Chapter 23

History of Development of Plasma Science and Technology in BARC

– *Asoka K. Das*

Historically, plasma science and technology made its first appearance in DAE programs in one of the speeches of Dr. H. J Bhabha wherein he expressed his faith in plasma fusion's viability for future energy scenario in the first Geneva conference on peaceful uses of Atomic Energy. Immediately in 1957, a group was constituted by him in the Tata Institute of Fundamental Research (TIFR) to study theoretical plasma physics and the next year, Dr. Bhabha invited Prof Alfven to visit TIFR and give a series of lectures on "Magnetohydrodynamics and cosmic rays". The first experiments on toroidal plasma was also initiated at TIFR at the same time. However, the effort towards building a sustainable activity towards achieving plasma fusion did not take shape at that time. However, across the globe, along with plasma fusion, various low temperature plasma applications were taking shape for modernizing new tools in various manufacturing technologies.

Almost a decade later, during late 1960s and early 1970 saw resurgence in plasma science and technology when fresh efforts were initiated towards using plasmas as a technological tool for various materials processing applications. Development of underwater and air plasma cutting systems were initiated at the Bhabha Atomic Research Centre (BARC), primarily driven by the urgent requirement of cutting of thick **stainless steel plates for the variable energy cyclotron** project. The then Technical Physics Division (TPD) at BARC was entrusted with this task. Keeping to the BARC philosophy of technology development, work was initiated at the High Temperature Section of TPD through first principle designing and building of an air as well as underwater plasma cutting system. As a rule, BARC programs are planned and evolved through a synergistic route where the two major aspects, namely, basic science research and technology development activities are implemented together in a self consistent manner. In other words, the knowledge derived from basic physics research supports the various technology components of the self sustained nuclear fuel cycle and the needs of upgrading the technology drives further research on scientific issues. Development of various plasma physics programs in DAE have been no exception to this fact. This technology was indigenously developed and the design, manufacture and operational technology of the 100 kW plasma cutting torch was subsequently transferred to M/s Kirloskar Industries. As the plasma MHD generator program took shape, the plasma technology activities also included development of plasma spray coating of ceramic on metals. Plasma spray as an important surface modification technology has had a sustainable growth in DAE and has been serving many user groups since then.

A few of the other major programs in plasma science and technology that were initiated during the early seventies also included plasma and electron beam furnaces, Development of Plasma MHD generator with specific emphasis on Coal based systems and generation and transport of relativistic electron beams for plasma fusion technology. Over the years the BARC program on plasma science and technology has evolved to developing of high power plasma sources, process development on reactive spraying, metallurgical applications like melting, mineral dissociation and materials synthesis with particular emphasis on rare earth minerals, Low pressure plasma physical and chemical vapor deposition, plasma nano synthesis etc. BARC had also started working on high temperature plasma physics research that included laser produced plasmas, inertial confinement fusion, dense plasma focus devices and pinch systems

23.1 Basic Plasma Physics Research at BARC a Precursor to Technology Development

The Basic physics activities on both inertial and magnetic fusion plasmas involving lasers, magneto plasmas and relativistic electron beams were initiated in early seventies at the erstwhile Plasma Physics Section later made in to a Division, where the basic physics of particle beam generated plasmas was studied through relativistic electron beam (REB) generation, transport of beam energy, understanding of energy exchange between beam/ gas/ and plasma and issues in beam focusing etc at BARC. Interesting experiments using REB on collective ion acceleration were carried out for acceleration H, O, C and F ions to fractions of MeV. While the REB development activities established the foundation of pulsed power system development expertise at the Plasma Physics Division that now has far reaching impact.

Another area where plasma physics research in BARC has been of international standards is the field of Laser produced plasmas and laser plasma interaction where scientists at BARC have significantly contributed to the basic understanding of laser-plasma coupling, energy transport, relativistic self focusing, dense plasma focus devices, laser induced ablation of various targets, x-ray enhancement in laser produced plasma expanding in a background gas, shock wave propagation in thin foils, EOS measurements of variety of materials at high pressures etc.

