasma reactors according to the prevailing conditions

τ s	d μm	$S=\int_{T_s}^{T_p} KdT$	T_o K	Type of plasma reactor
10^{-3}	100	high	cold wall	a
10^{-1}-1	100	mean	cold wall	b_1
			2×10^3	b_2
10^2	∞	mean	2×10^3	c

In type a we find reactors able to treat fine particles in the discharge itself (high S) when injected at high velocity. The Ionarc type reactor which takes advantage of the magnetic pressure existing at the cathode tip to force the particles into the arc discharge belongs to type a (fluid convective cathode). It has been developed for the dissociation of $ZrSiO_4$ into ZrO_2 and SiO_2 (15), the fuming of silica (16) and the spheroidization of sand (17). The scheme of the reactor is shown on figure 3.
The sedimentating plasma furnace, able to operate co-current spheroidization of fine particles in the plasma flow, with large residence times (0.1, 1 s) has been described in (18). It belongs to type b_1. The scheme is on figure 4. A counter-current version of type b_1 has been developed by Segsworth (19), for the reduction of iron oxides. The ore undergoes a pre-reduction in the plasma. Further reduction and purification of the metal take place in a liquid bath at the bottom of the reactor. Version b_2 concerns reactors of the same type, equipped with a vertical hot wall ($T_o > 2000$ K) for direct heating of particles by radiation from the wall. Such an arrangement has been already suggested in (2) but has not yet been developed, to our knowledge.
By the end type c is concerned with liquid wall reactors receiving in the entrance section a particulate feedstock which is forced to the wall. Many versions of this reactor have been developed, for melting of refractory oxides, (18), (19), for fuming of silica, (20), and for the direct preparation of iron (4) or ferrovanadium (21).
In the last reference, the cylindrical cavity is fixed and vertical (figure 5). It is also vertical but the crucible is spinning in the arrangement which has been experimented in (19) (figure 6).
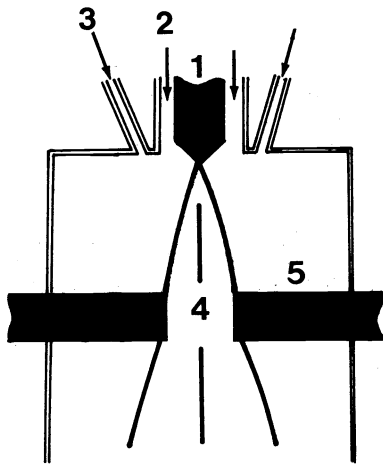
Fig. 3. after (15). Ionarc type reactor
(fluid convective cathode). The particles
injected at the tip of the cathode are
forced into the arc due to the magnetic
pressure. 1 : cathode ; 2 : protective
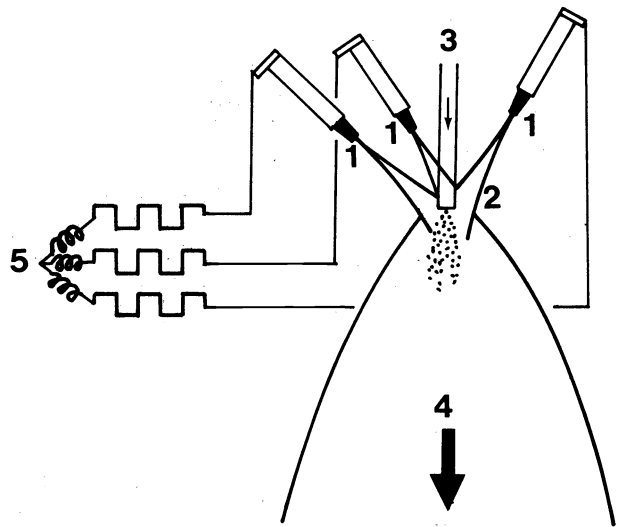gas injection ; 3 : particles injection;
4 : arc ; 5 : multiple anode.

