Manufacturing and material processing based on plasma technologies*

Plasmas are ionized gases containing free electrons, ions and excited neutrals. The charged particles can respond to external electric and magnetic fields and transport energy. A plasma can be created, for example, by striking a discharge between two electrodes; the ohmically heated plasma at temperatures more than 10,000 degrees can be ejected out, resulting in a 'plasma torch'. This torch can melt or vaporize any material. Plasma metallurgy, synthesis of ceramics, waste pyrolysis, etc. result from the high temperature gradients that aid in rapid quenching and selective reactions.

In low-pressure molecular gases, a different type of plasma referred to as 'non-equilibrium plasma', can be created by glow discharge. The electrons in this plasma have temperatures in the region of 10–50,000 degrees, whereas the ions and neutrals are left cold. One can use the resulting plasma for synthesis of thin films and for surface coatings and modification.

Since plasmas can localize electric fields, one can derive high flux beams of energetic ions and electrons; these beams can be used for implantation, ion-etching and micro machining.

Plasma science and technology has been used in a variety of modern technologies as it offers unique and novel opportunities for high value-added material processing.

The Institute of Plasma Research (IPR) of the Department of Atomic Energy at Gandhinagar is primarily concerned with fusion research using Tokamak facilities. In addition since 1990, the institute has also been developing plasma-based industrial technologies and created a Facilitation Centre for Industrial Plasma Technologies (FCIPT) in 1997. With the creation of FCIPT, IPR has ventured into converting the vast R&D knowledge base relating to plasmas into technology products to be marketed to the industry. This activity involved moving away, to some extent, from concepts such as pursuit of knowledge for its own sake, importance of publications and a relaxed open-ended research work-culture. It also meant that one had to realize commercial value of knowledge, protect commercial interests along with confidentiality. essential in interaction with industries.

Although new technologies lead to new products and better products along with the common belief that markets have insatiable hunger for new technologies, there is considerable resistance to technological change. This is because new technologies mean additional capital, new work-culture, reorientation of personnel and/or fresh recruitment.

Over the years IPR, through the FCIPT, has promoted spread of awareness of plasma-based technologies through several meetings, workshops, trade fairs and an in-house newsletter, *Plasma-Processing Update*. A few thrust areas have been diligently pursued. These are:

(i) Surface engineering to enhance wear/corrosion resistance, hardness and finish related to plastic dyes/moulds, automobile parts, tools and brassware, using ion implantation, plasma nitriding and Sioux coatings, etc. A case study of plasma nitriding of critical hydropower components, that otherwise undergo considerable erosion because of action of sand and silt, is noteworthy.

(ii) Processing of minerals where a specific case study relates to a single-step, viable and efficient plasma dissociation of zircon sand into zirconia. Zirconia being a high-strength, high-melting point material with good chemical resistance, is used in several sintered products like wire-drawing and extrusion dyes, automobile engine parts, bio-medical components, anti-corrosion coatings and for refractory linings. Hence its importance.

(iii) Plasma pyrolysis and remediation of medical and other wastes. As a case study, detailed study of treating medical waste is taken up. Conventionally, landfill or incineration is adopted for medical waste disposal. This can result in contamination of groundwater, pathogen survival, toxic pollutants and air pollution.

In plasma pyrolysis, using plasma torches, the intense plasma heat arising out of temperatures of the order of 10,000 degrees in the plasma, fragments a variety of organic and inorganic molecules found in the waste. The hot by-product gases are burnt, scrubbed and ultimately quenched. The recombination of the plasma produces intense UV radiation, that can destroy pathogens completely. Wet or dry and unsegregated hazardous waste can thus end up in toxic by-products much below emission standards.

There are other thrust activities related to plasma vapour-deposited coatings, efficiency improvement of solar photovoltaic cells, etc. which are also being pursued at FCIPT.

As pointed out in the report: 'we have shown that it is possible to develop and transfer advanced plasma-based technologies to industry by following a road-map, which recognizes various factors inhibiting such an activity. This has culminated in the creation of a self-financing technology development, incubation, demonstration and delivery facility, namely FCIPT'.

*Based on a research report entitled 'Commercialization of plasma-assisted technologies: The Indian experience' by P. I. John, Institute for Plasma Research, Gandhinagar 382 424, India.

RESEARCH NEWS

A paradigm shift in the electrowinning of metals

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In the electrowinning of metals, a metal compound is electrolysed as a solution or as a molten salt with appropriate electrodes. The metal ion discharges at the negative electrode (cathode) to produce the metal. This traditional approach to metal electrowinning is given a paradigm shift by the discovery of the FFC (Fray, Farthing and Chen) Cambridge process by researchers led by Derek J. Fray of the Materials Chemistry Department of the Cambridge University, England. In this process, instead of being dissolved in the electrolyte, the metal compound remains in the solid state and is the cathode during electrolysis. Chemical changes are induced in the compound by combined thermal and electrochemical means to produce the pure metal at the cathode.

