Plasma spouted/fluidized bed for materials processing

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Abstract: Plasma when coupled with spout/fluidized bed reactor for gas-solid reaction brings in several advantages such as high rate of heat and mass transfer, generation of high bulk temperature using a thin jet of plasma itself as a heat source. The science and technology of plasma and fluidization or spouted bed are well established except of these two put together for high temperature application. Plasma heating of fluid/spouted bed can bring down the size of the equipment and increase the productivity. However the theory and practice of the hybrid technology has not been tested in a variety of applications that involves high temperature synthesis of materials, TRISO particle coating for nuclear fuel particle, thermal decomposition of refractory type ore, halogenations of minerals, particulate processes and synthesis of advanced materials. This paper gives an account of the use and exploitation of plasma coupled with spouted/fluidized bed especially for material processing and also addresses the issues for adapting the same in the era of developing advanced high temperature materials.

1. Introduction
Material processing by and large is carried out in a highly reactive high temperature zone. The term ‘high temperature’ refers to operating temperatures in the order of a few thousand degrees centigrade. Certainly, the achievement of such temperature requires significant power consumption and specific reactor geometry. The control of such high temperature reactor is itself a matter of great exercise. In some cases, selectivity of the desired product is itself a key factor to adopt the process. Furthermore, the issue of mass transfer, continuous removal of by-products and the yield of desired product dictates the choice of the appropriate reactor type.

A fluidized bed reactor (FBR) has been popular since last four decades. Its application on fluid solid processing is the most successful on very large industrial scale. The key features, which enhanced its application further in almost all other kinds of process industries, are associated with the high rate of mixing coupled with excellent heat and mass transfer.

Therefore the understanding on the applicability of plasma fluidized bed as a new generation clean reactor for particulate processing and coating technology is beneficial to fully exploit its advantages. The features of the reactor itself attract deliberate investigations in core process industries like metal, polymer, printing, semiconductor, gasification etc. Hitherto a number of satisfied technologies are implemented in the field of plasma enhanced chemical vapour deposition (PECVD). Already CVD

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technology in fluidized bed (spouted bed) has received a lot of credit in bulk synthesis of carbon nano-
tube production. Several research scientists have already reported successful growth of films on solid-
granular polymeric materials. Several nano-technologists have recently presented their success stories
on processing of ceramic nano-particles and carbon nano-tubes, using circulating plasma fluidized bed
reactor.

1.1. Plasma generator basic
Plasma is a very distinct state of matter (some times called as fourth state of matter). It consists of
electron, ions, radicals and some neutral fragments of corresponding matter. Plasma can be produced
by the use of either high temperature or electromagnetic discharge. The latter is most often practiced
in industries. Generally the electromagnetic field is created by using direct current (DC) electrodes,
radio frequency (RF) or by microwave (MW) in a plasma generator. The ultimate effect of the field is
to remove the outer most electron(s) from the gaseous species at reduced pressure. Therefore this
plasma created by electromagnetic field considered as collection of active species has only few ten
degrees more in temperature than the normal gas whereas thermal plasma has temperature of more
than 2 orders of magnitude. Any material is therefore subjected to energy transfer while its interaction
with plasma. A comparative view of the efficiency of plasmas drawn from arc heated (electromagnetic
field) air and naturally heated thermal air is shown in figure 1.

![Figure 1. Efficiency for high temperature rating. (From Fey, M.G., Heat, 2, 1976)](image)

1.2. Plasma fluidized bed reactor
In a typical plasma fluidized bed reactor (PFBR) as depicted in figure 2, the plasma state of fluid is
used instead of corresponding fluid as a carrier or/and reactant (precursor) for fluidizing the bed
material. The commonly used plasma generator devices deal with argon, helium, nitrogen and argon.
The generated plasma along with the carrier gas and precursor is further accelerated and energised by
either the thermal or electromagnetic arc generator. The plasma generator attached to a fluidized bed
can continuously deliver plasma flows as a fluid source. The varieties of proposed geometries of
fluidized bed coupled with the plasma source have been examined widely and a brief description of
their application was reported by Flamant [1]. The plasma spouted bed reactor has a lot of advantages
over classical fluidized bed reactors for its steadiness of solid circulation and therefore mass and heat
transfer. Its uniform mixing characteristics help to attain thermodynamic equilibrium between
different species within the reactor [1].
Figure 2. A typical laboratory scale plasma fluidized bed reactor. (From Goldberger, W.M, Chem. Engg. Pros. Symp. Ser., 62(62), 42, 1966).