Ion sources and ion beam research is one of the major research areas in BARC due to the emphasis on development of accelerators. The physics of resonance energy transfer between a microwave source and a low pressure gas under a confining magnetic field has been utilized for development of ECR ion sources for accelerators and ion beam production), Coulomb explosion and physics of highly charged states, physics of transient photoplasmas have also been fields which occupied interests in plasama physics.

Though in the area of low temperature processing plasmas, the physics research is driven by the need of the technology to become sustainable in terms of robustness, long life, energy efficiency and environment friendliness, BARC has made significant contributions towards understanding of Glow and arc discharge fluctuations (BARC, SINP), Mechanism of arc connection at the electrodes (BARC), non equilibrium phenomena in high pressure plasma jets (BARC), plasma nano-synthesis (BARC), Understanding of MHD generator flows, physics of combustion plasmas (BARC) etc.

In the computational plasma physics, notable advancements have been made in BARC towards developing and using 3D Particle in Cell (PIC) codes, radiation hydrodynamic codes, molecular dynamic codes, Plasma thermodynamic and transport property codes, Monte Carlo based algorithms, Computational fluid dynamics programs including shock wave propagation, multiphase thermo physical and Nonlinear dynamic codes to analyze data and predict plasma system behavior.

23.2 Physics and Technology of Low Temperature Processing Plasmas

While high temperature and magnetized fusion plasmas have been the focus of attention for many years, the non fusion low temperature plasmas otherwise known as processing plasmas or industrial plasmas had been gradually making inroads due to their immense value addition to advanced materials processing and energy generation. These plasmas are extremely useful in industrial applications related to advanced surface engineering, materials processing, metallurgy, chemical synthesis, waste remediation and more recently targeted nano material generation. In fact, a survey published a few years back put the annual value of products that owe their existence to plasma technology to be well beyond the 500 billion dollar mark.

The processing plasmas are endowed with highly concentrated energy flux (CEF) (density $= 10^{10}$ W/m^2), high temperatures, velocity, electromagnetic fields, currents, steep gradients resulting in ultra rapid heating/cooling (10^{7-8} K/sec), exotic reactive species, precursors for new synthesis routes and extremely broad ranges of space and time resolutions. It is therefore, possible to have (i) access to non-equilibrium operating regime, (ii) achieve submicron scale in temporal and spatial resolutions, (iii) obtain large throughputs with high efficiency, ultrahigh purity and specificity and above all (iv) conform to eco-friendly technology. One of the major advantage of the low temperature plasma beams lies in their versatility to perform in any of the three material processing regimes; be it physical modification, chemical reaction or thermal processing. At BARC the research and development program on low temperature plasmas are being carried out mainly at Beam Technology Development Group (BTDG). In the following, a few of the major technological applications that have found use in DAE or other strategic sectors are described briefly.

23.2.1 Magnetohydrodynamic power generation and MHD phenomena

When a fast moving plasma interacts with a magnetic field, a voltage is induced and an emf is generated. With appropriate configuration of electrodes in contact with the plasma, electrical power can be extracted from the high velocity plasma. This concept was utilized to develop a gasified coal based MHD power generator in India under a DST-DAE joint effort executed by BARC and BHEL with Russian collaboration. The idea was to use MHD as the topping cycle and the conventional thermal plant as the bottoming cycle leading to an improvement of about 10% in efficiency. In this context, a Open cycle MHD experimental plant was established at BHEL Thiruchirapalli and proof of concept established. A large number of accessory technologies including development of large electromagnets, combustor and air preheater Design, Material development for electrodes and insulators, Comprehensive computer codes for multiphase Plasma properties and MHD flow/heat transfer characteristics and development of various MHD plasma diagnostics targeting high gas temperature combustion plasmas were. The high points of the program included the Joint test of Indian Channel at IVTAN, Moscow and The plasma run at BHEL. The Figure below shows the horizontal section of a long duration channel design for Indian MHD plant to operate with seeded combustion product of blue water gas. This design used hybrid structure of water-cooled copper and high-density controlled porosity alumina in contact with plasma. The basic design features and fabrication technology was validated through the joint Indo-USSR experiment on Indian-built channel at UO_2 installation in Moscow in 1980. The electrode current density of 0.8 –1.0 A/cm^2 and heat fluxes of the order of 100 W/cm^2 simulating commercial generator conditions were recorded during experiment. The test channel performed satisfactorily for test duration of 64 hours.

