CHAPTER 1

INTRODUCTION

1.1 SURFACE ENGINEERING

Surface engineering is a sub-discipline of Materials Science which deals with the surface of solid matter. It has applications in the area of Engineering, Space Science, and Chemistry and so on.

Solids are composed of a bulk phase and covered by a surface phase. The surface phase is an interface to the bulk of the material and the surrounding environment. The surrounding environment interacts with the bulk phase through the surface phase. Variations in the nature of environment such as acidic, alkaline, etc., can degrade the surface phase over time. Environmental degradation of the surface phase over time can result in surface wear, corrosion, fatigue, creep and oxidation. Surface engineering involves altering the properties of the surface phase in order to reduce the magnitude of degradation over time. This is accomplished by making the surface robust to the environment in which it will be used. Surface engineering techniques are used to develop a wide range of changes in functional properties including physical, chemical, electrical, electronic, magnetic, mechanical, wear resistance and corrosion resistance properties at the required substrate surfaces. Almost all types of materials including metals, ceramics, polymers and composites can be coated on different materials. It is also possible to form coatings of newer materials such as metallic glass, functionally graded deposits, multicomponent deposits, diamond, etc., on various substrates.
Surface engineering of aluminum is an offshoot of the major field of surface engineering of metals, where developments are taking place at a rapid rate. Aluminum has proved to be a very useful material for aerospace and automobile applications, owing to its good strength and low density. For example, IC engine pistons, cylinder blocks, pump bodies, gear box casings etc., are being made by aluminum alloys.

Applying coatings on surfaces is one discipline of surface engineering. Coatings are applied to surfaces of materials for various reasons. Corrosion, oxidation and wear resistance are only a few examples. There are different techniques for applying a coating onto a substrate, such as chemical and physical vapor deposition, sol-gel, electro-deposition, dip coating, and thermal spray. For different applications, a specific method should be chosen according to deposition rate, desired microstructure, cost, final surface finish and so on.

1.2 METHODS OF SURFACE TREATMENT ON ALUMINUM

In order to improve surface properties of final products, such as wear resistance, corrosion resistance, reflectivity, color etc., different types of surface treatments were designed. The large number of treatments in existence can be broadly classified into electrochemical methods, chemical methods, coatings and some latest techniques.

1.2.1 Electrochemical Treatment

Electrochemical brightening, electro polishing, anodization and its variants, like clear anodization, color anodization, bright anodization, protective anodization, decorative anodization, architectural anodization, hard anodization etc., fall in this category. All these methods use the electrolysis process for improving the decorative finish of objects or for enhancing the
mechanical properties like wear resistance, corrosion resistance or hardness of the surface.

1.2.2 Chemical Treatment

Chemical brightening, chemical polishing, degreasing, etching and pickling fall in this category. These methods use chemical methods to enhance the finish or roughen surfaces.

1.2.3 Coating

Organic coating, coil coating, chemical conversion coating, priming, single coat system, multiple coat system, film coating, lacquering and painting fall in this category. The coating methods include liquid or powder coating, priming, painting, film coating, dipping, spraying, etc., to improve the finish, appearance, corrosion resistance of the base metal. These methods again suffer from lower performance and life for demanding engineering applications.

1.2.4 Other Methods

Laser induced surface modifications enhances the wear and scuffing resistance by micro structural changes in the surface, but other properties like corrosion resistance and thermal shock resistance are not improved.

1.3 CERAMIC COATINGS ON ALUMINUM

Ceramic composite coatings have been developed which is a low cost method with tribological effectiveness. Heat treatment of the ceramic coated components is generally not required. Aluminum properties are such that one must carefully observe changes in physical properties of aluminum such as creep, aging, stress/strain and other important properties dependent
upon temperature. Therefore a ceramic coating possessing low curing temperatures is highly desirable. Ceramic coatings methods on aluminum can be grouped as follows:

- Plasma spraying of ceramic powders using a plasma spray system
- Laser cladding of yttria partially stabilized zirconia (YPSZ) ceramic coatings on aluminum alloys.
- Micro arc oxidation in an alkali silicate electrolytic solution for wear, corrosion resistance and microstructure improvement. Thick and hard ceramic coatings are produced in this method.
- Organo-metallic phosphate coating developed recently is a low cost and improved method for engine applications.
- Laser surface engineered (LSE) ceramic coating
- Micro plasma technology
- Ion Plasma deposition of coatings
- Electron beam powder metallurgy technology
- PEO (Plasma electrolytic oxidation ) coatings

Among these methods, thermal spray process sales are increasing regularly. Thermal spraying techniques may continue to grow as they are more environmentally friendly than some competitive coating techniques and full of undiscovered potentials. The air plasma spray technique (APS) is the most commonly used thermal spray process.

