CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

The various techniques of materials processing involve contact between molten metals and refractory materials to get the high purity end product. The interaction of the final product of molten metal is closely related to surface properties of the refractory material. Thus, surface properties of refractory materials play a key role in selecting suitable material to handle molten metal. Uranium has an important role in both military and nuclear energy industries for civilian applications. Uranium is highly reactive with most refractory materials when it is in molten state (Jonathan et al. 2013, Masaru et al. 1997). Since molten uranium is not chemically compatible with base/ container material, lifespan of crucibles and components used for processing of uranium reduces due to corrosion by uranium. Consequently, protective ceramic coatings are required on the container to prevent its reaction with uranium. These protective ceramic coatings should be chemically inert to liquid/vapour uranium and at the same time should not introduce any undesirable impurities in the processed uranium. Many refractory oxides, carbides and nitrides have been suggested for this task (Lee et al. 2010, Kim et al. 2011, Holcombe et al. 1978). Among them, lanthanum phosphate (LaPO$_4$) has been identified as a promising candidate for corrosion barrier applications since it has phase and chemical stability at high temperature.

In nature, there are 300 mineral phosphates classified into many groups depending on the element constituting the cationic part. Among these, rare earth
phosphates with monazite structure are important by virtue of their chemical and thermal stability. Naturally occurring phosphates, ABO (where, A = Ln (lanthanides), or (actinides), Zr, Y, Hf, Pb; B = P, Si) have the monazite or zircon crystal structure and they are important because of their high actinide content. Among these, studies of orthophosphates of rare earths are an exciting field of research in ceramics and materials science due to their intrinsic property of high thermal stability and chemical inertness.

Lanthanum phosphate (LaPO₄) is a member of rare earth phosphate family, whose geological history shows that it can exist with actinide content for several millions of years. Like LaPO₄, natural monazite [(Ln, Th)PO₄] can contain more than 17 wt.% ThO₂ and remains crystalline for 2 to 3 billion years (Byrappa et al. 1986, Randall et al. 1990, and Meldrum et al. 1997).

LaPO₄, also known as monazite, is ideally suited for high temperature molten metal corrosion and thermal barrier applications for the following reasons.

1. LaPO₄ is geologically very stable with excellent thermal and chemical stability
2. It has very high melting point
3. Its thermal conductivity is low
4. LaPO₄ has high thermal expansion co-efficient compared to other ceramic materials
5. It shows excellent corrosion resistance in many reactive environments containing molten metals, carbon, sulphur and vanadium salts

1.2 Phase stability of LaPO₄ and La₂O₃ - P₂O₅ system

Figure 1.1 shows the phase diagram of La₂O₃-P₂O₅ system reported by Naoyuki et al. (2013). This system has seven compounds, viz. La₃PO₇, La₅PO₁₀, La₇P₃O₁₈, LaPO₄, La₂P₄O₁₃, LaP₃O₉ and LaP₅O₁₄. As per the normal
nomenclature followed in literature, La\textsubscript{3}PO\textsubscript{10}, La\textsubscript{3}PO\textsubscript{7} and La\textsubscript{7}P\textsubscript{3}O\textsubscript{18} are called as lanthanum oxy-phosphates and La\textsubscript{2}P\textsubscript{4}O\textsubscript{13}, LaP\textsubscript{2}O\textsubscript{9} and LaP\textsubscript{2}O\textsubscript{14} are referred as lanthanum poly-phosphates. Among these compounds, La\textsubscript{2}P\textsubscript{4}O\textsubscript{13} and La\textsubscript{5}PO\textsubscript{10} are the least studied. The work by Park and Kreidler (1983) is the only literature available on synthesis of La\textsubscript{2}P\textsubscript{4}O\textsubscript{13}. Similarly, the works available on preparation and characterization of La\textsubscript{5}PO\textsubscript{10} reported by Kropiwnicka et al. (1988) and Kropiwnicka (1990), are the only literatures available on La\textsubscript{5}PO\textsubscript{10}.

Apart from these authors, no other group has yet reported about these compounds (La\textsubscript{5}P\textsubscript{4}O\textsubscript{13} and La\textsubscript{5}PO\textsubscript{10}) to the best of our knowledge. Efforts by other authors to prepare these two compounds were not successful (Naoyuki et al. 2013). Among the seven compounds, lanthanum orthophosphate (LaPO\textsubscript{4}) is the most stable compound (Damien et al. 2007), which is commonly known as monazite. Monazite is a line compound that melts congruently at 2040 °C (Cao et al. 2004).

**Figure 1.1**- Phase diagram of La\textsubscript{2}O\textsubscript{3}-P\textsubscript{2}O\textsubscript{5} system (Naoyuki et al. 2013).
1.3 Structural aspects

Based on the crystalline structure, the rare-earth orthophosphates LnPO₄ are divided into two groups viz. monazite and xenotime (Begun et al. 1981). The monazite structure occurs for first half of the lanthanide series from La to Gd and xenotime structure occurs for the elements from Tb to Lu.

Lanthanum phosphate exists in two structures, the hexagonal phase with rhabdophane structure and the monoclinic phase with monazite structure. Rhabdophane (LaPO₄ nH₂O) has primitive lattice with hexagonal structure. The crystallographic parameters of rhabdophane structure were reported by Morgan (1995). In this structure, the lanthanide atom has eight-fold coordination with eight oxygen atoms forming LnO₈ polyhedra, which is further linked to PO₄ tetrahedra. This structure was characterized by the existence of large tunnels parallel to the c axis in which the water is present and appears to be localized, which gives an impression of stabilizing the structure (Horvath et al. 1988). The degree of hydration for it is variable; and the value of n lies between 0.5 and 1.