Fig. 4. after (18). Three phase sedimentating
plasma furnace. The particles are injected by
gravity at low initial velocity into the plas-
ma flow. 1 : gas sheathed electrodes ; 2 : arcs;
3 : particles injection ; 4 : plasma flow ;
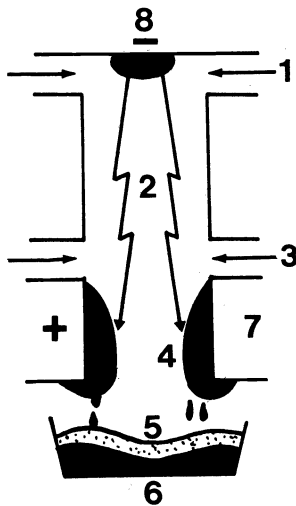5 : three phase current source and inductances.

Fig. 5. after (4). Dripping film, vertical
axis, plasma furnace. The tangential intro-
duction of the oxide ore forces the parti-
cles to stick to the liquid dripping film
at the surface of the anode. Further reduc-
tion and slagging are achieved at the bot-
tom, in the liquid bath. 1 : hydrogen and
methane mixture injection ; 2 : d.c. arc ;
3 : ore injection ; 4 : dripping film ;
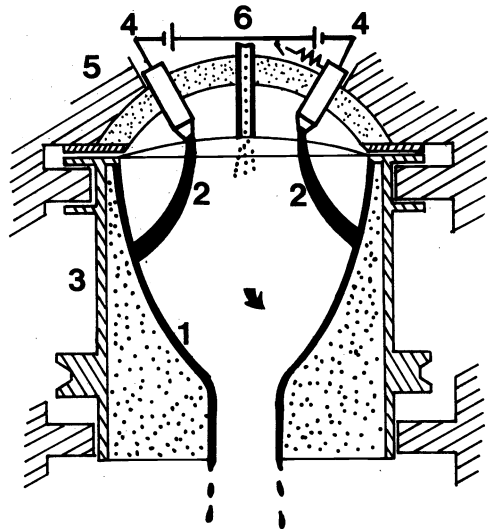5 : slag ; 6 : liquid iron ; 7 : anode ;
8 : cathode.

Fig. 6. after (19). Vertical axis, spinning
crucible, plasma furnace. Heat is supplied
by the main transferred arcs struck between
the 2 plasma guns.
1 : liquid wall ; 2 : arcs ; 3 : rotating
furnace ; 4 : plasma guns ; 5 : fixed flange ;
6 : material injection.

On figure 7 the tilted furnace illustrates the scheme of the plasma installation developed and described in (18).
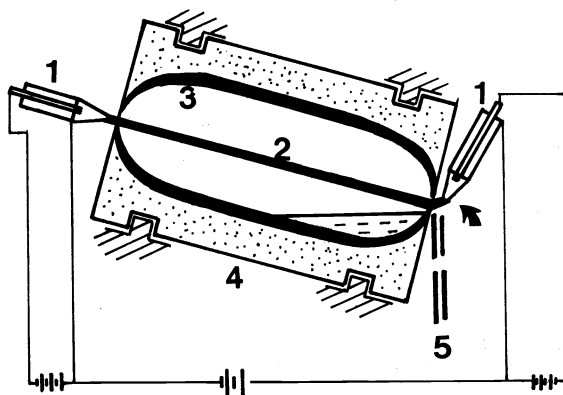

Fig. 7. after (18). Tilted axis, spinning crucible, plasma furnace. The furnace is heated by a d.c. transferred arc which is struck between the plasma guns installed on each side of the furnace.
1 : d.c. plasma guns ; 2 : transferred arc ; 3 : liquid wall ; 4 : rotating furnace
5 : liquid material poured out.