Ceramic materials generally applied are aluminum oxide, silicon nitride, titanium nitride, silicon carbide and titanium carbide. One such application of the plasma spray process is the coating of IC engine components.
1.4 IC ENGINE APPLICATION

The idea of thermally insulating the engine is as old as the internal combustion engine itself and is based on the knowledge that only 30-40% of the entering fuel energy is converted to useful work on the output shaft (Evans 1987). Thermal barrier coatings (TBC’s) applied on the piston crown and skirt and cylinder head of an engine made of cast aluminum, completely insulate the combustion chamber and allow improved combustion of the fuel, thereby improving the thermal efficiency of the engine and at the same time reducing the emission of unburnt carbon and other hazardous elements through the exhaust (Parvathi 2003). TBC’s when applied to the top of the pistons will increase the combustion temperature, due to the ceramic nature of the coating. It acts like a thermal barrier, reducing the amount of heat transfer into the piston and combustion chamber (Parvathi 2003). This effect produces more power and better fuel efficiency. Reducing the temperature at the top of the piston allows cooler running pistons, rings, oil and water, maintaining ring tension and leading to higher compression and lower oil consumption over a wider operating range. Temperature reductions of 50 to 80°C is possible in the metallic parts under normal operating conditions which is useful to achieve longer engine lives and to improve the performance of the engines at higher operating temperatures (Parvathi 2003). One of the major causes of piston failure is detonation. When a ceramic coating is applied to a piston top and the combustion chamber, it will increase the heat retained by combustion and this in turn may cause bad detonation.

In the 1980’s there was an effort to use thermal barrier coatings in diesel engines in pursuit of advantages, including higher power density, fuel efficiency, reducing specific fuel consumption, emissions and noise, improving the engine life and cold start reliability, and multifuel capacity due to higher combustion chamber temperature- 650°C to 900°C (Ramaswamy et al 2000,
Zhu and Miller 1999, Winkler and Parker 1992, Beardsley 1997). The goal was to have an engine with 48% thermal efficiency rather than the ordinary 33% (Churchill et al. 1988). Plasma spraying has been observed to be the most common method of depositing TBCs for diesel applications. It creates a splat structure with 10-20% volume fraction of voids and cracks. The high porosity of this structure makes it an ideal choice for TBCs.

Surface engineering, in general, and plasma surface engineering, in particular, can play an important role in helping to achieve both objectives of enhancing the engine efficiency and of decreasing the vehicle weight (Merlo 2003). Thermal barrier coatings were evaluated for component durability, as well as providing a means of lowering heat rejection (Pierz 1993). Partially stabilized zirconia ceramic thermal barrier coatings were plasma sprayed over a MCrAlY (M = metal – iron, nickel or cobalt) bond coat on the valve faces and tulips, piston crowns and cylinder heads of two medium speed diesel engines to a specified total thickness of 0.015 inches (0.4 mm). Coating performance analyses were carried out on several parts after service. Coatings applied to piston crowns and cylinder heads generally performed in an acceptable manner. One type of coating on a valve face performed well without coating loss or degradation. Two other types of coatings on valve faces failed for identifiable reasons. Overall, the durability of the coatings in a diesel engine combustion zone operating environment was promising (Allan Levy and Stuart Macadam 1987). Impregnation of plasma-sprayed Y$_2$O$_3$-ZrO$_2$ with chromium markedly improved its wear resistance (Allan Levy et al. 1985). 250 μm thick 8YPSZ (8% yttria partially stabilized zirconia) TBC on 50 μm NiCrAlY bond coat was deposited on the top surface of the piston and cylinder head of a two-wheeler motor vehicle consisting of a two-stroke engine. Endurance tests and laboratory performance tests were conducted. A trend of marginal improvement in the hydrocarbon emission levels was
reported by Parvathi (2003). In one study, a single cylinder engine with variable ER/CR ratio was analyzed for its performance when copper coating is done on the surface of cylinder head-piston combination. Improvement was noticed in the brake thermal efficiency of 4% compared to that of standard engine. The SFC of the copper coated engine was reduced by 0.8 kg per Kw-h compared to that of standard engine, reported by Krishnamoorthy and Chandrasekeran (2007).

1.4.1 Turbine Engines, Diesel Engines and Petrol Engines: Similarities and Differences

The service environment of the coating in the turbine is markedly different from that in the diesel engine. In the former, the service temperature is high (1000-1100°C). The super alloy substrate’s maximum service temperature is about 800°C (Padture et al 2002). The thickness of coating is a few hundred microns and the coating is applied to protect it against oxidation, hot corrosion, thermo mechanical fatigue, and creep. Due to the high substrate temperature, oxidation of the bond coat and creep play major roles in coating failure.

