Mathematical Modelling and Measurements of Plasma Spraying

Mohammad Miyan

Department of Mathematics, Shia P. G. College, University of Lucknow, Lucknow, India.

Email: miyanmohd@rediffmail.com

Abstract

The plasma spraying has a huge industrial development and users want much sophisticated properties of the deposit material. If plasma re-melting, purification and extractive metallurgy are still in their infancy, the results obtained are promising and raise a great interest for industrial developments. That is why a better knowledge of the phenomena involved is needed specially for modelling different plasma devices configurations which on taking into account chemical reactions, mixing, non-equilibrium effects, and if possible using 3-D configurations. But, due to the complexity of the models and to the various assumptions the results are meaningless if they are not compared with measurements and a great effort has to be done to computerize all the devices already available to start a systematic study of the mixing of a cold gas with a plasma, of the reduced pressure spraying devices, of particles injection and behavior, of heat transfer to electrodes or walls, of chemical kinetic. Now, after a brief description of the industrial developments of Wermal plasmas in the fields of extractive metallurgy and thermal spraying, the state of art of the knowledge in the following subjects is reviewed: modelling of the plasmas, plasma transport properties (LTE or two temperatures conditions) and cold gas mixing, modelling of the plasma particle momentum and heat transfer measurements of plasma jet velocity distributions and temperatures measurements of particles in the flight for the plasma jet : surface temperature, velocity, size evolution, trajectory etc. are correlated between measurements and calculations. In the present paper, there is a comparative analysis between the mathematical modelling and actual measurements using experiments.

Keywords: Plasma spraying, Modelling, Plasma measurement.

1. Introduction

The formation of the protective coating by the plasma spraying stream of ceramic particles or molten metal was developed during the sixties. The major advantage of plasma compared with the higher particle velocity obtainable up to 500 m/s and the high temperatures achieved i.e., above $10,000^0$ K making possible for melting the much refractory materials. The rapid solidification by plasma deposition cooling rates up to K/s combines melting, quenching and consolidation in a single operation and that cooling rates result in the grain of the sizes 0.25 to 0.5, μm for metals and alloys. However the quality of the coatings obtained depends strongly on one hand on the heat and momentum transfer between particles and plasma (the particles must be melted upon impact) controlling also the chemical reactions of the particles with their environment during their flight and also their decomposition and on the other way of heat transfer control to the substrate and deposit while spraying. For a long period, industrial development of the plasma sprayed coatings has been empirical, the physical and chemical understanding of the phenomena lagging far behind. So, with the important development of the plasma sprayed deposits in the fields of aeronautics, nuclear engineering, mechanics, electrical engineering etc., a better understanding of the phenomena involved is needed to improve the quality of the coatings as well as the spraying yields; the properties of such deposits required by industry being more and more sophisticated. That

improved the knowledge of phenomena is also needed with industrial development of plasma jets or of transferred arcs for the following:

(i) Melting and purification by transferred arcs (100 ≤P ≤1000 kW) struck in the controlled atmosphere chamber between a cathode and a water cooled crucible; the material to be treated being introduced as particles, pellets, rods, hollow pieces etc.

(ii) Heating of steel billets, blast air injected at the tuyeres of blast furnaces.

(iii) The scrap melting with the power levels.

(iv) The extractive metallurgy, still at its very beginning, using mostly transferred arcs but with high power pilot plants for example in South Africa.

(v) The plasma reformer for direct reduction developed either for smelt reduction or for the direct reduced iron production.

The aim of this paper is to make a brief review of the state of the art in the fields of modelling and measurement of plasma jets, seeded or not, with the solid particles and trying to underline where lacks are and what is still needed.