As a conclusion we have been able to propose a simple classification of heterogeneous plasma reactors, based upon the control of heat transfer to the condensed phase through the relevant operating parameters (τ, d, S, T_O) - Note b -

Note b - Further development of the plasma process at the laboratory scale will require different steps. Let P be the plasma power, $\dot{m}$ the mass flow-rate of material under processing, X the yield of the reaction in the collection unit (or the relative quantity of material successfully treated).
The first stage to be considered is the demonstration of feasibility. It can be expressed by the following energetic figure :
$$E \geqslant E_t \quad \text{and} \quad X_o \leqslant X \leqslant 1 \text{ (where } X_o \text{ represents a lower limit)}$$
for purposely selected values of P/$\dot{m}$.
The second step is concerned with the demonstration of the energetic viability.
It is expressed as following :
$$E \geqslant E_t \text{ and } X_o \leqslant X \leqslant 1 \quad \text{with} \frac{P}{\dot{m}} \leqslant E_c$$

where E_c represents an upper energy consumption value which in any case may not be transgressed.
In the third step economic constraints will be added (operating cost, investment) as well as the scaling up features. In any case the overall experimentation will consist in appropriate variations of the 4 parameters which have been identified, in order to optimize the process.

ELECTRODE EROSION IN PLASMA ARC REACTORS

Most reported examples and detailed analysis pertain to d.c. arcs (22), (23), (24), in order to separate cathode and anode phenomena. Indeed each electrode is characterized by its own properties : heat balance, current density, temperature.
We have reported on figure 8, after (25), erosion data versus current density. The horizontally hatched zones characterize cathodes, while anodes are represented by vertically hatched areas. The 5 zones are described as follows :
- in zone I, are located the operating data for thermoionic cathodes. The current density is between 10^2-10^3 A.cm^{-2}. Erosion is essentially due to evaporation and sublimation of the cathode.
- in zone II, are the cathodes presenting a stationary constricted cathodic spot. Current density is between 10^3-10^5 A.cm^{-2}. Erosion is only 10^{-8}-10^{-10} g.C^{-1}. Indeed the temperature of the spot is higher than in case I, but its area is considerably less. Consequently the loss of material by evaporation or sublimation is decreased.
- in zone III are located the cathodes presenting a non-stationary constricted cathodic spot. The current density is very high (10^6 A.cm^{-2}) and the loss of material is due to boiling and sputtering of the surface. Indeed the temperature of the cathode is very high and can reach the boiling point of the metal.
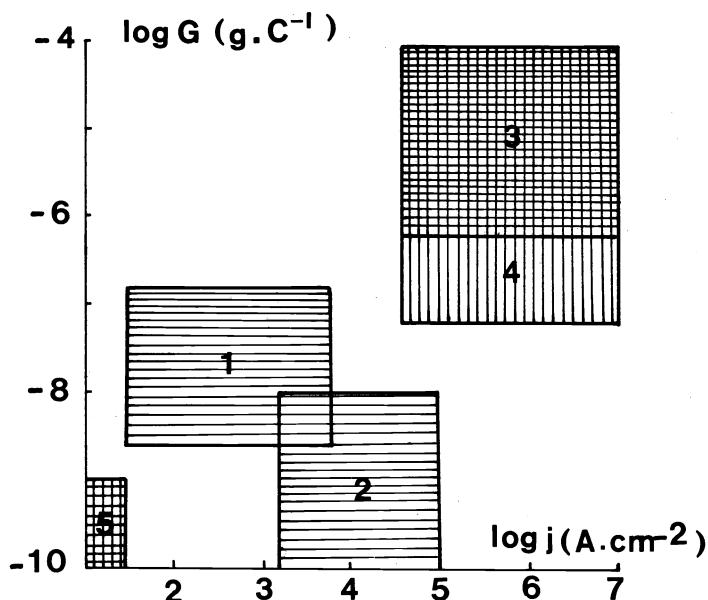
Fig. 8. after (25). Specific erosion (G) and current density (j) data for electrodes operating under neutral or reducing atmosphere according to the regime.
Zone I : cathode in a thermoionic regime ; zone II : cathode in a stationary constricted regime ; zone III : cathode in a non stationary constricted regime ; zone IV : anodes ; zone V : diffuse regime for both cathodes and anodes.

- the behaviour of anodes is illustrated in zone IV. They generally exhibit a non-stationary spot.
- by the end, the figure shows in zone V data for electrodes at low current density, operating in a diffuse regime for both cathode and anode. The erosion is then very low.