In the diesel engine the gas temperature, currently less than 650°C, would ideally approach 900°C (Ramaswamy et al 2000, Zhu and Miller 1999). The substrate temperature is limited to approximately 200°C and therefore a thick coating (at least 1 mm) is required, which leads to a large thermal gradient. In a thick thermal barrier coating (TTBC), the bond coat temperature is too low for severe oxidation and creep (Kokini et al 1996). Due to the frequent on/off nature of the diesel engine operation, the thermal barrier coating in a diesel engine experiences more transient mode conditions than in a turbine engine. These differences in service conditions and coating thickness result in different failure mechanisms, primarily thermo cyclic
fatigue and thermal shock in the TTBC. Although several systems have been used as TBCs for different purposes, yttria-stabilized zirconia with 7-8% yttria has received the most attention (Samadi and Coyle 2004, Cao et al 2004). Several factors play important roles in overall TBC performance including thermal conductivity, micro structural and chemical stability at the service temperature, creep resistance, and the coefficient of thermal expansion (CTE).

In the case of petrol engines, the combustion temperatures are still lower and hence not much of performance enhancement can be expected, but the ceramic coating improves the emissions and the life of the substrate and a thicker coating is preferable as in the case of diesel engines. In any case, an attempt has been made in this thesis, to study an alternate material to stabilized Zirconia, i.e., mullite and its effect on the petrol engine performance. If tangible results are obtained, the same coating can be applied on diesel engines as well to have a still better performance of these engines.

The performance testing of the engine in this study has been tested as per the text written by Michael Plint and Anthony Martyr (1999), and standard laboratory practice.

1.5 INTRODUCTION TO MULLITE

1.5.1 Need for Mullite

Its low oxygen diffusivity, low creep rate at high temperatures, high thermo-mechanical fatigue resistance makes it an ideal choice for many applications.

In thin coatings (up to a couple of hundred microns) on top of a metallic substrate, the durability of mullite as a TBC has been reported to be
better than that of zirconia (Pierz 1993). The low CTE of mullite is an advantage relative to YSZ (Yttria stabilized zirconia) in high thermal gradients and under thermal shock conditions. However, the large mismatch in CTE with metallic substrate leads to poor adhesion. This problem can be solved by using a bond coat. Mullite has excellent creep resistance. The strain rate for mullite was reported to be $1.32 \times 10^{-20}$ s$^{-1}$ vs. $3.25 \times 10^{-7}$ s$^{-1}$ for YSZ at 800°C and $\sigma = 100$ MPa (Pask et al 1987). Like cordierite, mullite is sensitive to cooling rate and mostly amorphous as deposited (Schneider et al 1994). In service recrystallization occurs at 750 -1000°C, which is accompanied by a volume contraction, cracking, and top coat debonding. A solution is to heat the substrate to 1000°C, which is, however, not possible for most metallic substrates. However if the service temperatures are well below 600°C, the coating is safe.

Mullite is one of the most important ceramic materials used in applications of ceramic science and technology. Mullite is a strong candidate material for advanced structural applications at both low and high temperatures, because it has high strength at high temperature, good creep resistance, low thermal expansion and good chemical stability. Owing to its high temperature-low pressure formation conditions mullite occurs only very rarely in nature, although it sometimes can be found in high temperature metamorphosed rocks. Mullite is mainly a synthetic oxide, rare in nature, with three different preparation methods: sintered-mullite, fused-mullite and chemical-mullite -high purity mullite (Juliana Anggono 2005 ). Mullite is deposited on SiC as an oxidation resistant layer to form an environmental barrier coating (EBC). Its low oxygen diffusivity, low creep rate at high temperatures, high thermo-mechanical fatigue resistance and close CTE match with SiC ($4-5 \times 10^{-6}$K$^{-1}$ vs. $5-6 \times 10^{-6}$ K$^{-1}$) makes it the ideal choice for this application (Basu et al 2007)
1.5.2 Chemistry of Mullite

The composition of mullite is commonly denoted as \(3\text{Al}_2\text{O}_3 - 2\text{SiO}_2\) (71.83 wt. % of \(\text{Al}_2\text{O}_3\)). It is actually a solid solution with the equilibrium composition limits of 60 – 63 mol% \(\text{Al}_2\text{O}_3\) below 1600°C. However, commercially available mullite which is a solid solution generally consists of 71-76 wt. % \(\text{Al}_2\text{O}_3\), 23 – 24 wt. % \(\text{SiO}_2\), and small quantities of \(\text{TiO}_2\), \(\text{Fe}_2\text{O}_3\), \(\text{CaO}\) and \(\text{MgO}\). Stoichiometric (\(3\text{Al}_2\text{O}_3 - 2\text{SiO}_2\)) mullite can be produced without a glassy grain boundary phase which results in high strength being maintained at high temperatures. As the composition moves away from stoichiometry a glassy grain boundary phase forms, reducing the material’s strength, and lowering the maximum use temperatures (Juliana Anggono 2005). Mullite is the mineralogical name given to the only chemically stable intermediate phase in the \(\text{SiO}_2\)- \(\text{Al}_2\text{O}_3\) system. Mullite is a good, low cost refractory material which can be prepared easily.