In monazite structure (LaPO₄), all the four P–O bonds in the PO₄ tetrahedron are equivalent and are of the terminal type due to the isolated arrangement of the tetrahedral. Compared to other rare-earth orthophosphates (RPO₄, where R = Pr, Nd, Eu, Gd and Sm), the monazite structure of LaPO₄ is isomorphic and belongs to a monoclinic crystal system with a space group: P2₁/n (No. 14), and lattice parameters: a = 6.8313 Å, b = 7.0705 Å, c = 6.5034 Å, and β = 103.27°. Lanthanum phosphate is identified as a potential candidate for high temperature coatings due to its unique thermal properties in comparison to other ceramics. It has high melting point, high thermal expansion coefficient, low thermal conductivity, and good temperature stability.
Lanthanum phosphate in the form of coatings by various methods such as pulsed laser deposition (PLD), electron beam physical vapor deposition (EBPVD), sol gel, ultrasonic-based coatings etc., is used for the aforementioned applications (Sinha et al. 2009, Sudre et al. 2001, Zainurul et al. 2013, Romankov et al. 2008). Today, there are a number of coating techniques available with each technique having its own advantages as well as disadvantages. The advantages and disadvantages of each technique are discussed in the following sections.

1.4 Overview of coating processes

Corrosion, heat, wear and abrasion resistance of the substrate materials can be improved significantly by applying suitable coating on them. There are a number of coating techniques available for corrosion, wear and thermal protection. These include chemical vapour deposition, physical vapour deposition, and plasma enhanced chemical vapour deposition. These deposition techniques require vacuum chamber. On the other hand, thermal spray deposition techniques are efficient tools to deposit a variety of materials on any desired substrate. Thermal spray deposition can be carried out at normal atmospheric conditions and its enormous heat content can be used to melt a wide range of materials from metal to ceramics.

1.4.1 Physical vapor deposition (PVD)

Evaporation is one of the simplest techniques of PVD. In this technique, the material to be deposited is melted and vaporized in either tungsten or molybdenum boat by resistive heating or electron beam and the vapor is condensed on the substrate to form a coating. This method is suitable for metals, alloys and compounds, which melt congruently. PVD can be used for almost any inorganic or organic material. The coating is uniform and having good adhesion with substrate. The PVD coatings are developed in inert atmosphere and
therefore show no chemical reactions. These are some of the advantages of PVD techniques. Disadvantages of PVD process include slow deposition rate and very small final coating thickness of only about Angstrom unit (Å) to nano meter (nm). It is difficult to coat larger and complex shaped substrates (because of chamber size limitation) and inner surfaces of the cylindrical substrates uniformly (Mikell 2010). RF/DC sputtering, electron beam, and laser ablation are some of the widely used methods for physical vapor deposition of metals, alloys and ceramics.

1.4.2 Chemical vapor deposition (CVD)

Unlike PVD, the nucleation and coating growth/process in CVD techniques involve chemical reaction of the precursors. The chemical reaction occurs on the substrate surface, which is kept at high temperature. Here the deposition rate varies with concentration of the precursor gases. In generally, the rate of deposition depends on the kinetics of the reaction, rate of crystallization of the decomposition products on the reaction surface (Mikell 2010) and the substrate temperature. Various applications of CVD involve applying hard coatings on to cutting tool surfaces to improve wear resistance, for producing high-purity bulk materials, preparing large band gap semiconductor materials such as gallium arsenide, indium phosphide and other compound semiconductor materials in powder form (Heimann et al. 1995). The major disadvantages of CVD are the presence of highly toxic (Ni(CO)_4), corrosive (SiCl_4) and explosive (B_2H_6) precursors. Also the deposition of the film requires a high temperature, which can distort the substrate shape and geometry (Yongdong et al. 2010).
1.4.3 Laser ablation technique

Laser ablation technique is extensively used for depositing thin coatings of various target materials on different kinds of substrates at room temperature. The process involves the following steps,
1. Focused laser beam interacts with the surface of the solid target material.
2. Absorption of energy and localized heating of the surface
3. Material evaporation and deposition on the substrate at room temperature
The main disadvantage of the laser ablation is the high cost of the laser source and low rate of deposition (Bunshah, 1994).

1.4.4 Thermal spray techniques

Thermal spray techniques are employed for preparing an overlay coating onto desired surface and are most widely used to prepare composite structural parts with improved properties and augmented lifecycle. These coatings should withstand in extreme corrosion environments, high temperature and also protect the machinery compounds from wear and tear. Thermal spray is a highly versatile technique that can be used to deposit metals, ceramics and composites. The equipment is simple and does not require sophisticated training procedures for the operator. Thermal spray technique is used to develop various types of metallic and non-metallic coatings on different types of substrates for various applications. In thermal spraying, the material to be deposited (very often in powder form) is heated to the molten or semi-molten state in the plasma/hot gas jet. The stream of heated particles issuing out of the heat source are accelerated and driven toward the surface to be coated using either the process gases or atomization jets (Powlowski 2008).

Depending on methodology, thermal spray techniques can be generally classified as:
1. Flame spraying
2. Wire arc spraying  
3. Detonation-gun spraying  
4. High velocity oxy-fuel spraying  
5. Arc plasma spraying  

Flame spraying (FS)

Flame spray is the simplest method among the family of thermal spray technologies. In this technique, the injected coating material can be either in powder, wire or rod form. The molten particles are accelerated and propelled towards the substrate to be coated. In wire flame spraying, the primary function of the flame is to melt the feedstock material. Coating material in the form of wire is fed into the flame with constant speed and a stream of air atomizes the molten material and propels it toward the work piece. The flame is produced by fuel and oxygen and occasionally compressed air is also used instead of oxygen.