The equilibrium temperature reached by the electrodes results from the heat balance at the surface, and partly explains the observed erosion regime (in the case of a neutral atmosphere). But the measurement of the electrode temperature is difficult, due to the spot size and to its motion. These measurements are easier to perform with thermoionic cathodes, which exhibit a large and stable zone for emission of the electrons.
On figure 9 are presented experimental values (hatched zone) and theoretical (solid line curves) for thermoionic emission of tungsten and graphite electrodes. The theoretical curves
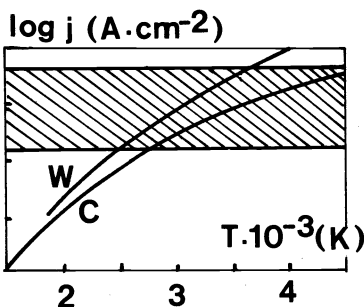

Fig. 9. after (25). Theoretical (solid line) and experimental (hatched zone) emission data for W and C cathodes. T is the surface temperature, j is the electronic current density.

express the well known Richardson-Dushman's law, which correlates the saturation current density j to the surface temperature of the cathode T. Agreement between the theoretical and experimental results is valid only above 10 A.cm^{-2}. The temperature of the cathode lies then in the range 3000 K-4000 K.
Pustogarov (26) has described detailed temperature measurements of plasma generator electro-

des by optical pyrometry, using fast optical micropyrometers (10^{-2}-10^{-6} s).
Such measurements can be performed in the presence of the plasma, only at selected wave-
lengths for which it is optically thin ; its contribution can then be neglected.
When its contribution is not negligible, the pyrometric measurements are carried out after
the arc extinction. The following conditions are then required :
- very fast circuit breaking (20×10^{-6} s)
- very fast deexcitation of the plasma (t)
- fast pyrometry
- thermal inertia of the electrodes large enough.
For instance, the error in measurements is evaluated at 10 K in the case of a deexcitation
time of the plasma t = 10^{-5} s and a cooling rate of the electrode 10^6 K.s^{-1} ; t depends upon
mechanisms which control the exchange of energy between the excited species in the plasma,
the relaxation time of which is variable, and upon the pressure and the energy in the dis-
charge.
At last, these measurements require the knowledge of the monochromatic emittance of the ca-
thode material. Extrapolated values from the solid lead to large discrepancies, since the
emittance shows an important variation at the solid-liquid transition.
As an example of these methods we give on figure 10, after (26), the axial temperature dis-
tribution of a tungsten cathode in Ar and He at I = 100 A. The solid line has been establis-
hed by a photographic method and the dotted line corresponds to optical micropyrometry at
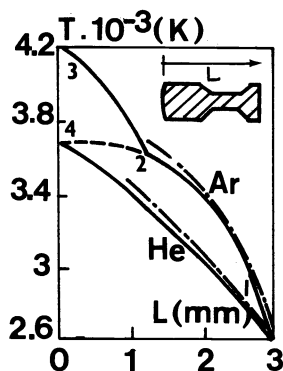λ = 0,65 μm.

Fig. 10. after (26). Axial temperature distribution of a constricted W
cathode in Ar and He at a current of I = 100 A. The dotted lines correspond
to measurements in presence of the plasma by optical micropyrometry. The
solid lines correspond to photographic pyrometry. The portion 2-4 along
the Ar curve takes into account the correction for the plasma contribution.
Under He, the plasma contribution is negligible.

The part 2-3 along the Ar curve shows the contribution of the argon plasma. Part 2-4 has
been constructed by eliminating its contribution. In the case of He, no contribution of
the plasma has been found.
The spatial distribution of the radial temperature of the cathode has also been determined
by optical pyrometry, associated to a scanning mirror (2 m.s^{-1}) installed in front of the
optical system of the pyrometer. The radial temperature distribution of a tungsten cathode
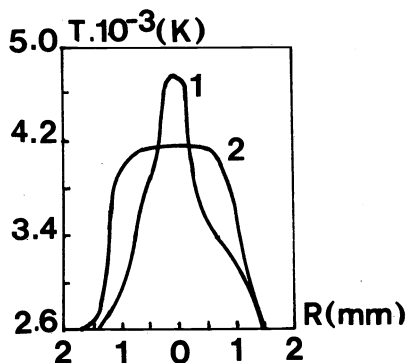in He at I = 150 A is reported on figure 11, after (26), for various cathode geometries.