2. Plasma Processes Modelling

2.1 Plasma Flows

In spite of the intensive research effort that has been devoted over the last three decades to the study of electric arcs, mathematical modelling has developed slowly due to the difficulties encountered in the analytical description of the electrode regions. The regions are organized by very steep temperature gradients, low dimensions and useful non-equilibrium effects. It seems that the arc is capable of producing a vast variety of different phenomena induced by the minor changes of mechanical properties of electrodes, of the geometry, of small impurities at their surface. If at a moment the cathode phenomena are still far to be well understood, specially for the emission phenomena of cold cathodes i.e., cylindrical copper electrodes widely used now in arc gas heaters, some phenomena have been emphasized for cold anodes with argon as plasma gas such as negative anode drop, instead of positive one generally supposed and strong non equilibrium effects, phenomena permitting to understand the heat transfer. So, what happens when anode material evaporates (of primary importance for smelting, melting, extractive metallurgy, welding with transferred arcs) has to be studied. The experiments of Tsantrizoo et al. with the transferred argon arc on the molten copper anode have given an important evolution of the voltage as soon as the anode evaporates. After sometimes spectroscopic measurements performed in Limoges with a TIG stroked onto an iron plate show that two plasma regions can be distinguished as the quasi "pure argon" plasma region in L.T.E. and a "metallic vapor plasma region" near anodic molten bath. In the latter region, a strong disequilibrium between the "argon temperature" values and neutral iron excitation temperature values is observed. The results suggest that the amplitude of the thermal transfer to the work piece depends largely on efficiency of elementary processes which govern the exchanges of energy between the "argon" plasma and the metallic "vapor" plasma within the arc plasma column. The phenomena of electrode must take into account elementary processes i.e., collisions and non equilibrium effects as well as the flow problems to model the balance between the drag force due to the cold gas flow near the walls and the electromagnetic force due to the bending of the plasma column when the arc strikes at nozzle anode of the plasma torch and this is at the moment far too complex to be included in the flow models. The flow models are developed either for the arc column or for plasma jets exiting the nozzle. The main suppositions of such models are such that the plasma is in L.T.E., the jet is steady and possesses cylindrical symmetry, and radiation transfer is negligible as compressibility effects except for the supersonic plasma flows as these used for

spraying w. r. t. reduced pressure. Two types of approaches are then possible the plasma jet is supposed to be laminar and the flow is described by the Navier Stokes equations, continuity and conservation of energy for high Reynolds numbers, obtained with rather low temperature plasmas (T=6000^0 K), the dependent variables are broken into mean and the fluctuating parts and resulting equations are the time averaged to produce the equations for the evolution of the mean quantities. Usually density weighted averaging is used and the mean flow equations are closed by assuming the gradient diffusion for turbulent correlations and using the K-C turbulence model for Reynolds stresses. The governing equations are then put in a finite difference form and solved numerically using iterative procedures due to the coupled nature of the equations. The numerical solutions are generally classified as parabolic and elliptic.

The parabolic and very simple case corresponds to the one-way behavior i.e., the flow is said as boundary layer type without influence of downstream on upstream because axial convection dominates axial diffusion. The forward marching solutions algorithms such as those of Gemmix program extended to plasmas by numerous authors, greatly reduces computational time. Most of transferred arcs or plasma jets are relevant of this type of the parabolic solutions. However when a plasma jet exiting in a pipe is considered, for example to heat the blast air in the tuyeres of a blast furnace, recirculation problems, participating to heating of whole gas, have to be for consideration and then elliptic solutions must be used for example with the simple program. In this case the downstream boundary conditions must be needed. Typically these are taken zero axial gradients but if the boundary is not far enough downstream, the jet decay rate will be affected and the computational domain should increased until the results are not affected, but grid must remain fine sufficient to resolve steep gradients. In these heating flows with the elliptic models the problem of the heat transfer to surrounding walls is also of primary importance. For the conductive-convective fluxes, the choice of the proper grid and of the velocity distributions in the viscous area near the wall, in the transition region and the fitting with their fully turbulent area far from the wall is complex and the radiative fluxes cannot be neglected. Other problems arise from the boundary conditions and for example up to now the surrounding gas pumped by the fast plasma flow has always been supposed to be of the same nature as the plasma gas, thus avoiding the calculation of complex transport properties available for the gases such as N_2, 0_2, Ar, He, H_2 and for some mixtures N_2 -H_2, N_2-0_2, Ar-H_2. These transport properties are much sensitive to choice of interaction potentials. The anode evaporation also requires the knowledge of transport properties plasma gas" metallic vapor and up to now results are only available for Ar -Cu and Ar-Fe, the unknown interaction potentials being assumed to be hard core ones. Chen and his co-workers have also demonstrated that the symmetrical injection of a cold gas into the plasma jet modifies strongly the equilibrium, the temperature discrepancy between heavy particles Th and electrons Te being most severe at location of the cold flow injection (cold argon in argon plasma). The present effect is introduced in governing equations by splitting the equation of energy in two: one for electrons and one for heavy particles with the closure equation relating Te to Th via elastic collisions. The corresponding thermodynamic properties are calculated using the Modified Saha Equations (MSE) method introducing the ratio θ = Te/Th and the transport properties by extending the work of Devoto developed at equilibrium. However, Bonnefoi had proposed a new definition of the diffusion forces in a two temperatures (2-T) model and a different approach of the reaction term. It is important to note that the formulas developed for the transport properties in the 2-T model make use of the collision integrals calculated at equilibrium. Aubreton had demonstrated that this approach is valid for $\theta \leq 3$ i.e., special ratio for atmospheric thermal plasmas for which a cold gas is injected or for reduced pressure plasmas down to about 40 Torr. For $\theta > 3$ it is necessary to use a kinetic approach for which the nature of the gas mono-atomic or diatomic has a great importance. However for heat transfer between plasma and particles the integrated