The material to be coated is taken in powder form and is used as the feedstock in powder flame method. The powder is injected into the oxy-fuel flame. The particles get melted and are accelerated towards the substrate by the hot stream of gas. Particle velocity is relatively low (<100 m/s) compared to other thermal spraying techniques. Average feed rate is 0.5 to 9 kg/h for most of the coating materials. However, materials that melt at lower temperatures can be sprayed at significantly higher feed rates. The bond strength of coating to substrate is found to be relatively lower compared to that obtained by other methods (Pawlowski 2008, Davis 2002).

Detonation gun (DG) spraying

The Detonation gun spray process was developed by Union Carbide12 (Poorman et al. 1955) in early 1950. Oxygen and acetylene combustion gas mixture is fed through a tubular barrel closed at one end. The gas mixture inside
the chamber is ignited by a simple spark plug and combustion of this gas mixture generates high pressure shock waves. Nitrogen gas is used as blanket cover gas in order to prevent the back firing. The powder is injected into back side of the combustion chamber. Gas temperature depends on the ratio of oxygen to the combustible gas. The DG can produce gas temperatures up to 4000 °C. The velocity of DG wave can reach up to 3500 m/s. The Coatings produced by denotation gun spraying are characterized by low porosity. (Lakhwinder et al. 2012, Ramnarayan 2004).

High velocity oxy fuel spraying (HVOF)

HVOF spray coating technique is based on the heat and pressure generated from the combustion chamber where liquid or gas fuel is mixed with oxygen. Coating material is fed axially or radially into a hot gas stream where they are melted and propelled to the prepared surface of work piece to be coated. Combination of thermal and kinetic energies is used to melt and accelerate the powder particles. In general, HVOF coating is a high-velocity, low-temperature spraying process. Due to the high velocities of propelled particles, high bond strength is obtained between coating and substrate and the coating porosity is very low. These are the main advantages of the HVOF process (Ramnarayan 2004, Bunshah 1994).

Wire arc spraying (WAS)

In this arc spray technique, a pair of electrically conducting wires is fed into the spray gun, where these wires serve as the feedstock material. An electric arc is struck between these electrically charged wires with opposite polarity and the wires are melted and atomized by externally compressed air and finally the stream of atomized melted particles are propelled onto the prepared surface to be coated. The electric arc spray coatings are denser and stronger when compared to flame spray coatings. Low running costs with high deposition rates are the main
advantages of the wire arc plasma spraying. Metal and metal alloys can be coated on large surface area with high production rate (Davis 2002).

Arc plasma spraying (APS)

Plasma is commonly called as the fourth state of matter. Besides solid, liquid and gaseous states, partially ionized gas is termed as the plasma state because of its distinct behavior from gas. According to Professor Chen (1985) “plasma is quasi-neutral gas of charged and neutral particles which exhibits collective behavior”. The striking feature that distinguishes plasma from a gas is that plasma responds to externally applied electric and magnetic fields, whereas a gas does not. Plasmas can be classified as thermal or equilibrium plasma and non-thermal or cold plasma. In non-thermal plasmas, the electron temperature is different from that of ion and neutral species temperature. In contrast to this, thermal plasmas are characterized by a single temperature; the electron, ion and neutral species are in local thermodynamic equilibrium (LTE) and therefore, they have the same temperature.

Plasma spray process uses thermal plasma medium to produce metal and ceramic coatings for various applications. In plasma spray process, an electric arc is struck between a rod type cathode and nozzle anode. When the plasma gas flows through the arc, it gets heated and plasma is initiated when electrons are accelerated from the cathode to the anode. As the electrons move towards the anode, they collide with the gas molecules and ionize the atoms or molecules in the gas. The additional electrons freed by the ionization process are also accelerated causing further ionization. These collisions transfer the kinetic energy of the electrons to the other species and raise the temperature of the gas. The hot gas comes out of the nozzle in the form of a jet, whose temperature is of the order of 15000 K.
Plasma spray technique has been used since the last four decades for development of coatings to protect critical components in corrosion and thermal barrier applications. For example, plasma sprayed yttria stabilized zirconia (YSZ) coating is widely applied as thermal barrier coatings in turbine blades and aircraft engines (Tamura et al. 1999, Cao et al. 2001, Stover et al. 2004, Vassen et al. 2008). This technique is applicable for wide range of coating materials from metal to ceramic without changing their chemical properties. The deposition rate is very high when compared to other techniques such as PVD, CVD and PECVD.

Plasma spraying utilizes the high temperature and high velocity of the thermal plasma medium to heat the coating material to a molten or semi-molten state. Any powder which is to be sprayed is injected into the plasma plume, where it is melted and accelerated towards the substrate. The stream of molten powder particles is propelled towards the desired substrate and strike the substrate surface with high velocity (~100-200 m/s). As the molten particles strike the substrate, they get anchored together to form a strong adherent coating. This technique is mainly used for preparing many protective coatings on metals and alloys for applications like corrosion barrier, thermal barrier coatings, erosion, abrasion resistant coatings, and special coatings like superconductive coatings etc (Heimann 1995). The main advantages of plasma spray process are

- Any powder which melts without sublimation can be deposited
- The substrate temperature can be as low as 50°C
- There is no restriction on the size and shape of the job
- The coating process is comparatively fast
- Coating thickness can go from few microns to millimeter. In additional reinforcement, ceramic coatings with more than 10 mm thickness can be prepared
- Adherent mechanical as well as metallurgical bonding is obtained
1.5 Operating modes of arc plasma torch

Depending on the operational necessity and the mode of current transfer, arc plasma torches are divided into two types (Fig. 1.2)
1. Transferred arc plasma torch
2. Non-transferred arc plasma torch

Figure 1.2 Schematic of operating modes of plasma torches

1.5.1 Transferred arc plasma torch

In transferred arc plasma torch, the arc is transferred from the cathode directly to the work piece. The work piece can be metal plates (plasma cutting) or metal powder or metal scrap (plasma melting). This system is normally employed in metallurgical processes, cutting, welding, melting and verification of hazardous wastes and also for preparing overlay coatings by plasma transferred arc welding. The transferred arc plasma torch has a much higher efficiency than
the non-transferred type, since almost all the heat is directly transferred to the material to be treated.