Through its participation in the Indian MHD program, the BARC group also developed a large number of spin off technologies that are being widely used in nuclear fuel cycle programs. The plasma spray technology, initiated then for insulation coatings, is one of the most used technologies for thermal barrier and corrosion resistance coatings for various programs. The liquid metal MHD expertise developed is now being fully utilised in the ADS and ITER programs.

23.2.2 Development of high power plasma torches

High power plasma torches are designed to efficiently convert electrical energy to thermal energies in the form of a well stabilized plasma column in a sustained manner. Normally the non transferred arc plasma torches are aimed to operate >70% electrothermal efficiency and the transferred arc torches above 90%. These torches are routinely exposed to high electric fields, currents and heat fluxes. Design development of a robust plasma torch is an exercise in computational simulation and experiments. BARC has been developing high power plasma torches from few kW to hundreds of kW ratings for spray, melting, gas heating and space reentry applications. It has, over the years, built high power test stands (few kW to 1 MW) equipped to test and characterize these torches. The high power plasma torch program, in particular, has been instrumental in actively helping Indian Space Research Organization (ISRO), Defense Research and Development Organization (DRDO) etc. in setting up High Enthalpy Facilities and plasma probes for space reentry applications.

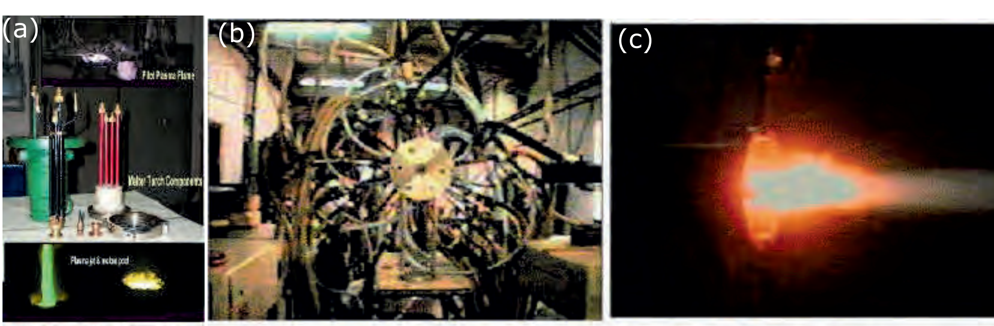

Figure 23.1: Various Plasma Devices developed in BARC: (a) 300 kW Plasma melter, (b) plasma tube (14 ring) and (c) the constrictor arc plasma jet.

23.2.3 Plasma cutting of thick metal plates

Plasma cutting of thick metal plates of MS, SS, Al as well as many other metals is today considered a matter of routine. As mentioned earlier, during very early seventies, BARC undertook development of transferred arc plasma cutting torches and both underwater as well as air cutting systems for its in-house needs. Apart from metal plates, underwater cutting of alpha active piping and aluminum jacket of burnt fuel bundles have also been demonstrated.

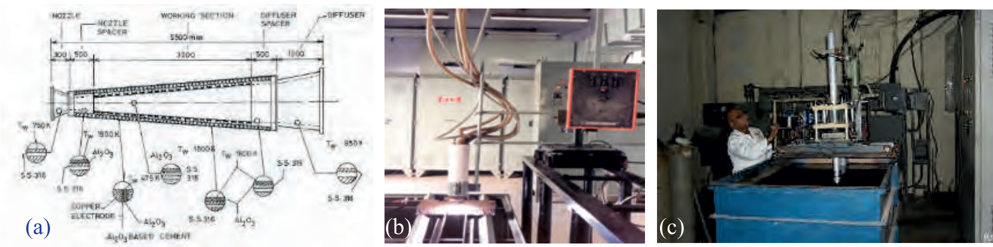

Figure 23.2: (a) Horizontal Section of MHD Channel Designed at BARC, (b) Air Plasma Cutting machine at BARC, and (c) Under Water Plasma Cutting system at BARC