Fig. 11. after (26). Radial temperature
distribution of a W cathode under He.
Current I = 150 A. 1 : diameter d = 2 mm,
length l = 2 mm ; 2 : d = 4 mm, l = 15 mm.
The measurements are performed by scanning
optical pyrometry.

The previous erosion data which have been presented do not take into account possible chemical reactions between the material of the electrode and the species present in the arc. If such reactions can exist, the behaviour of the electrodes is then considerably modified, depending on the physical properties of the products formed (melting point, electronic emission properties, for oxides in the case of the interaction metal-oxygen). Such an evidence is represented on figure 12, after (25), which reports erosion data of tungsten cathodes under various conditions (vacuum, nitrogen, oxygen).
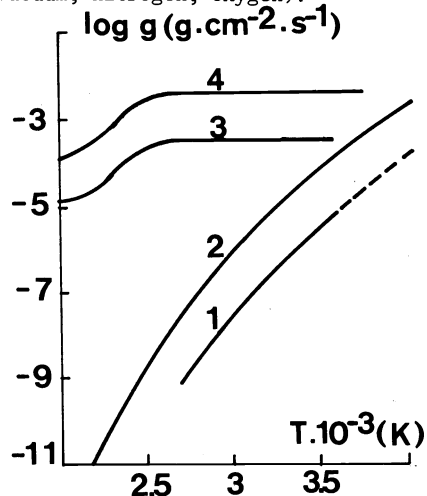

Fig. 12. (after 25). Erosion data (evaporation and oxidation) and temperature of W cathodes under different conditions. 1 : N_2, p = 10^5 Pa ; 2 : in vacuo ; 3 : O_2, p = 1,3 Pa ; 4 : O_2, p = 133 Pa.

These results clearly illustrate the problem to solve for the utilization of oxidizing gases (air, O_2, CO_2) in arc plasma generators. It requires the design and study of special electrodes, purposely adapted for operating under oxidizing conditions.
2 types of solution have been investigated :
- the first one consists in the utilization of copper electrodes (generally oxygen free high conductivity). The cathodic and anodic spot are continuously rotated by a gas vortex at low current and by a superimposed magnetic field at higher current. The erosion rate is then decreased down to 10^{-6}-10^{-7} g.Cb^{-1} for currents up to some hundreds of Amperes.
- in the second solution, the authors utilize special materials for the cathode, either Zr or Hf (25) or systems containing ZrO_2 (27).
The erosion of Zr and Hf cathodes in air is illustrated on figure 13 after (25). The erosion lies in the range 10^{-6}-10^{-8} g.C^{-1} between 100 and 500 A. The reported life of the electrode is about 30 h at 300 A.
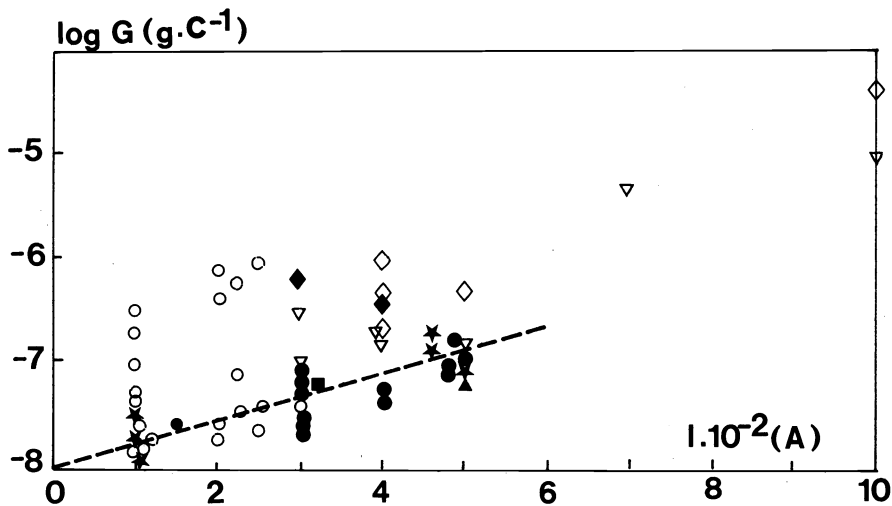