values of the thermal conductivity are not really affected by the differences between the two methods. So, these 2-T calculations have been developed for H_2, Ar, O_2 and Ar-O_2, Ar-H_2 mixtures. the injection of the cold gas chemically distinct from plasma gas can induce important chemical reactions such as those obtained when injecting cold oxygen into nitrogen plasma. With the high temperature gradients encountered in thermal plasmas (heating rates up to 10^9 K/s, cooling rates up to 10^8 K/s due for example to fast expansion of jet) the kinetic observations should be included in flow models, so making them very complex with the stiffness of the solutions of the kinetic equations. That is why, up to present none of the calculations have been developed in normal case.

The first results obtained will be limited to flows with the uniform radial velocity and temperature distributions. At last it should be underlined that all the developments of the flow models are 2-D but that the more practical problems are 3-D (the particle injection for the spraying, plasma torch blowing in tuyere of the blast furnace etc.) and up to present time only big companies like Westinghouse of U.S.A., E.D.F. of France have developed a 3-D models for the gas heating, but the simplified models where plasma properties are kept constant to reduce the computing time.

2.2. Plasma Particle Momentum and Heat Transfer

Due to the importance of the thermal treatment of powders in plasma torches and furnaces the considerable attention has been given to plasma particle momentum and the heat transfer. These works underline the necessity to take into account corrections terms or integrated thermal properties for the steep gradients in the boundary layer round the particles, non continuous effects for particles smaller than about 10 m at atmospheric pressure, turbulent dispersion, charging effect, evaporation effect. For the given temperatures and velocity distributions of a plasma jet, the trajectory and the temperature history of individual particles, assumed to be spherical, are calculated. So that in practice what is needed is statistical behavior of injected particles which have size and velocity distributions. For a given injector diameter and a given carrier gas flow rate the particles will have (due to their size distribution) different injection velocities and even with the proper injection velocity, particles passing nearer to injector wall will have the velocity tends to zero. That is why the trajectories and temperature histories of the particles must be calculated for the different sizes and velocities and results averaged according to starting distributions and the particles flow rates. Moreover, when the particle mass flow rate increases too many the particles start to cool down the plasma jet as well as when small particles evaporate consuming a large amount of energy and this has to be included in the calculation program rending it very heavy. So, one has to underline that all the calculations neglect cold gas injection that should requires the 3-D calculation to take its effect on the plasma flow.

3. Measurements and Comparison with Modelling

3.1 Needs of Measurements

Quite a lot of data are needed temperature and velocity distributions of the plasma flow as well as non-equilibrium effects concentration of the different species excited or not trajectory, velocity, surface temperature of the particles to compare the calculated distributions with the measured ones, to have reliable models and to obtain relevant data either for the particles (drag and Nusselt coefficients accounting for various phenomena) or for plasma gas itself (chemical rates, diffusion coefficients etc.).