The FFC Cambridge process is a high-temperature molten salt electrolysis process and is named after the inventors Fray, Farthing and Chen. The process was patented[1] in December 1999 for the production of a host of metals/semi-metals such as Ti, Si, Ge, Zr, Hf, Sm, U, Al, Nd, Mo, Cr, Nb or their alloys with their oxide, sulphide, carbide or nitride as the starting material. The extraction of titanium from titanium dioxide has been reported as a case study[2,3]. Titanium dioxide is used as the solid cathode and graphite as the anode in the high-temperature (~ 950°C) FFC cell with molten calcium chloride, which possesses the required electrochemical and thermodynamic properties for the metal extraction, as the electrolyte in the process. During electrolysis, the oxygen present in the solid cathode is reduced to oxide ions. Under the influence of the applied potential and the thermal conditions existing in the cell, the oxide ions leave the cathode, which finally gets converted to pure metal. The oxide ions are transported through the molten electrolyte to the graphite anode, where they are discharged as oxygen or carbon dioxide.

The process can be expressed as follows:

$$TiO_2 \text{ (solid, cathode)} \rightarrow \text{molten } CaCl_2 \text{ electrolysis} \rightarrow Ti \text{ (cathode)} + O_2 \text{ (anode)}$$

In their article in *Nature*, Chen *et al.*[2] have examined two possible mechanisms for the deoxygenation of TiO_2.

(1) Reduction of TiO_2 by calcium deposited at the cathode

$$TiO_2 + 2Ca \rightarrow Ti + 2CaO$$

(2) Ionization of oxygen at the cathode

$$TiO_2 + 4e^- \rightarrow Ti + 2O^{2-}$$

By careful voltammetric experiments, they have established that the electrochemical deoxygenation (reaction 2) is the mechanism.

At present, the largest potential application of FFC Cambridge process is identified for production of titanium and titanium alloys. The special interest in titanium is due to its potential use as light, strong and corrosion-resistant alloy for aerospace and other strategic applications. In spite of the very attractive properties, its use has been restricted due to the very high cost of production by the conventional Kroll process. In this process, titanium dioxide and carbon are heated together, at around 500°C, in a stream of chlorine to produce a volatile and corrosive liquid, titanium tetrachloride. This is reduced to the metal by reaction with metallic magnesium (Kroll process) or sodium (Hunter process) at high temperatures (700–900°C). The batch processes are slow, demanding in terms of health and safety criteria, and require prolonged high-temperature vacuum distillation of the product to remove excess alkali metal and its chloride from titanium.

In the new process, by controlling the potential of the cathode, oxygen can even be removed from solution in the metal, allowing a high purity metal to be obtained. The major difference in this process is that the titanium metal is left behind at the cathode and at no stage is it in the liquid or ionized state, as in conventional electrolysis. Another uniqueness of the process is that it is possible to use the readily available oxide ore directly in the metal production.

According to Fray, the new technology has many other advantages apart from metal production. Mixtures of oxides can be blended together and reduced, electrochemically, to alloys. This overcomes many of the problems such as segregation and oxidation, commonly associated with alloying of reactive metals. Furthermore, the product may be of a form suitable for powder metallurgy that eliminates casting, machining and other expensive fabrication processes. In practical terms, the new technology offers dramatic savings. Fray is optimistic that the non-polluting and energy-efficient process may become generic for the production of many metals and alloys in future, especially those that are difficult and expensive to prepare or are highly reactive.

A company, British Titanium plc (BTi), was incorporated in 1998 to develop and exploit the FFC Cambridge process for titanium metal production. Under a teaming agreement with the Defence Evaluation and Research Agency (DERA) of UK, the company funded the Phase II test programme to produce 1 kg batches of titanium metal by the process. The results achieved are reported as 'beyond the best expectations'. Encouraged by the Phase II results, BTi is now proceeding with plans for a Phase III plant. The new plant will be used to optimize the FFC Cambridge process and to establish the design parameters for an eventual commercial plant. If the claims of the inventors turn true in the commercial level, titanium metal will become considerably cheaper in future and this may possibly make this remarkable metal the mainstream engineering metal of tomorrow. It is reported that the FFC technology is sought by some of the leading metal and minerals companies in the world.

The new discovery is of great significance to India. Based on the early laboratory and pilot plant studies carried out at Bhabha Atomic Research Centre (BARC), Mumbai, the Nuclear Fuel Complex (NFC), at Hyderabad has been a major producer of zirconium alloy components for nuclear reactors through the Kroll process to produce sponge zirconium. The Defence Metallurgical Research Laboratory, Hyderabad has followed the early BARC work to set-up a pilot plant for titanium production, also through the Kroll route. Department of Atomic Energy (DAE) and Defence Research and Development Organization have plans to set up a commercial plant for production of titanium based on the above experiences. Many private industries have also shown interest in a possible 'joint venture' for production of titanium. DAE and NFC have plans to set-up new plants (based on the Kroll process) to meet the increasing demand for zirconium alloys from our growing nuclear power programme. With the possible emergence of a cheaper and superior technology, these plans have to be reassessed.

1. International Patent (PCT), WO 99/64638, 16 December 1999.
2. Chen, G. Z, Fray, D. J. and Farthing, T. W., *Nature*, 2000, **407**, 361–364.
3. Flower, H. M., *Nature*, 2000, **407**, 305–306.

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