23.2.4 Plasma spray processing and deposition

Plasma spray deposited coatings of metals, alloys, ceramics and composites to meet the specialized requirements of the department of atomic energy in general and BARC in particular was developed in the seventies for MHD generators and is one of the most utilized plasma processes today. Besides development of ceramic-alloy duplex coatings for handling corrosive melt and ceramic-alloy composite coatings for strategic and specialized nuclear applications, research on advanced thermal barrier coating (TBC) systems has been a major R&D area. A TBC system, usually, consists of two layers –a metallic bond coat and top ceramic coat. The function of the bond coat is to protect the substrate from oxidation and provide sufficient bonding of the top ceramic coat to the substrate. The insulating ceramic layer provides a reduction of the temperature of the metallic substrate, which leads to improved component durability. Thermal barrier coating system employs a duplex design consisting of a bond coat and top ceramic layer. Some of the state-of-the-art TBC material developed at BARC are yttria-stabilized zirconia (YSZ) containing 7-8 wt% of yttrium oxide, which is deposited over MCrAlY(M=Co, Ni) or Pt modified aluminide. For use above 1200 °C, R&D efforts are presently directed towards development of new class of ceramic materials for the top layer of TBC with improved thermal and chemical stability and lower thermal expansion coefficient. The rare earth phosphates, lanthanum zirconium oxide and yttrium oxide have many desirable features, which are not exhibited by the other materials. These materials have high melting points (> 2400 K), thermal stability and do not react with many molten metal including molten uranium and molten lead. Lanthanum phosphate has excellent thermal stability and corrosion resistance against many molten metal and other chemically corrosive environments. Plasma spheroidization and melting studies at BARC on Lanthanum phosphate and its compatibility with molten uranium have established that these phosphate coatings are effective in high temperature containment of molten uranium. The rare earth phosphates are resistant to corrosion by molten slag, glass and are ideally suited coatings for containment of radioactive waste. In addition, yttrium oxide and lanthanum phosphate are not wetted by molten lead and bismuth and are therefore ideal candidate materials for ADS applications. The plasma group at BARC had also developed an arc wire spray technique for preparing metallic nickel coating on carbon electrodes.

23.2.5 Reactive plasma spray processing and plasma chemistry

Reactive plasma spraying developed in early twenty first century provided a powerful technique that takes advantage of the high temperature and high enthalpy of the plasma jet to effect 'in-flight' chemical reactions in the presence of a reactive gas. The unique feature of reactive thermal plasma synthesis is independent control of plasma power and the reactive environment. The high temperature gas phase chemistry and temperature of the plasma medium can be customized to promote the desired chemical reaction. Some of the promising opportunities that reactive plasma synthesis offers include development of novel coatings, processing of advanced ceramics and conversion of industrial wastes to value added materials. This technology can also be extended for synthesizing nano-sized powders of advanced ceramics. Reactive plasma processing has been successfully applied to synthesize nano-crystalline titanium oxide by 'in-flight' oxidation of micro-sized TiH_2 powder in a DC non-transferred arc thermal plasma reactor designed and developed at BARC. Complete conversion of the injected TiH_2 powder to nano-sized TiO_2 that is functionally as effective as commercially available photocatlytically active titania powder could be accomplished. The same technique has been applied to synthesize Nickel aluminide, an excellent bond coat material in a plasma torch operating in a non transferred arc mode using premixed powders with excess aluminum as precursor material, argon as carrier gas and argon and nitrogen as plasma gas The reactive plasma processing technique has also been extended to generate metallic and ceramic aerosols of importance in the Nuclear Industry. A 20 kW plasma torch based aerosol generator has been integrated with the nuclear aerosol test facility (NATF) and used for study of aerosol generation and settling behavior.