1.2.1 Plasma fluidised/spouted bed reactor in CVD Process. Chemical vapour deposition (CVD) process involves the reaction of gaseous reactants in an activated (heat, light, plasma) environment followed by the formation of a stable coated solid product. The deposition involves homogeneous gas phase reactions, which occur in the gas phase or heterogeneous chemical reaction, which occur near the vicinity of a heated surface leading to the formation of powders or films. The fluidized/spouted bed reactors as shown in the figure 2 are commonly used in thermally activated CVD (TACVD) to deposit PyC, SiC coating on solids. The selection criterion for the spouted bed reactor follows the same rationale, as that of fluidized bed reactor for processing small particles (<500 µm). However, the processing of coarse/dense particle (for which \((\rho_s - \rho_f) d_p^2 \geq 10^6\) \[2\]) using fluidised bed is ineffective due to large slug formation signifying poor gas-solid contact. The requirement of good gas-solid mixing, particle re-circulation, isothermal conditions needed for uniform coating by CVD technique are provided by the spouted bed especially for coarse and dense particulate solids. The fluidisation technology offers choice of reactor types to handle a wide range of particulate solids and also the flexibility in operational conditions based on applications. On the other hand the plasma itself is a versatile fluid and can be manipulated from equilibrium to non-equilibrium plasma. Non-equilibrium plasma is a promising tool when low bed temperature is required [3]. Thus, the combination of fluidised/spout bed along with plasma open-up new vistas in material processing of particulate solids.

2. Thermal behaviour

2.1. Process temperature and heat transfer
Highly energised plasma is fed into the fluidized bed where heat is transferred from plasma to granular solid materials [4]. At this stage the active radicals of precursor(s) take part into the reaction at the desired temperature. Therefore plasma acts as source of heat as well as precursor for the reaction. High thermal diffusivities of plasma and fluidizing arrangement result in rapid quenching [5] and hence the desired product at desired temperature is achieved quickly by efficient the heat transfer due to vigorous solid circulation. It is reported that power consumption for heating the solid materials to
attain the reaction temperature is much less while using plasma [4-8]. The effective use of heat carried by plasma for reaction is a responsible factor for the high efficiency of plasma fluidized bed reactor [6-8]. Furthermore, the active radicals increase the effective surface area and hence the reaction rate [9-11].

2.2. Temperature and plasma effect on hydrodynamics

The popular Wen and Yu [12] correlation for predicting the minimum fluidizing velocity ($U_{mf}$) was experimentally supported by Pattipati and Wen [13] for high temperature operation of fluidized bed and it was demonstrated that $U_{mf}$ decreases with increasing temperature. On the other hand, plasma has higher temperature than non-ionized gas and experimental observations support the same. Therefore one can expect the minimum fluidization velocity would be less in a plasma fluidized bed. But the trend reported using experimental data by Wierenga et al [14] showed exactly the opposite as seen in the table 1. An iterative procedure to calculate the pressure drop with temperature through a fixed bed was used by the authors Wierenga et al [14] and presented in figure 3. On the other hand, the unexplained change in the fluidizing conditions for different particle and fluid properties may be due to the lack of basic understanding of inter-particle forces at very high temperature while interacting with plasma. Also, the distinct nature of hydrodynamics in plasma fluidized bed reactor is not well explored till date.

| Table 1. Minimum fluidization velocities and inferred gas temperatures for argon and hydrogen plasma fluidized bed. (From Wierenga et al. AIChE, 1989) |
|-----------------|---------|---------|----------|----------|
|                 | Gas used | P (Pa)  | T (K)    | Measured $U_{ms}$ | Predicted $U_{ms}$ |
| Hydrogen        | 2,000    | 300     | 49.0     | 60.0      |
| Argon           | 266      | 300     | 17.0     | 23.0      |
|                 | 500      | 27.0    | 18.0     |
|                 | 650      | 57.5    | 13.0     |
|                 | 1,333    | 22.5    | 23.0     |
|                 | 450      | 25.0    | 18.0     |
|                 | 700      | 26.0    | 13.0     |
|                 | 2,000    | 21.0    | 23.0     |

Figure 3. Pressure drop versus gas velocity in the presence of argon plasma [14]
3. Material processing in PFR

The basic requirement of high temperature reactor for processing the granular materials is to provide a controlled heat environment. The excellent solid circulation system accomplishes this feature in a fluidized bed condition. As a result, beside classical treatment of plasma, its combination with fluidized bed is finding increased trend of application in the advanced materials technologies. Some of such applications are briefed in the following.