1.5.2 Non-transferred plasma torch

The schematic diagram of non-transferred plasma torch or atmospheric plasma spray torch is shown in figure 1.3. The non-transferred arc plasma torch consists of a central cathode and an anode that is usually shaped in the form of a nozzle. The torch operates at high current and gas flow rates. The arc is generated between these electrodes, the working gas extracts the arc energy and comes out of the anode nozzle as a high temperature high velocity plasma jet. This mode is mostly used for plasma spray deposition and fine powder processing, where the thermal energy is transferred from the hot gas to the powder to be sprayed. The power of torch can vary from 1 kW to 6 MW (Pawlowski 2008).

![Figure 1.3 The schematic of cross sectioned atmospheric plasma spray (APS) torch](image)

1.6 Literature Review

Literature relevant to synthesis of lanthanum phosphate and its characterization, production methods of spray grade powders, plasma spray deposition and coatings for molten metals containments is surveyed in this section.
1.6.1 Synthesis of lanthanum phosphate and its characterization

Hexagonal hydrated LaPO$_4$ (LaPO$_4$.0.5 H$_2$O) was successfully synthesized by Horvath et al. (1988) by precipitation method. The authors followed the chemical route of synthesis and used 0.2 M solutions of Ln(NO$_3$)$_3$ and NH$_4$H$_2$PO$_4$ at pH 8-9. Thermogravimetric analysis and differential thermal analysis (TGA-DTA) results showed that two distinct steps of dehydration occurred during heating up of the hydrated powder to 300 °C. The first step (~200 °C) indicated the release of physically bound water, whereas the second step (~250 °C) indicated the escape of zeolitic water at higher temperature. This dehydration temperature is found to depend on ionic radius of rare earth phosphate and it is found to decrease with decrease of the ionic radius of Ln$^{3+}$ in the sequence of La>Nd>Eu>Gd>Tb.

Glorieux et al. (2004) synthesized lanthanum phosphate by chemical route and the starting materials used were lanthanum nitrate solution and aqueous phosphoric acid. Hydrated lanthanum phosphate having the rhabdophane structure (LaPO$_4$.0.5H$_2$O) of lanthanum phosphate was formed in this process by the following reaction (1.1):

$$\text{La(NO}_3\text{)}_3 + \text{H}_3\text{PO}_4 \rightarrow \text{LaPO}_4 \text{ 0.5H}_2\text{O} + \text{HNO}_3$$  (1.1)

X-ray diffraction (XRD) results indicated hexagonal structure in the temperature range of 100-400 °C and it transformed to the monoclinic structure formed beyond 700 °C. TGA showed substantial weight loss from room temperature to about 280°C and the weight loss associated corresponds to 0.5 mol of water molecules from hydrated LaPO$_4$. The authors carried out differential thermal analysis from room temperature up to 1200 °C to study the phase stability of lanthanum phosphate. The endothermic peak with less intense was
observed at 450 °C might be mainly attributed to the evaporation of hydroxyl groups. No exothermic or endothermic peak indicating phase change or reaction was observed beyond 700 °C and this evidenced that LaPO₄ is stable compound at higher temperature. The DTA result did not show any thermal effect during cooling suggesting that the monoclinic phase was stable and did not transform to the hexagonal phase. In other words, it was observed that the transition from hexagonal to monoclinic is thermally irreversible. The authors also conducted melting studies on 1 g of LaPO₄ using 2 kW solar heating furnace for different time periods of melting. According to the XRD results of melted samples, samples melted for one second showed LaPO₄ but with a change in crystallinity. However, continued melting for longer duration led to formation of new phases accompanied by loss of P₂O₅. It was observed that samples melted for 30 seconds showed other phases like La₇P₃O₁₈ and La₃PO₇ due to loss of P₂O₅ molecules from LaPO₄.

Onoda et al. (2002) showed that it was possible to synthesize monazite-type orthophosphate at lower temperature by reacting La₂O₃, lanthanum chloride, nitrate and other compounds of La and H₃PO₄. LaPO₄ was formed in all systems except for LaF₃–H₃PO₄. FTIR spectrum of LaPO₄ prepared by La(NO₃)₃·9H₂O–H₃PO₄ indicated a new absorption peaks at 1400 cm⁻¹ and this peak was attributed to the unreacted or residual nitrate (NO₃) present in the sample.

Nano powder of lanthanum phosphate was prepared by Lucas et al. (2004) using aqueous solutions of rare earth chloride LaCl₃·7H₂O, (NH₄)₂HPO₄ and H₃PO₄. The precipitates thus obtained were washed and centrifuged until excess of phosphoric acid was removed from the precipitate, then finally the precipitates were dried at 80 °C. FTIR spectra of precipitated samples showed absorption peaks at 542, 570, 615, 960, 1015, and 1050 cm⁻¹. These bands are characteristic of phosphate groups in the hexagonal phase, whereas the bands around 3550 and
1630 cm\(^{-1}\) were assigned to vibration peaks of H\(_2\)O molecules. Lanthanum phosphate annealed at 1000 °C confirmed the monazite phase. The authors also observed a minor diffraction peak at 2\(\theta\) of 24.1° due to the presence of polytrioxophosphate (LaP\(_3\)O\(_9\)) in very small quantity. Formation of this secondary phase may have major influences and play a major role in properties of the final product.