3.2 Plasma Jet Measurements

3.2.1 Temperature Distributions

What can be reached easily with emission spectroscopy, is the excitation temperature (through atomic spectra), the electron density (through line profiles of Stark enlarged lines), the vibrational and rotational temperatures (through rotational spectra), but the electron temperature has to be observed with the help of the preceding data. Of course these measurements give averaged values (for times of the few tens ms) masking the fluctuations of the arc. So, due to steep radial gradients, Abel's inversion has to be performed. That is why all measurements have been done for axially symmetric jets and a big effort has been made to automates these measurements, by moving the plasma, using rotating mirrors displacing rapidly a metal strip into the jet, devices allowing rather fast measurements for atomic line intensities, by using 2D optical multichannel analyzers (OMA) allowing fast measurements of rotational spectra (up to 40 lines) or of line profiles. It is worth to notice that rotational spectra will give temperatures in the range 3500 - 9000 K about and atomic lines in the range 8000 K - 13000 K, whereas the ionic lines lie between 15000 and 21000 K and the precision is around 10%. The temperature ranges encountered in the various plasmas are the following:

For heating 3000 - 9000 K about, for spraying 3000- 12000 K, for transferred arcs 7000 - 18000^0 K and one has to remind that, according to the fast variation of the volume emission coefficients with temperature, a range of three decades about is accessible for a given set of the measurement device corresponding to $\partial T = 4000^0$ K at the maximum. In a transferred argon arc at atmospheric pressure, where the electron density is rather high ($n_e = 10^{22}$ e /m^3), the measured excitation temperatures are in reasonable agreement (within 15%) with the calculated distributions. However for a nitrogen d. c. plasma jet where cold nitrogen is introduced symmetrically, the measurements have shown that when increasing the cold gas flow rate, the temperature iso-contours (measured from rotational spectra corresponding, due to the fast relaxation translation rotation, to the heavy particles temperature) are pinched and lengthened - the cooling of the fringes result in a fast diffusion of the electrons from the plasma center to the periphery of the jet the population of the levels close to ionization limit is thus no more in thermal equilibrium with the one of the levels close to the resonant one the diffusion phenomena, very important in this case, have to be included in the models where they have been neglected up to now of course these first results obtained for the cold gas injection emphasize the non- equilibrium effects already taken into account in the models, but where effects of diffusion have to be introduced. It could be also important to develop measurements in the non-symmetrical plasmas where these effects are probably enhanced. Non-symmetrical Abel's inversions are now possible with the use of computers on line to account for the quantity of data to be treated. They have already been developed in a simple case for thermal plasma jets, the use of OMA being very promising for such measurements. If the problems of investment costs are not considered, CARS technique could probably be used in the thermal plasmas for measuring the heavy species temperature, extension of the temperature range (developed for combustion up to 3000^0 K), being quite possible (up to 7000^0 K). The advantage of CARS over emission spectroscopy is the possibility to obtain a very good spatial resolution (avoiding the problems of Abel's inversion), an important signal (even in the plume of jet) and most probably to measure temperatures in the plasmas seeded with particles (in the combustion flame temperature seems to be insensitive to presence of soot particles). Laser induced fluorescence (LIF) gives signals proportional to the number density difference ∂N_u of the upper level due to laser pumping and the problem is to relate ∂N_u either to temperature or to density of the lower level (a fundamental level or a meta stable one). Such relationships in the general case are obtained through the matrix density and it is only in particular conditions, generally not full filled in thermal plasmas, that the approximation of the rate equations can be used. That is why in thermal plasmas such measurements can give only relative values, however much instructive; showing for example

that NO in the fundamental state is produced mainly in periphery of a nitrogen d. c. plasma jet where cold oxygen is injected symmetrically. However LIE is the only mean to obtain information about reaction or quenching routes via experiments performed at reduced pressure (0.1 - 10 Torr.) in the flowing afterglow where different species to react are excited through collision transfers with various meta stable atoms.