3.1. Methane decomposition and methane pyrolysis

High temperature chemical vapour synthesis by plasma was explored from the initial stage of plasma discovery. The gas phase conversion of methane was the prime interest for synthesizing acetylene. The gas phase reaction in plasma and hence the formation of intermediate compound was realised by development of a coating on aluminium particles in a fluidized bed reactor. Pyrolysis of methane in the presence of hydrogen gas was also realized by the deposition of carbon on zirconia, graphite and silica particle using inductively coupled plasma in FBR [15, 16].

3.2. Extractive metallurgy

Metallurgical plants are operated at very high temperatures and hence consume a significant amount of energy. The power efficiency and reduction of furnace size are the key advantages for raw metal process plants operating at very high temperatures. It has been reported that the plasma fluidized bed reactor can replace the conventional reactor by its multitude of advantages at very high temperature [17-20]. A developed technology claimed that a 100 MW plasma reactor could have a modest steel production rate of 250,000 tons/day [20].

Gauvin and Choi [21] reviewed the uses of plasma in the extractive metallurgy and reported the feasibilities of producing refractory metals including a special mention on plasma production of zirconium by Kroll process. The report contains the variety of plasma reactor used for production of titanium, tungsten, chromium and vanadium. The feasibility of Kroll process for zirconium production modified by plasma fluidized bed had been well demonstrated by authors in the same literature.

3.3. Particulate processing

Spheroidizing is an important process for making spherical particles, which have attractive features like large surface area, maximum apparent density, close size range and controlled porosity. Potter [22] first introduced a technology for spheroidizing metals and non-metals including alumina, zirconia, columbium, zirconium, uranium oxide, uranium monocarbide, tantalum and zirconium dibromide by applying DC plasma jet. This DC plasma jet can be coupled with fluidized bed to provide a better quenching medium.

On the other hand, plasma jet heated reactor are now being favourably considered for coating technology due to its advantage of ultra high temperature surface deposition. Further requirement of this process deserves continuous quenching and maintenance of uniform thickness of coating. Plasma spouted (fluidized) bed is one of the best choices for bulk production of coated particle.

3.3.1. PECVD deposition on powders at low temperatures in CFB. Karches and Rohr [23] have introduced a circulating fluidised bed (CFB) for plasma-enhanced chemical vapour deposition (PECVD) of powders. Low-temperature plasma is generated in a riser tube by coupling microwaves. As a model application, sodium chloride crystals were coated with a thin silicon oxide film and the deposition rate was measured.
The plasma reactor is a glass tube [40 mm internal diameter (ID) and 0.5 m length, figure 4(a)], which is surrounded by a ring-shaped slotted antenna for the output coupling of microwave energy. This glass tube replaces one part of a steel tube [40 mm ID and 1 m total length, figure 4(b)], where the particles are fluidized with a high gas flow rate (riser). Total riser volume is 1.5 l. The bottom of this tube is sealed by a sintered metal disc for supply and dispersion of the reaction gas. The particles leaving the tube through an opening at the top are separated from the gas by cyclone and L-valve combination. The circulating solid mass flux of sold is controlled by the flow rate of the aeration gas (argon). The gas exit of the cyclone is connected with the vacuum unit. The circulating fluidised bed (CFB) was operated with NaCl crystals ($d_p =0.21\text{mm}; \rho_s=2.16 \text{kg l}^{-1}; c_p=0.87 \text{Jg}^{-1}\text{K}^{-1}; a=16 \text{m}^{2} \text{kg}^{-1}$) and mixtures of argon, oxygen and hexamethyldisiloxane (HMDSO) as reaction gas at 400 Pa process pressure. PECVD of thin SiO$_x$C$_y$ films was achieved in which HMDSO and oxygen are decomposed in the plasma and react on surfaces to form thin films.