Reactive plasma synthesis can be most gainfully employed for processing of minerals. Plasma dissociation of zircon (zirconium silicate mineral), conversion of ilmenite to titanium oxide, titanium carbide and titanium nitride, plasma conversion of fly ash to value added materials are some of the interesting applications. The principal advantage of this direct method is that it uses cheap raw material. At BARC, DC plasma torch based reactors have been developed for dissociation of zircon to zirconium oxide and silica. The process consists in feeding zircon particles into the thermal plasma jet, where they undergo thermal dissociation to zirconium oxide and silicon dioxide and the high quench rate associated with the process prevents recombination of the oxides, leading to the formation of a product that consists of the individual oxides. Zirconium oxide is suitably extracted from this oxide mixture by acid or alkali treatment. Recent innovations that include the addition of carbon and use of air as the plasmagen gas have resulted in one-step process, eliminating the down-stream wet chemical operation and thus, leading to improved process economics. The technique can also be extended to convert industrial waste such as fly-ash into value-added materials. Fly-ash is a waste product from coal-based thermal power plants. The major chemical constituents of fly-ash are silica and alumina and its disposal is a matter of great ecological concern. Only a very small percentage (5-7%) of fly-ash is utilized for gainful application. By proper control of the flame chemistry and plasma power, fly-ash can be converted to silicon carbide and nitride based composites.

23.2.6 Low-pressure plasma surface modification and deposition

Low-pressure plasmas are characterized by high reactivity due to the presence of highly energetic electrons, free ions and excited species. Due to high internal energy of low-pressure plasma, processes, which are thermodynamically allowed but kinetically hindered in a conventional process, proceed with a high rate under plasma conditions. In low-pressure plasmas it is possible to effect the deposition at low deposition temperature, low ion temperature (less bombardment), which results in small grain size. There are two general classifications of how low-pressure plasmas are applied in surface modification. The first involves the use of the

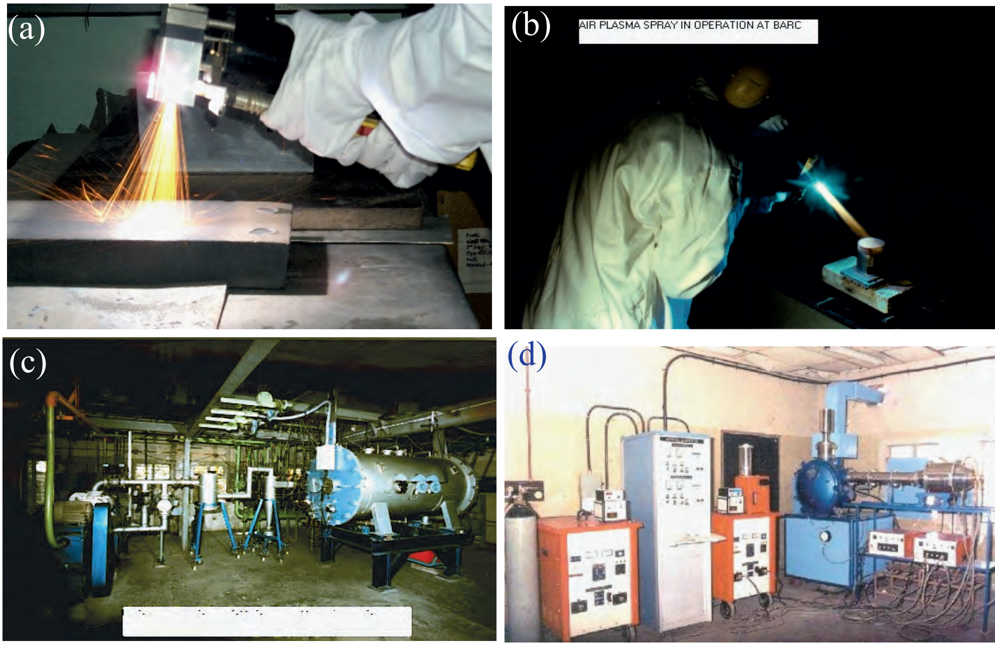

Figure 23.3: (a) Arc wire Spray at BARC, (b) Plasma Spray System in operation, (c) Vacuum Plasma Spray Equipment, and (d) Plasma Chemical Reactor at BARC.