3.2.2 Velocity Distributions

The methods using the Doppler shift of lines are limited to the supersonic jets at low pressure (below 50 Torr.) and up to present the seeding of the jet with small particles that velocity is measured by LDA has been used in thermal plasmas. However the precision of the measurements is questionable due to measurement difficulties with small particles and to the problems of momentum transfer between plasma and small particles (Knudsen effect among others underlined by the results presented at Montreal for 40 μm particles in plasmas at 50 Torr). Such uncertainties in the measurements may partly explain the discrepancies between measured and calculated temperature and velocity distributions in thermal spraying jet. It is necessary to emphasize the importance of having a reliable velocity distribution at nozzle exit to obtain the correct results with models developed for the spraying plasma jets where particle heating occurs in a few tens of millimeters. That is why a recent method of resonant Doppler velocimetry with alkali atoms seeded in flames might be very interesting if it is possible to extend it to thermal plasmas. Now the problem is different when one wants to heat a cold gas injected round the plasma jet, the influence of initial velocity and temperature distributions of the plasma being negligible for distributions obtained at the distances comprised between 6 and 10 times the diameter of pipe.

3.3 Particle Measurements

3.3.1 Velocity

LDV is the main technique used; it allows high spatial resolution (less than 1 mm^3) and high temporal resolution (down to 5 ns). Among different detection devices, only frequency trackers and counters are able to associate a velocity with a single given particle. To perform the measurements in the plasma core itself requires on one hand the use of mono chromators with band pass round 1 A^0 in order to eliminate, as much as possible, the light emitted by the plasma and on the other hand either to increase the power level of the laser or to increase the dimensions of measurement volume by performing it within the angle close to laser beam direction to obtain the maximum emission of the scattered light.

3.3.2 Surface Temperature

The up-to-date technique is that of discrete in flight color pyrometer, first developed with absolute flux measurements which precision was poor (the result depends on the emission coefficient of the particle and on its diameter which varies as soon as evaporation starts). Recently this technique has been developed by measuring the ratio of fluxes emitted at two wavelengths (two color pyrometer) thus eliminating the problem of the diameter and reducing the one of unknown emission coefficients (assumption of grey body). Actually such measurements, performed in volumes of ϕ = 160 μm, 1 = 15,000 μm, are statistical measurements and give in fact surface temperature distributions. So, it is important to underline that, whatever will be the future technique, it will never be possible to perform the measurements in the core of the plasma jets, heating zone of the particles and where the flux can't overcome the plasma flux as their temperature is not higher enough (around more than 2 200^0 K for 20 μm particles).

3.3.3 Particle Trajectories and Concentrations

The number of particles travelling at different locations in plasma jet may be measured by the counting, for the given time, pulses resulting from the light scattered by the particles passing through a focused laser beam. A measurement volume of less than 10^{-3} mm^3 is achievable. The particle mean trajectory is observed by the position of maximum concentration of particles. It is worth to notice that, even with very narrow size distributions (Al$_2$O$_3$ particles 18 $\pm$3 μm) injected with the optimum velocity, the trajectory distribution is large: 20 mm downstream the injector, that covers about 33% of surface of a plasma jet "slice".

3.3.4 Particle Sizes

The combined measurements of size of particles and velocity are achieved by the extended laser Doppler anemometers: the amplitude and modulation depth of the LDA signals depend on size of the scattering particles, optical properties of the particle material, wavelengths of the employed laser radiation, angle between the two incident beams and size and location of the receiving aperture. These sizing methods are essentially the visibility and pedestal calibrations methods where size and velocity measurements are getting on the same signals and power calibrations methods for which the optical probes for velocimetry and sizing are distinct.