Fig. 13, after (25). Erosion of cathodes versus current, under air at normal pressure ; ● Hf ; ✶ Zr ; ▲ , ■ , O , ◆ Zr other works ; ◇ Hf ; ▽ cermet.

Phenomena involved with such electrodes are still poorly understood, because excited and ionized nitrogen and oxygen from the arc can react with the metal to form Zr and Hf oxide and oxinitride phases.

The oxide cathodes allow operation under varied gas conditions (Ar, Ar+H$_2$, N$_2$, Air). They have been described by Vallbona (27), at first with the system 0.87 ZrO$_2$-0.13 CaO. Reported data are then : i) current density 100-200 A.cm^2 (Ar and N$_2$), ii) temperature 2800°C-3000°C $\pm$ 100°C.

The further experiments described in (28) are concerned with the behaviour of pure ZrO$_2$ with different gas compositions. The stabilization of the arc and of the liquid cathode are performed by rotation of the cathode around its axis (rotation speed $<$ 1000 r.p.m.). Different new phases are formed during the interaction between the molten oxide and the arc. The composition of the cathode after operation is indicated in table 3.

Table 3. Composition of the ZrO$_2$ electrode under different arc atmospheres (I = 150 A ; gas flowrate Q = 10 STP l.min^{-1} ; rotation speed ω = 900 r.p.m.).

	Ar	Ar + 5% H$_2$	N$_2$	Air
Upper part of the cathode	ZrO$_2$ (M) Zr (c.h)	ZrO$_2$ (M) Zr (c .h)	ZrO$_x$N$_y$ (C) ZrO$_2$ (M) ZrN (C)	ZrO$_2$ (M) ZrN (c) ZrN (c)
Bottom of the cathode	ZrO$_2$ (M) Zr (C.H)	ZrO$_2$ (M) Zr (c.h)	ZrN (C) ZrO$_x$N$_y$ (C) ZrO$_2$ (M)	ZrO$_x$N$_y$(C) ZrN (C) ZrO$_2$ (M)
Duration of the run (h)	2	1	1	1

M : monoclinic ; C : cubic ; C.H. : compact hexagonal ; O : orthorhombic.
m, c, c.h., o : idem but in faint quantities.

During the operation of the cathode under argon, Zr$_\alpha$ (a solid solution ZrO$_x$) is formed, and oxygen is evolved from the surface of the liquid into the arc. We have represented on figure 14 the evolution of the molar flowrate of oxygen (measured as O$_2$ at the exit of the tubular anode, through an oxygen gas analyzer) as a function of time, under constant conditions.
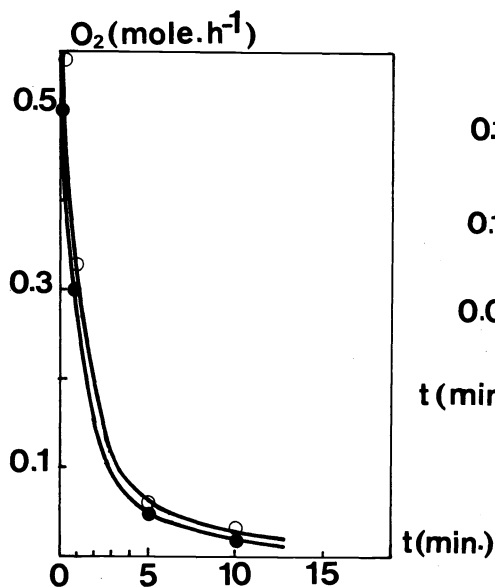