3.3.2. Metal powder granulation in a plasma spouted bed reactor. D.C. plasma-spouted/fluidized bed was applied to the granulation of spherical alloy grains from metal powder mixtures. From a mixture of iron powder ($d_p=149-210 \mu m$) and aluminium powder ($d_p=74-88 \mu m$ and 125-149 \mu m) alloy grains of 1-5 mm in diameter was reported by Goto et al [24]. The concept of plasma spouted bed and the experimental arrangement used are shown in the figure 5 and figure 6 respectively. The cathode top was made of a pointed tungsten rod of 5 mm in diameter. The water-cooled anode made up of copper, was the conical bed bottom with an orifice of 4 mm ID. The voltage and current of arc discharge were maintained at about 30 V and 30 A respectively. In order to inject additional reactive gas or fine particles, two auxiliary injection nozzles were located above the orifice. Granulation of Fe-Al binary powders was feasible in a laboratory scale plasma-spouted/fluidized bed (PSFB). Spherical alloy grains 1-5 mm in diameter were obtained successfully.
Figure 5. The concept of plasma spouted bed [24]

Figure 6. Experimental plasma spouted bed set-up for metal powder granulation [24].
3.4. Ultra fine powders: chemical vapour deposition

Chemical vapour deposition (CVD) is the most conventional way to produce the ultra fine powders. Recent researches have been demonstrating that circulating solid fluidized bed reactors are the efficient option for successful operation of chemical vapour deposition process [25-28]. P.R von Rohr and Borer [25] have reported that the combination of circulating fluidized bed reactor with the PECVD is very efficient for thin film deposition process on particles with high deposition rates and high precursor conversion ratios. Tap and Porada [26] were successful to produce self-sustained microwave plasma to process granular material using a PECVD circulating FBR. Kim et al [27] concluded that PECVD on powders in the CFB reactor is a more effective way to deposit TiO$_2$ thin films than the sol-gel method.

Kojima et al. [15,16] have extensively studied the fluidized bed CVD reactor for particle coating and surface treatment. A low pressure microwave plasma jet was fed into the fluid bed containing silicon and alumina as bed materials. The hydrodynamic studies concluded that roughly unchanged pressure drop occurred while plasma bubble penetrated into the bed material. In this process the methane conversion was influenced by type of bed materials. However, they claimed economical and practical advantages of FBCVD process over an atmospheric process [28]: such as (i) reduction of cycle time during CVD process, (ii) relatively low capital and operational costs, (iii) very fast adjustment of reactor, (iv) uniform heat transfer coefficient and (v) good mixing results and (vi) uniform coatings.

3.4.1. Deposition of diamond coatings on particles in a microwave PECVD. Diamond is one of the most attractive industrial materials because of its excellent mechanical, electrical and chemical properties. To date, most work has been focused on the deposition of flat two-dimensional surfaces. While flat films have many uses, there are other applications where it is necessary to uniformly coat small, three-dimensional objects (for example, powders, fibers, bearings, sensor components, or small machine parts). This is hard to do with standard diamond chemical vapor deposition methods, since it is difficult to expose the entire surface area uniformly to the activated gas or plasma. Due to the excellent mass transfer characteristics of a fluidized bed, transport of reactive radicals to the particle surface has been achieved easily to deposit diamond coating on particle using microwave PECVD [29].

![Diagram](image-url)

**Figure 7.** Schematic of experimental set-up to deposit diamond coating on Si and SiO$_2$ particles [29].
Shin [29] et al. has used apparatus as shown in figure 7 to deposit diamond coating on small (<1mm dia) Si and SiO₂ particles. The experimental set-up consists of a 12 mm OD, 10 mm ID quartz flow tube with tapered bottom. The tube is connected to 2.45 GHz microwave facility. The gas was introduced from the bottom of the quartz tube to fluidize the particles. The reactant gases were mixtures of CH₄ and, in some cases O₂ in a H₂ carrier gas. The CH₄ concentration was in the range of 0.5 to 2.0% and O₂ concentration was in the range of 0 to 3% by vol. The total gas flowrate was 160sccm and pressure of 9 torr. The SEM images of diamond coating on SiO₂ particles at different process conditions are shown in figures 8 and 9.

3.4.2. PECVD on Powders in a Low Temperature Plasma Fluidized Bed (figure 10). Coating techniques for the deposition of thin films received much attention and significance in several fields of applications such as microelectronics, automobile industry and biomaterials. With the help of energetic species from the plasma, gaseous monomers are dissociated or modified to form precursors, which chemically react and yield the desired film. An electric field is applied to accelerate the free electrons in the discharge, which then deliver energy to the atoms or molecules through collisions. Typically the degree of ionization is less than 0.1%. This allows gas temperatures to go below 200°C and treatment of temperature sensitive materials such as polymers.
Bayer et al [30] has demonstrated the feasibility of SiO$_x$ coating at 200°C on NaCl particles (d = 551mm) using microwave fluidized bed reactor as given in figure 11 and has successfully modified the surface property (hydrophobic nature) of the NaCl particles as shown in the figure 11.