The rare earth phosphates (RPO\(_4\), R- La, Ce, Pr, Nd, Sm, Eu and Gd) were also prepared by solid state reaction method by Damien et al. (2007). In this process, lanthanide oxide and phosphate precursor (NH\(_4\)H\(_2\)PO\(_4\)) were used as the starting materials. The resulting synthesized powder was characterized by XRD, magic angle spinning NMR (MAS NMR) and TG/DTA. The preparation of orthophosphate from NH\(_4\)H\(_2\)PO\(_4\) and lanthanide oxide was described by the following reaction (1.2)

\[
\frac{1}{2}\text{La}_2\text{O}_3 + \text{NH}_4\text{H}_2\text{PO}_4 \overset{1350 \degree\text{C}}{\longrightarrow} \text{LaPO}_4 + \text{NH}_3 \uparrow + \frac{3}{2}\text{H}_2\text{O} \uparrow
\] (1.2)

According to the XRD results, the secondary phases (LaP\(_3\)O\(_9\) and La\(_3\)PO\(_7\)) were also formed along with LaPO\(_4\) up to 1300 °C. Single phase lanthanum orthophosphate was obtained when the reactants were heated at 1350 °C for 2 hours.

Thermal stability of rare earth phosphate (RePO\(_4\) nH\(_2\)O) was studied up to 1100 °C using high temperature XRD by Lucas et al. (2004). Phase transformation of the hexagonal rabdophane phase to the monoclinic monazite phase was observed at 600 °C. High temperature XRD results also confirmed phase stability of LaPO\(_4\) up to 1100 °C. TG-DTA results showed the formation of anhydrous monoclinic LaPO\(_4\) at about 600 °C and also confirmed that this transition was irreversible.
Ruigang et al. (2003) prepared anhydrous lanthanum phosphate by solid-liquid chemical reaction of lanthanum oxide and phosphoric acid with weight ratio of 1:1 (La:P). They studied the microstructure of sintered LaPO$_4$ and bonding characteristics of Al$_2$O$_3$/LaPO$_4$ composite to obtain machineable ceramic.

Dong-Hau et al. (1996) investigated weak interface of LaPO$_4$ with Al$_2$O$_3$, Y$_3$Al$_2$O$_{12}$ and LaAl$_{11}$O$_{18}$ for high temperature applications using tape-cast laminates and fiber model systems. LaPO$_4$ and composites of laminates were found to be chemically stable-up to 1600 °C. However, some chemical reactions were found to occur in the LaPO$_4$ and Al$_2$O$_3$ system after firing at higher temperature (> 1600 °C).

Ananthapadmanabhan et al. (2009) synthesized lanthanum phosphate by chemical route using lanthanum oxide and phosphoric acid. The prepared powder was characterized by XRD and TGDTA. Formation of LaPO$_4$ can be represented by the following chemical equation (1.3)

$$\text{La}_2\text{O}_3 + 2\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow 2\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O} + 3\text{H}_2\text{O} \quad (1.3)$$

The conversion of rhabdophane LaPO$_4 \cdot 0.5$ H$_2$O to monoclinic LaPO$_4$ was reported to occur at about 550 °C. The authors sintered the resulting powder at 1600 °C for 4 h and confirmed no phase change after sintering. The authors also reported that monoclinic to hexagonal phase transition is irreversible. The resultant powder was used for preparing plasma spray coatings.

In summary, many authors reported the preparation of lanthanum phosphate by various methods like chemical route, solid state synthesis, and sol-gel method etc., for various applications. The authors mainly concentrated on
preparation of LaPO₄ powder with particle size in nano scale range. Among the various methods studied to synthesis of LaPO₄, chemical reaction route using lanthanum oxide and phosphoric acid has certain advantages as listed below

1. It is simple and fast process
2. No reaction by-products are formed except water
3. No secondary phase has been obtained after calcination at different temperatures (within the detectable limit of XRD)
4. Finally, the yield of resultant LaPO₄ powder is very high and can be easily scaled up to large commercial quantities.

1.6.2 Production methods of spray grade powders for thermal spray deposition

Feedstock powder for thermal spray applications should meet several specifications (Nicoll and Eschuauer 1987). Particle shape, size, distribution and powder flow characteristic are important parameters of thermal spray feedstock powders. Particle size and its distribution are important parameters that decide the microstructure of the coatings. Free flowing powder ensures high efficiency of spray deposition and reduces the process cost.

There are many methods available to make thermal spray grade powders of ceramics, alloys and metals. The production methods used to produce metallic, alloy and ceramic spray grade powders are listed in table 1.1. The various methods for production of thermal spray grade powder are discussed in the following sub sections.

Spray drying method

Spray drying is used to make spray grade powder for thermal spray applications. Spray drying is a one step process involving particle formation and drying. The input of feedstock can be used as solutions, emulsions, gel or slurry. Final end-product of spray drying depends on the physical and chemical
properties of the feedstock, process parameters of spray dryer and design of atomizer as well as drying chamber. Many authors (Berger-Keller et al. 2003, Qian et al. 2009 and Bian et al. 2012) have successfully prepared plasma spray grade powders (TiO₂, Y₂SiO₅, Al₂O₃/TiO₂) using this method for plasma spray deposition.

The strength of this process is its versatility, fast processing, high quality and large volume of powder production. The disadvantages are high capital and overhead costs. Feedstock material has a tendency of clogging and sticking at the nozzle mouth and therefore, maintenance of the spray dryer’s nozzle is a major issue to be taken care of.