Fig. 14. after (28). Evolution of the oxygen flowrate (measured as O$_2$ at the exit) evolved at the surface of a ZrO$_2$ cathode, under argon at normal pressure. Current I = 205 A ; Argon flowrate Q = 10 STP l.min^{-1} ; rotation speed of the cathode ω = 900 r.p.m.
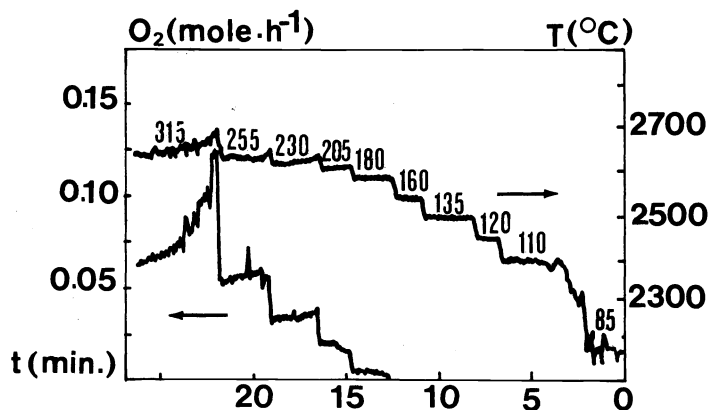
Fig. 15. after (28). Evolution of the apparent temperature (right scale) of a ZrO$_2$ cathode after 15 minutes at I = 205 A, under argon, when increasing the current from 85 A up to 315 A step by step. On the left scale the equivalent O$_2$ flowrate evolved at the cathode surface and measured at the same time is reported.
Q = 10 STP l.min^{-1}
ω = 900 r.p.m.

As soon as the arc is struck, the O_2 flowrate is maximum (0,5 mole.h^{-1}) then decreases rapidly down to a constant value (~ 0.02 mole.h^{-1}).

The apparent temperature of the ZrO_2 cathode is reported on figure 15. After 15 minutes in operation under constant conditions (I = 250 A, Q = 10 STP l.min^{-1}), the current is decreased to 85 A then increased step by step up to 315 A.

On the right scale of figure 15 is indicated the apparent temperature of the cathode, measured by optical pyrometry at λ = 0,65 µm, through the argon arc and plasma. It depends mainly upon the current, but should be corrected for taking into account the plasma contribution. We have recorded at the same time the evolution of the O_2 flowrate, which is indicated on the left scale. A decrease of the current from 205 A (fig. 14) down to 85 A blocks the oxygen departure. At I = 205 A, the value corresponds to the previous one under the same conditions (fig. 14). At higher current, more and more oxygen is evolved. Such a system is therefore able to liberate a controlled quantity of oxygen according to the current value and the duration of the current peak.

Electrolysis of the liquid oxide might be responsible for the oxygen emission at the surface of the cathode, associated to the deposition of Zr_α at the bottom. But the evaporation of the oxide may also contribute to the oxygen departure, possibly as the limit phenomenon which can be observed after 15 minutes in operation.

Another step to overcome is the study of electrode phenomena with a.c. in the presence of oxidizing gases. The litterature is much less abundant in this latter case. (29) reports results of electrode erosion for a.c. arc heaters and test electrodes. They are made either of O.F.H.C. copper or chrome-copper alloy (Cup-alloy). These data are of great interest since they show that electrodes with magnetically driven arc roots exhibit very low erosion. Furthermore erosion is less in oxidizing media (air) than in non oxidizing gases (CH_4, $CO+2H_2$, N_2).