3.4 Correlation and Calculation of Measurements

First one has to remark that the measurements on the particles and on the plasma flow are performed separately and second that, to get reliable information, the measurements on the particles should be performed at same location and time. If previous comparisons between the calculated and measured velocities gave a reasonable agreement (within 15%) for the measurements along axis, the discrepancies between calculated and measured temperatures have been reduced with two color pyrometer. However the last measurements underline the importance of various effects: evaporation, heat propagation for ceramics, Knudsen etc., but also necessity to make statistical calculations of trajectories and velocities, surface temperatures and diameters for comparing measured distributions with the calculated ones.
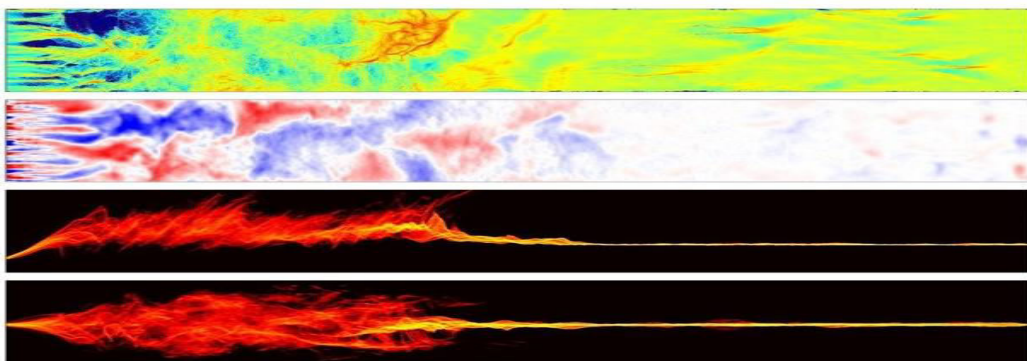
4. Experimental Diagrams

Figure-1 (A snapshot of plasma turbulence and ion acceleration at the first stage)
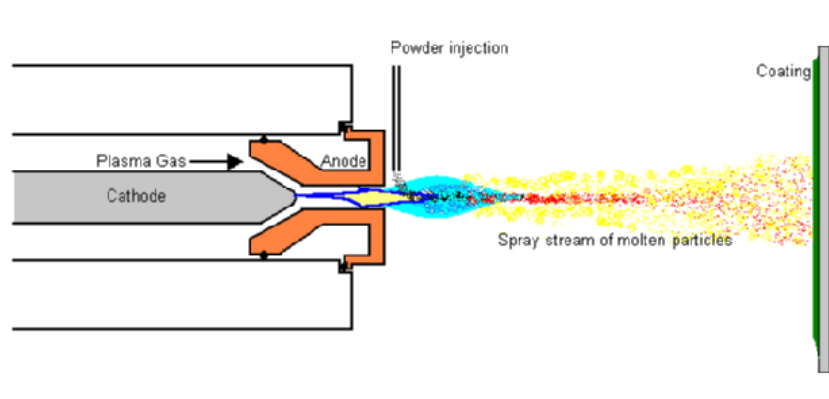
Figure-2 (Schematic Diagram of the Plasma Spray Process)
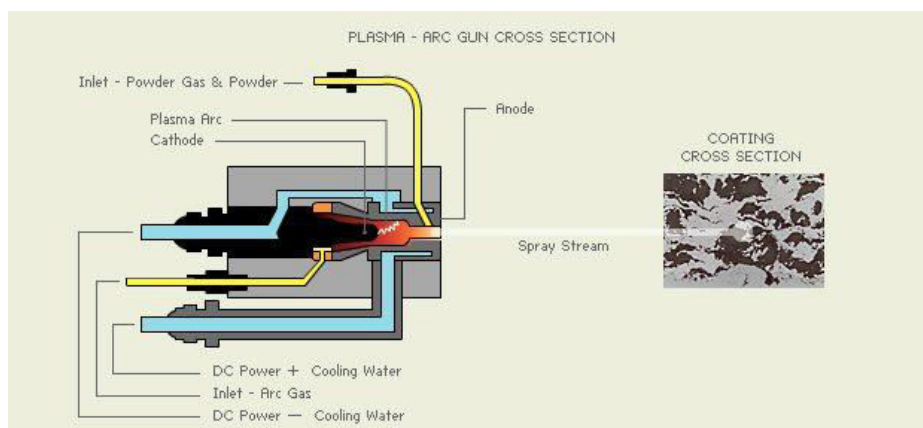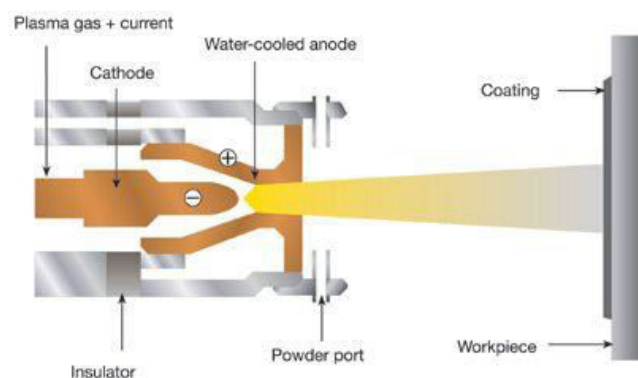