**Table 1.1** Common methods for production of spray grade powders (Padmanabhan et al. 2007)

<table>
<thead>
<tr>
<th>Methods for production of spray grade powder</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray drying</td>
<td>CrO₂-SiO₂, MoCrSiZrY, WC-CO</td>
</tr>
<tr>
<td>Atomization technique</td>
<td>Al, Ni, Cr, Si, Fe, B</td>
</tr>
<tr>
<td>Plasma processing</td>
<td>Al, Ni, Cr, B</td>
</tr>
<tr>
<td>sol-gel (liquid–phase technique)</td>
<td>Y₂O₃-ZrO₂, ZrO₂-Cr₂O₃, Al₂O₃-SiO₂-ZrO₂</td>
</tr>
<tr>
<td>Fusing or sintering, crushing and sieving</td>
<td>Al, Ni, Cr, Si, Fe, B, Y₂O₃, LaPO₄</td>
</tr>
</tbody>
</table>

Atomization method

Atomization process is used commonly in the manufacturing of metal and alloy spray grade powders. At first, the raw material for atomization is melted by induction heater. The melted liquid metal is then constantly supplied from the
reservoir to nozzle where the molten liquid disintegrates into individual particles by means of high pressure atomizing medium. Generally, atomizing medium used is gas or water. The stream of molten metal is split into fine droplets and fall freely through collection chamber. Atomized particles are solidified during free fall. Surface morphology of these resulting powders is spherical or near spherical (Pawlowski 2008).

Spheroidization method

Thermal plasma synthesis has been applied to generate spheroidized powders of a variety of metal and ceramic powders. The high temperature and highly concentrated enthalpy available in the plasma jet can melt and vaporize virtually any refractory material (Ananthapadmanabhan et al. 1996). The high quench rate favors homogeneous nucleation resulting in spheroidized particles. The degree of spheroidization depends on many parameters such as the plasma power, plasma gas flow rate and powder feed rate. In general, any parameter that enhances particle melting increases the extent of spheroidization. For example, as the input power increases, the extent of melting increases and therefore the spheroidization also increases. Thermal plasma spheroidization offers a viable route to synthesize free flowing powders for thermal spray applications.

The main advantages of this process are

✓ Spherical particle shapes of resultant powder
✓ High density
✓ Good flowability
✓ Versatile technique which virtually applies to metals as well as ceramic materials.

The major drawbacks are

✗ High capital equipment cost
- High power requirement
- Powder production efficiency is less
- At high temperatures of plasma jet, decomposition and change in stoichiometry of resulting spheroidized powder can take place
- High quenching rate may induce the meta-stable state.

Sol-gel method

Sol-gel process is generally used to prepare glasses and ceramic powders. In this process, metal alkoxides and nitrates are used as starting material which undergoes hydrolysis followed by condensation polymerization reactions to give product in the form of gel. This gel is finally heated to obtain the desired powder with enhanced properties. Chetterji et al. (1993) had successfully prepared thermal spray grade powder by using sol gel process for plasma spray deposition.

Advantages of sol gel process are
- Control on particle size and shape
- High purity of final products
- Minimization of the dust hazards normally associated with crushing and sieving.

Demerits of the process are
- High cost of raw materials
- Internal porosity reduces heat and momentum from plasma jet to particles
- Longer reaction times
- Organic solvents and by-product may be harmful to the human body.

Sintering and crushing method

It is a very simple and versatile technique for spray grade powder production. Oxide, carbide and cermet powders can be manufactured by fusion (or sintering) followed by crushing and sieving. Virtually any material can be
processed via this method. Here sintering is a process of heating a solid compact of fine powders at a temperature below its melting point. Sintering temperature of the compact varies with the material. Spray grade powders produced by this method are generally blocky and irregular in shape which reduces the flowability (Padmanabhan et al. 2007) of powder.

However this method has following advantages

- Very simple method
- High density powder
- Low capital equipment cost
- Possible to produce in bulk quantity.

Disadvantages include the following

- Final product is blocky and irregular
- Relatively low flowability
- Difficult to control the particle shape and size.

In this dissertation work, crushing and sieving method is used for production of spray grade lanthanum phosphate powder for plasma spray deposition.

1.6.3 Plasma spray deposition and coating characterization

Plasma spraying has been applied to develop metal, alloy and ceramic coatings for a variety of high-tech applications (Cao et al. 2001, Julie et al. 2001, Anand et al. 2005, Stover et al. 2006, Vassen et al. 2007, Vassen et al. 2008, Julie et al. 2010). Literature on plasma sprayed coatings is so large that it would be difficult to cover the entire spectrum of coating studies carried out for various applications. Therefore, literature on plasma sprayed coatings relevant to the subject matter of the thesis is covered in this section. In particular, the deposition process and influence of various input parameters on phase, and microstructure and corrosion properties of the coatings are discussed.
Yin et al. (2011) discussed the effect of thickness of plasma sprayed Al$_2$O$_3$ coatings on stainless steel substrates. It was observed that porosity of Al$_2$O$_3$ coating increased with increasing thickness of the coating. Hence, the microhardness and corrosion resistance of the coating were found to decrease with increasing thickness. Low porosity and high hardness with good corrosion resistance against H$_2$SO$_4$ solution were achieved with 160 µm thick coating.

Guoliang et al. (2011) prepared WC-(W,Cr)$_2$C-Ni coatings using atmospheric plasma spray technique with different input powers. They investigated microstructure and mechanical properties (friction and wear behaviors) of the plasma spray coatings. They observed that at higher power level decomposition of WC was promoted, which decreased the hardness whereas coating prepared at moderate spraying power gave the highest fracture toughness and hardness.