ions from the plasma, which can be accelerated from the edge of the plasma by an electric field. The kinetic energy of these accelerated ions can be used to physically erode a surface or to implant the ion below the bombarded surface. The second general use of plasma is to generate energetic or metastable species from the gas, such as excited states of atoms and ions, active chemical species from molecules and photons. The presence of these energetic metastable species will cause various surface phenomena, such as reactive etching or deposition that would not have occurred thermally in the absence of the plasma medium. In DAE, Low pressure plasma deposition activities are mainly being carried out at BARC, IGCAR and IPR. The work at BARC and IPR are more holistic as they range from device to process to characterization activities. At the IGCAR, work is more focused on the use of plasma devices for coating development.

At the Laser and Plasma technology Division (L&PTD) of BARC, a 2 kW, 2.245 GHz large volume microwave electron cyclotron resonance (ECR) system had been developed for large area deposition of highly adherent nonporous coatings of diamond, diamond like carbon (DLC), cubic boron nitride and superhard nanocomposites coatings. The system had been used to deposit diamond like carbon (DLC) films on silicon (111) substrates using methane and argon gas plasma. The energy of the ions impinging on the substrate during deposition is varied by changing the rf self bias voltage developed on the substrate to get highly adherent films. This Microwave ECR plasma CVD system was adapted to grow thin films of yttrium oxide on Si (111) and s.s. substrates by metal organic chemical vapour deposition (MOCVD) using a Y(thd)3 (thd = 2,2,6,6,-tetramethyl-3,5-heptanedionate) precursor. The technique was optimised to deposit yttium oxide and yttria stabilized zirconia coatings on various substrates including stainless steel and tantalum. In addition, R&D efforts on in situ plasma diagnostics, Carbon nanostructures for electron emitter applications and oriented diamond films were also reported.

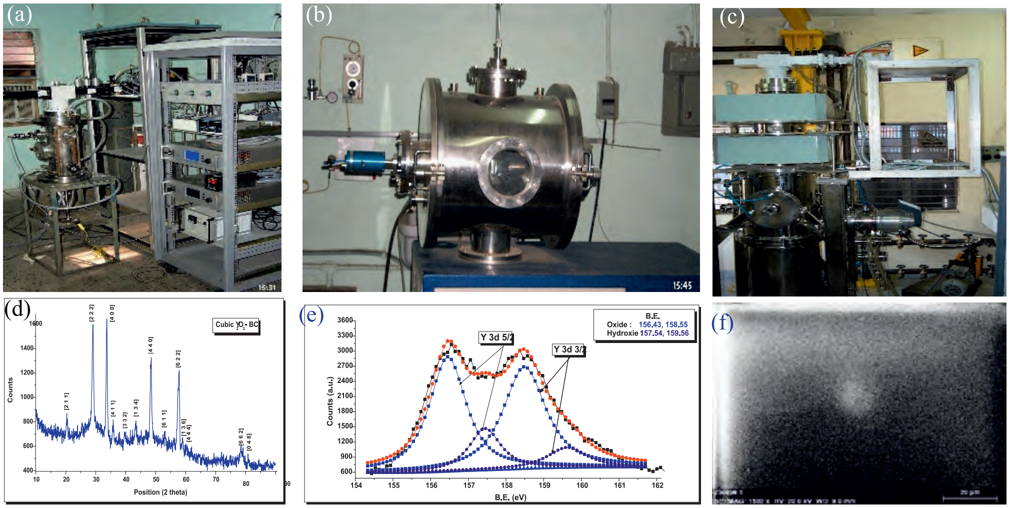

Figure 23.4: (a) Microwave Plasma CVD Reactor (2.45 GHz, 2 kW) for Oriented Diamond Thin Film Deposition, (b) Radio Frequency Plasma CVD Reactor (13.56 MHz, 250 kW) for Deposition of DLC-SiOx Thin Films, (c) Low pressure large volume plasma source – Microwave – ECR Plasma, (d) X-Ray diffraction pattern taken on Y_2O_3 deposited on Si (111), (e) XPS spectra of Y_2O_3 deposited on Si (111), and (f) SEM Image on Y_2O_3 on Tantalum (Annealed sample).