The available results are presented in figure 16, after (29). The corresponding power for the arc heaters lies between 1 and 3 MW.
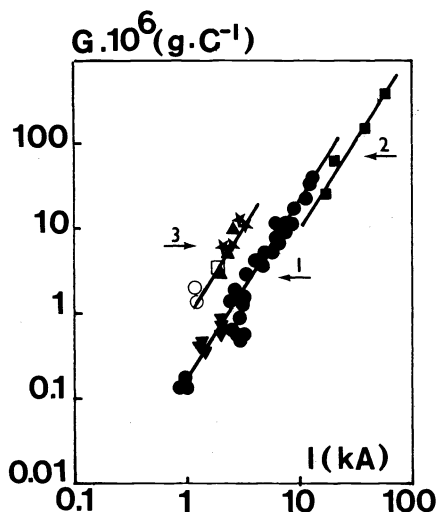

Fig. 16, after (29). Experimental erosion data versus single phase current for arc heaters and test electrodes (OFHC copper and cupalloy) operating under different atmospheres. 1 : Air, 100 mm Diameter electrodes ● and Arc heaters ▼ ; 2 : ■ , Air, 200 mm Diameter electrodes ; 3 : Arc heaters, ▲ N_2, O $CO+2H_2$, ▫ steam, ✱ CH_4

The estimated electrode life is between 170 and 1000 hours at 1500 A. This value has to be compared to the cost of each electrode, which is by nature a rather expansive system, since it shall present for the arc rotation (10^3 r.p.s.) a track of sufficient area to support erosion.

Gold has reported in (18) results for operating   a three phase plasma generator consisting of very simple and cheap gas-sheathed electrodes. The main advantages of the system (which is described on figure 4) is its simplicity, easiness for scaling up, and low investment cost.

But the erosion results with copper electrodes (electrolytic copper) in the presence of clay particles (silico-aluminate) indicate much more severe erosion rates than those previously reported. The results are indicated in table 4.

Table 4, Electrode erosion data for the three phase plasma generator (electrolytic copper ; plasma and clay particles). Power 100 kW.

gas	Erosion rate in g/h per electrode	Erosion rate in $g/C \times 10^6$	Estimated life h
$N_2 + 1.5\% \ O_2$	4-17	34-62	1.5-3
$N_2 + 2.5\% \ O_2$	12-20	40-70	
Air	26-41	88-142	0.5-1

It is noticeable that the presence of oxygen is necessary for preventing arc extinction at zero current. Indeed, as reported in (29), erosion with pure N_2 is more important and operation is unstable. The role of oxygen may be correlated to the formation of : i) metastable species able to store energy at zero current and avoid arc extinction, ii) oxidized sites favourable to electron emission, (24).
The utilization of neutral gases (even N_2) for thermal treatment of raw materials and particularly oxides, has been proved to be detrimental for the economic viability of the plasma process. Therefore the direct utilization of air, and if possible a.c., is required for processing of cheap materials, when it can be indifferently performed under neutral or oxidizing conditions. Reported erosion rates with copper electrodes and magnetically driven arc roots are quite acceptable. Another solution under present investigation, (18), is the utilization of simple and cheap gas-sheathed electrodes, provided that the erosion rate is such that the ratio cost of the electrodes/life is acceptable compared to the cost of electric energy. In such a view graphite may represent as a cheap material, a possible alternate solution.

CONCLUSION

The complete description of the plasma reactor for the thermal processing of refractory materials requires an important basic knowledge in the following directions :
- interaction between the plasma and the condensed phase (transport phenomena and microscopic interaction in terms of excited species).
- diagnostics for i) temperature and velocity measurements of particles in flight, ii) temperature measurement of the neutral species in complex polyatomic plasmas containing vapors and impurities.
- electrode phenomena (a.c. and oxidizing media).
- data for radiative and transport properties of the plasma and for physical properties of the materials at high temperature.
We have tried to demonstrate that a description based upon the analysis of the major phenomena in view of the process, namely heat transfer, allows a simple identification of some wellknown plasma reactors.
Cheap raw materials have become candidates to plasma processing (spheroidization, melting, fuming, decomposition) but they demand a special requirement for the control not only of the energy consumption but also of the operating cost. In this view the utilization of air as a plasma gas, when possible, shall be considered as an attractive route. The design and study of electrodes able to operate with oxidizing gases have to be developed for such a purpose.

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