Plasma-sprayed coatings of alumina-titania powder (60%:40%) was prepared by Ananthapadmanabhan et al. (2003) and Shanmugavelayutham et al. (2006) at different power levels. The input power of plasma spray deposition influenced the chemical composition of the resultant coatings. At high power, the aluminium oxide content in the coating increased. The hardness and wear resistance of the coatings were strongly influenced by coating composition and plasma input power. They increased with increasing plasma input power and alumina content in the coating.

Ramachandran et al. (1998) prepared different compositions of alumina-titania composite coatings by atmospheric plasma spraying at different power levels. The phase, microstructure and mechanical properties of the coatings were evaluated and correlated with input power levels.
Tong et al. (1996) and Cheang et al. (1996) studied the effect of particle size on crystallinity of hydroxyapatite (HA) plasma sprayed coatings. The results showed that crystallinity of coatings fluctuated with particle size and additional phases were found in coatings sprayed with smaller particles.

The effect of stand-off distances (SOD) (100–300 mm) on microstructures and mechanical properties of plasma sprayed neodymium iron boron (Nd–Fe–B) coatings was investigated by Gan et al. (2013). At chosen input parameters, the critical SOD was found as 150 mm and below which particles were not sufficiently melted and above which particles started to resolidify. At the SOD below and above 150 mm, the deposition efficiency and porosity of the coatings were decreased and increased respectively.

The effect of plasma spraying parameters (viz. power, powder feed rate, scanning speed of torch and number of cycles) on microhardness, thickness and porosity of alumina - titania composite coatings as well as deposition efficiency were studied by Forghani et al. (2013). As discussed earlier, higher power enhanced the fraction of melted particles in feedstock powder, which produces dense coatings with higher deposition efficiency. Hardness and thickness of the coatings also increased with increasing plasma input power.

The effects of critical plasma spraying parameters (CPSP) on different crystallographic forms of alumina were investigated by Aruna et al. (2011). They reported the influence of CPSP on microstructure, microhardness, surface roughness and wear behavior of the plasma sprayed alumina coatings. The coating prepared using γ-alumina powder exhibited a change in the preferred orientation from [113] to [104] with increasing CPSP whereas α-alumina did not exhibit any such change in preferred orientation. The coating deposited with a moderate CPSP exhibited maximum wear and corrosion resistances, moderate microhardness and less than 10% spallation for 700 thermal cycles.
Padmanabhan et al. (2007) prepared thermal spray grade yttrium oxide powder by sintering, crushing and sieving. The reported flowability (tested as per standard method) of $Y_2O_3$ was 30 g/min. The synthesized $Y_2O_3$ powder with particle size in the range of 38-75 μm was used for plasma spray deposition. The deposition efficiency was found to increase with increasing input power. The maximum deposition efficiency of 40 % was obtained with 26 kW of input power.

1.6.4 Plasma spray deposition for corrosion barrier applications

Corrosion is a more significant problem in industries and results in degradation and failure of many components, thus decreasing their service life. Various technologies can be used to deposit an appropriate surface protection layer that can resist the corrosion under specific conditions. Ashary et al. (1991) and Berndt et al. (1992) reported that atmospheric plasma spray technique can be used to deposit a corrosion protective layer of thickness ranging from 30 μm to several mm.

The effect of the plasma spray coating on components for corrosion resistance of sulfate-vanadate in molten salt environment at 900 °C in air was investigated by Longa-Nava et al. (1995). The Cr-Ni-2.5Mo-1Si-0.5B alloys containing 55 and 58 wt% chromium were coated by APS. Plasma spray coatings exhibited good resistance against molten salt film attack with a maximum penetration of 100 μm after 70 hours.

Plasma sprayed yttrium oxide coatings on graphite substrates were prepared by Chakravarthy et al. (2014). Coatings were characterized for phase composition, microstructure and thermal stability. Dense and adherent coatings could be deposited at 24 kW power. Corrosion behaviour of the coatings in
molten uranium was studied by using differential thermal analysis (DTA) up to 1473 K. The results showed that the coatings offered sufficient protection to graphite against corrosion by molten uranium. Penetration of liquid uranium into pores depends on the surface tension and the contact angle. The rate of capillary penetration of liquid metal into the pores can be explained using Washburn equation (1.4)

\[ \frac{dh}{dt} = \left( -\frac{1}{\rho g h} \right) [\Delta p - \rho gh] r^2 \]  \hspace{1cm} (1.4)

where,
- $\rho g h$ Static pressure exerted by the liquid,
- $\mu$ Viscosity of the liquid,
- $\rho$ Density of the liquid,
- $r$ Capillary radius,
- $h$ Distance of penetration of liquid into the capillary,
- $g$ Acceleration due to gravity,
- $\Delta p$ Capillary pressure.

The authors calculated that the pressure required for liquid uranium to penetrate into the pores is 0.169 MPa by using Washburn equation.

Atmospheric plasma sprayed yttrium oxide coatings were successfully prepared by Nagaraj et al. (2011) for uranium metal corrosion barrier applications. Yttrium oxide coating on tantalum substrate was prepared and it was found that the coating provides stable protective barrier against liquid uranium at 1573 K up to 80 hours. Reaction products were not observed at the uranium/yttrium oxide interface and it was confirmed from EDX results that uranium is unable to diffuse into plasma sprayed yttrium oxide coating.
Corrosion studies were performed by Jagadeesh et al. (2012) on coated and uncoated high density graphite in molten LiCl–KCl salt mixture at 600°C for periods of 250, 1000 and 2000 hours under inert argon atmosphere. Partially stabilized zirconia (PSZ) was coated on graphite using atmospheric plasma spray technique with a bond coat of NiCrAlY. There was no degradation or attack observed on the coated sample under the test conditions. However, Ananthapadmanabhan et al. (2015) reported using Gibbs free energy minimization data that ZrO$_2$ and Al$_2$O$_3$ may not be kinetically stable with molten metal for longer duration at higher temperature.