23.2.7 Plasma nanosynthesis

Plasma assisted synthesis of nanoscale structures is known to offer opportunities in terms of bulk production, purity and good alignment. The thermal plasma techniques offer high yield with prospects of production of both particles as well as rods/tubes/wires but with lesser degree of control on shapes and sizes. The low pressure, low temperature non-equilibrium plasmas on the other hand, have the capability to effect controlled growth and alignment in nano tubes and rods. This is the other emerging application of plasma-materials technology. The L&PTD in collaboration with University of Pune, Centre of Plasma Physics Guwahati and Bharathiyar University, Coimbatore had designed and developed transferred arc nanogenerators to synthesize nanostructures of AlN nano wires, Al_2O_3, TiO_2, ZrO_2, ZnO, γ-Fe_2O_3, Fe_3O_4 particles and single elemental materials like carbon nanotubes and nano sheets. Significantly a plasma parameter control regime in terms of plasma gas, flow pattern, pressure, local temperature and the plasma fields have been established to obtain the desired nano phase structures. Use of simple in situ measurements like heat fluxes, emission spectra, electron densities, arc voltage, pressure and temperature and an array of particle characterization techniques have indicated possibility of definite correlation between plasma parameters and characteristics of the nanomaterials generated. While pressure and arc current have shown definite controlling effect on phase structure and size, the magnitude of fluctuations have shown to be affecting the size of nanoparticles. In the case of arc synthesis of carbon nano structures, it has been demonstrated for the first time that high purity MWCNT and graphene can be synthesized with proper optimization of electric and magnetic fields. Work related to RF plasma Nanosynthesis was also initiated for ceramic oxide materials.

23.2.8 Plasma assisted waste remediation and pollution control

Waste remediation and pollution control emerged as one of the emerging and exciting large scale application of plasma technology in the 1990s. Thermal plasmas have been used as a single step solution for treatment of biomedical, municipal, hazardous plastic, ozone depleting and radioactive wastes whereas the non thermal plasmas are effective in flue gas and water purification. Plasma lamps are industrially being used for large scale water purification. The plasma waste treatment also provides value added material and fuel gas as by products. Applications of non-equilibrium atmospheric pressure plasma for gas phase scrubbing of volatile and non-volatile contaminants and environmental remediation is also a viable process. L&PT Division had initiated a program during early 2000 for treatment of biomedical waste using Plasma torches unlike IPR that used open graphite arcs. The program was continuing.

23.3 Concluding Remarks

It is apparent that over the last five to six decades, plasma science and technology has formed a part of many BARC Programs aiming at applications in various units of BARC and DAE. In fact, the eleventh and twelfth five year plans saw plasma reduction of UF6 gas being installed at CHTD of BARC, Coating of graphite crucibles for reactive metal melting, non thermal RF, microwave and DBD plasma jets for uranium etching and boron coatings for detector applications. It is significant to note that in most of these programs, the thrust has been in capacity building wherein the devices and the process equipment are indigenously developed. Simultaneously, a large number of innovative and path breaking theoretical, experimental as well as innovative diagnostics work has been carried out that had opened of new directions of research. This approach has provided a certain expertise and technological competence essential in these advanced areas. In future, fusion energy, plasma surface engineering applications in nuclear fuel cycle, Laser Plasma accelerators, Plasma nanosynthesis and plasma waste beneficiation might be the emerging technologies due to the increasing needs from energy, materials and environment sectors. On the basic plasma physics and chemistry aspects, (i) understanding and control of nonlinear waves and instabilities in all types of plasma systems, (ii) high temperature chemistry of plasma assisted reactions, (iii) understanding and controlling plasma nano synthesis are few emerging areas that will continue to be investigated in BARC. Plasma Device design at high powers is one of the much needed sectors and there is sufficient expertise developed in these groups to take up the challenges. Considering the application potential and environmental sustainability aspects it is absolutely essential that the science and technology of plasmas be nurtured and supported.

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