The low temperature plasma fluidized bed technique can be used for thin film deposition (e.g., SiO$_x$, Si$_3$N$_x$, TiN, TiC, TiO$_2$, diamond-like carbon), but also for non-coating processes (e.g., plasma cleaning, sterilization, activation, hydrophobic or hydrophilic finishing). Due to the treatment temperatures lower than 200°C a broad spectrum of applications is possible as listed in the following:

- Corrosion protection of metal pigments
- Diffusion barriers of pharmaceutical powders for retardation of active substances
• Hard coatings of abrasives
• Enhancement of chemical, thermal or mechanical stability of powders
• Reduction of adhesion for the avoidance of agglomeration
• Improved properties for tablet production
• Modification of electrical properties (conductivity) and
• Modification of wettability (e.g., color pigments by oxidation or roughening)

3.4.3 Nitriding. Okubo et al. [31] successfully nitrided the titanium particles using nitrogen plasma in a FBR at reduced pressure condition. The extent of nitriding of titanium particles was determined by the nitrogen concentration. A comparison between the use of nitrogen plasma and thermal nitrogen is presented in figure 12. It showed the variation of concentration of nitrogen in plasma and thermal state. While Kawamura et al [32] attempted to nitride the milled carbon fibre for their surface treatment they found poor wettability and dispersibility of raw carbon with respect to a polymer matrix. Oxidation of fibre and thereby nitriding in a plasma activated fluidized bed demonstrated a successful nitriding by nitrogen plasma.

Besides nitriding, there are so many thermo-chemical treatments like carburising, carbonitriding and nitrocarburising, which have successfully been carried out using fluidized bed reactor based CVD [34].

Figure 12. Comparison of nitrogen concentration in plasma with time of nitriding. (From Okubo et al. American ceramic. soc., 73(5), 1150, 1990)

4. Advanced material processing
Advanced material processing [33-40] by PFB includes very fine and selective/ controlled deposition of matter on growing particle or thin film processing for surface treatment of granular matter. High temperature and high pressure material processing require much attention on the geometry of reactor and types of plasma generator. Continuous removal of by-product is another key consideration in advanced processing of materials.

For example, the growth of artificial diamond on surface of the particles required much care to select the bed geometry and the source of plasma [39]. Additional requirement of removal of by-product is very essential [39, 40] during the growth of the diamond. In this case the preferred reactor is the FBR due to its frequent collision between particles and fast mass transfer. Matsumato et al [36, 37] claimed that up to 20 micron growth of diamond was achieved by 600 MW microwave plasma in 3 hours at 0.06 atm operating pressures.

The processing of nano particles also bears importance now. Some recent literatures on ceramic nano particles and carbon nano tubes reported the aspects of CFB while using plasma jet for their surface treatment [39-40]. A demonstration by Weimer et al. [39] gives an account of processing of
micron-sized high density polyethylene while coating with ultra thin alumina films by atomic layer deposition. The coating was done using a FBR at 77°C temperatures. Their results showed the success of an attempt for the formation of nano-composite using plasma FBR. On the other hand Shi et al [38] reported the successful uniform deposition (2~7 nm) of ultra thin film of pyrrole on nanotube surface using PFBR.

5. Conclusions
Several experimental works amply demonstrated the use of plasma environment couple with the fluidized bed or Spouted bed and established a number of achievements in high temperature material processing. The example of various processes includes some exotic processes like gasification, semiconductor etching, and painting using plasma fluidized bed or spouted bed reactor. In the advanced material processing including nano-technology, circulating fluidized bed is used and high rating of reactor performance is vouched in the literature. However, use of PFBR still stands mainly on the extensive hydrodynamic studies. Future attempts for application in large-scale industries are still underway. Future attempts for application in large-scale industries are still underway. A comprehensive treatment pertaining to materials processing at high temperature using some advanced high temperature reactors as a whole and the plasma spouted bed/ fluidized bed in particular can be seen in a book edited by Gutpa and Sathiymoorthy [40].

ABBREVIATION
FBR- Fluidized bed reactor
PFBR- Plasma fluidized bed reactor
SBR- Spouted bed reactor
CVD- Chemical vapour deposition
CFB- Circulatory fluidised bed
PECVD- Plasma enhanced chemical vapour deposition
TECVD- Thermally enhanced chemical vapour deposition
Ums- Minimum spouting velocity
PyC- Pyrolytic Carbon
T- Temperature (in °K)
P- Pressure (Pa)

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