Figure-3 (Diagram of Plasma spray)

Figure-4 (Diagram of liners sleeves thermal spray process)

5. Conclusion

The plasma re-melting, purification and extractive metallurgy are still in their infancy; the first results obtained are promising and raise a great interest for industry. That is why a better knowledge of the phenomena involved is needed specially for modelling the different plasma devices configurations using for chemical reactions, mixing and non equilibrium effects if possible by using 3-D configurations. However due to the complexity of the models and to the various assumptions the results are meaningless if they are not

compared with measurements and a great effort has to be done to computerize all the devices already available to start a systematic study of the mixing of a cold gas with a plasma, of the reduced pressure spraying devices, of the particles injection and behavior, of the heat transfer to the walls or electrodes, of the chemical kinetic.

References

1. A. S. Almgren, J. B. Bell, P. Colella, L. H. Howell, and M. L. Welcome, A conservative adaptive projection method for the variable density incompressible Navier–Stokes equations, J. Comput. Phys. 142, 1 (1998).

2. A. VARDELLE, P. FAUCHAIS, M. VARDELLE, Actualite Chimique, 10, 69 (1981).

3. H. Wu, B. W. Yu, M. L. Li, and Y. Yang, Two-dimensional fluid model simulation of bell jar top inductively coupled plasma, IEEE Trans. Plasma Sci. 25, No. 1, 1 (February 1997).

4. J. H. Ingold, Two-fluid theory of the positive column of a gas discharge, Phys. Fluids 15, No. 1, 75 (January 1972).

5. J. L. BESSON, M. VARDELLE, P. BOCH, L' industrie Ceramique 727, 249 (1979).

6. M. J. Berger and P. Colella, Local adaptive mesh refinement for shock hydrodynamics, J. Comput. Phys. 82, No. 1, 64 (1989).

7. M. A. Lieberman and A. J. Lichtenberg, Principles of Plasma Discharges and Materials Processing (Wiley, New York, 1994).

8. M. J. Berger and J. Oliger, Adaptive mesh refinement for hyperbolic partial differential equations, J. Comput. Phys. 53, 484 (1984).

9. N. N. RYKALIN , V.V. KUDINOV, Pure and Applied Chemistry 48, 229 (1976).

10. P. Colella, M. R. Dorr, and D. D. Wake, A conservative finite difference method for the numerical solution of plasma fluid equations, J. Comput. Phys. 149, 168 (1999).

11. P. FAUCHAIS, A. VARDELLE, M. VARDELLE, J.F. COUDERT and B. PATEYRON, Plasma spraying and extractive metallurgy, Pure &Appl. Chem., Vol. 57, No. 9, pp. 1171-1178 (1985).

12. P. L. G. Ventzek, M. Grapperhaus, and M. J. Kushner, Investigation of electron source and ion flux uniformity in high plasma density inductively coupled etching tools using two-dimensional modeling, J. Vacuum Sci. Technol. B 12, No. 6, 3118 (1994).

13. R. A. Stewart, P. Vitello, and D. B. Graves, Two-dimensional fluid model of high density inductively coupled plasma sources, J. Vacuum Sci. Technol. B 12 (January 1994).

14. R. J. Hoekstra and M. J. Kushner, The effect of subwafer dielectrics on plasma properties in plasma etching reactors, J. Appl. Phys. 77, No. 8, 3668 (1995).

15. S. D. Cohen and A. C. Hindmarsh, CVODE User Guide, Technical Report UCRL-MA-118618, Lawrence Livermore National Laboratory, September 1994.