Seung-Ho et al. (2011) prepared plasma sprayed composite coatings of 3YSZ/LaPO$_4$ for thermal barrier coatings (TBC) application. The authors also studied the phase structure of the plasma spray deposits and observed that LaPO$_4$ retained its monoclinic phase.

Ananthapadmanabhan et al. (2009) successfully prepared lanthanum phosphate powder (spray grade) using chemical route and coatings on stainless steel and graphite substrates using plasma spray technique. The adherence between coating and substrate achieved was reported to be good for coating prepared at 24 kW. The compatibility test between LaPO$_4$ and Uranium was conducted by using DTA. Author confirmed that no reaction was occurred between molten uranium and LaPO$_4$.

1.6.5 Summary

A comprehensive survey of literature including synthesis and properties of lanthanum phosphate, effect of plasma spray parameters on microstructure, hardness and phase etc of the coatings as well as corrosion studies on plasma spray deposited samples with different molten metals is given in this chapter. The salient research aspects derived from the literature are listed below:
Lanthanum phosphate can be prepared by chemical, solid state and sol-gel methods. Chemical method that uses La$_2$O$_3$ and phosphoric acid is the simplest process among all. This process can give lanthanum phosphate directly without any byproduct except water and can be easily scaled up for large quantities.

Plasma spray grade powder can be prepared by combustion, plasma spheroidization and sintering-crushing methods. The sintering and crushing is the simplest method among all. This technique is highly versatile and can be applied to any material.

Adherent coatings of LaPO$_4$ and its composite with YSZ have been prepared on stainless steel and graphite substrates by using atmospheric plasma spray technique.

Plasma sprayed coatings of various materials have been successfully tested against the molten metals. Penetration of liquid metal into pores is explained by Washburn equation and required pressure is found to be 0.169 MPa calculated by using this equation. Plasma sprayed yttrium oxide coatings and lanthanum phosphate coatings have been found to offer sufficient protection to the substrate against corrosion by molten uranium.

1.7 Objectives

Uranium is highly reactive with most of the refractory materials when it is in molten state. Therefore, lifetime of components used for processing of uranium reduces due to corrosion by uranium. Consequently, protective ceramic coatings are required on the container to prevent its reaction with uranium. Rare-earth lanthanum phosphate ceramics have been widely studied and their phase and chemical stability has been demonstrated up to 1600 °C. Lanthanum phosphate has high melting point, low thermal conductivity, high thermal expansion co-efficient (compared to other ceramics) and chemical
inertness to most of the chemical environments, which makes this material a promising candidate for corrosion and thermal barrier applications.

In this study, we anticipate that lanthanum phosphate coatings would exhibit significant properties and corrosion resistance against molten metal. Atmospheric plasma spraying (APS) technique is used for depositing lanthanum phosphate coatings due to the high enthalpy and temperature available in the plasma jet. In view of the advantages of APS, it has been identified as the most suitable method to prepare LaPO$_4$ coatings for high temperature corrosion resistance against molten metal.

There is hardly any literature available on plasma spray deposition of lanthanum phosphate. To the best of my knowledge there is no study on plasma sprayed coatings of lanthanum phosphate powder except Ananthapadmanabhan et al. (2009). However, the authors presented preliminary research work on plasma spray coated lanthanum phosphate and its characterization. Hence, detailed studies on the same are required. Therefore, it is decided to prepare and characterize LaPO$_4$ powder and coatings as well as to study the corrosion behaviour of the plasma sprayed coating with molten uranium. The objectives of the thesis work are

1. Synthesis and characterization of LaPO$_4$ powder
2. Preparation of sprayable LaPO$_4$ powder
3. Investigation of thermal stability of LaPO$_4$ powder by using transferred arc and non-transferred arc plasma techniques
4. Preparation of LaPO$_4$ coatings by atmospheric plasma spray technique and characterization of LaPO$_4$ coatings
5. Investigation on plasma sprayed LaPO$_4$ coatings for molten metal corrosion barrier applications.
The thesis is divided into six chapters and the contents of each chapter are given below:

**Chapter 1: Introduction and literature survey**

LaPO$_4$ properties and advantages as a corrosion barrier material are discussed. In addition to this, various coating methods are presented. Further it includes a detailed literature survey for the proposed work. The objectives of the thesis are listed at the end of the chapter.

**Chapter 2: Synthesis and characterization of lanthanum phosphate**

The synthesis and characterization of lanthanum orthophosphate and production of spray grade lanthanum phosphate powder are discussed.

**Chapter 3: Thermal stability of lanthanum phosphate**

Thermal stability of lanthanum phosphate is reported using transferred arc melting and non-transferred arc plasma melting techniques. In addition, the experimental setup of transferred and non-transferred arc plasma is also explained.

**Chapter 4: Plasma spray deposition and characterization of lanthanum phosphate coatings**

This chapter presents the preparation and characterization of plasma spray deposited lanthanum phosphate. Characteristic of coatings are studied by X-ray diffraction, FTIR, Raman spectroscopy, Scanning electron microscopy, Tensile adhesion test and the results are presented.

**Chapter 5: Corrosion and compatibility studies of plasma spray coated lanthanum phosphate against molten uranium**

Compatibility and corrosion studies of plasma spray coated lanthanum phosphate with molten metal uranium are presented.
Chapter : Conclusions and scope for future work

The conclusions derived from the present investigation are given. In addition to this, scope for future work is also added.