1.5.3 Crystal Chemistry of Mullite

The crystal structure of mullite (nominally \(3\text{Al}_2\text{O}_3 - 2\text{SiO}_2\)) is orthorhombic with unit cell dimensions \(a = 0.754 \times 10^{-9} \text{m}, b= 0.7680 \times 10^{-9} \text{m}\) and \(c = 0.2885 \times 10^{-9} \text{m}\) for the stoichiometric composition (Angel and Prewitt 1986). Mullite possesses a defect crystal structure (Burnham 1964), consisting of chains of slightly distorted Al-O octahedral which run parallel to the c-axis of the orthorhombic unit cell. These chains are linked by discontinuous double chains of Al-O and Si-O tetrahedral with randomly distributed aluminum and silicon atoms (Juliana Anggono 2005). Mullite (\(3\text{Al}_2\text{O}_3 - 2\text{SiO}_2\)) usually forms elongated needle-shaped crystals with a density of 3.03 g/cm. This defect structure accommodates no-stoichiometry and the average composition of mullite may range from close to \(3\text{Al}_2\text{O}_3 - 2\text{SiO}_2\) to \(3\text{Al}_2\text{O}_3 - \text{SiO}_2\), commonly denoted as 3:2 and 3:1.
1.5.4 Properties of Mullite (3Al$_2$O$_3$ . 2SiO$_2$)

Mullite has the following important properties (Juliana Anggono 2005):

- Good high temperature strength, stability and thermal shock resistance
- Low thermal expansion and thermal conductivity
- Excellent creep resistance
- Resistance to most chemical attack; it has excellent stability in acid metal slags and is insoluble in most acids
- Resistance to oxidation and attack by furnace atmospheres
- Resistance to abrasion
- Good electrical resistivity
- The approximate limiting temperatures of use are 1800°C in air and 1600°C in vacuum
- Low dielectric constant

Mullite has been used for high-temperature exposed parts because of its good creep resistance and high compressive strength at elevated temperature. The slow diffusion kinetics which makes the material so difficult to sinter also imparts excellent high temperature microstructural stability. Flexural strength and creep resistance at elevated temperatures are significantly affected by the presence of glassy boundary inclusions; in the absence of grain boundary glassy phase, polycrystalline mullite retains > 90% of its room temperature strength to 1500°C (Mah and Mazdiyasni 1983, Kanzaki et al 1985, Ismail 1986, Ismail 1987, Kumazawa 1990, Ohnishi 1990) with excellent thermal shock resistance, and low thermal conductivity (Becher 1991, Somiya and Hirata 1991, Nixon 1990). Depending on the
micro structural features, the low fracture toughness of mullite, typically of the order of 2 MPam$^{1/2}$ is regarded as a significant factor in limiting the potential applications. Moreover, the goal of high temperature stability requires the grain boundary to be free from glass. The processing of mullite is therefore especially important if a dense ceramic capable of fulfilling its high-temperature potential is to be achieved. A poly crystalline structure should not result during processing as this structure retains more glass. The grain boundary glass has a critical effect on high-temperature properties. Rapid softening of the glass and micro cracking can occur as the test temperature is raised. Mullite usually only has a minimal grain boundary glassy phase, if any, reducing the damaging effects of grain boundary sliding and micro-cracking. Bend strength values can vary from as low as 120 MPa to over 400 MPa. The differences can be partly explained in terms of the density achieved, the morphology of the grains and the presence of additional crystalline and amorphous phases, (Juliana Anggono 2005). Literature values of mullite are presented in Table 3.3.

1.5.5 Mullite Microstructure

The final phase constitution depends strongly on the processing conditions and substantial differences in behavior have been identified between mixing on the atomic scale compared with the 10-30 nm range (Pask 1987). These includes differences in transient phases and final phase, the presence or not of a grain boundary silica phase and the morphology of the mullite grains. The presence of a liquid silicate phase is associated with the development of microstructures having prismatic mullite grains. High aspect ratio mullite grains are typical of mullite with a residual glassy phase while equiaxed structures are associated with the absence of a grain boundary glassy phase.

Dense mullite ceramic following the fused mullite processing route results in an amorphous structure and minimal glassy phase at the grain boundaries (Juliana Anggono 2005).
Dense Mullite ceramic has an amorphous structure with few grain boundaries and defects. The grains are well interlocked. Porosity does exist in the structure due to which it has a composite structure. Mullite grains have an equiaxed structure which is associated with the absence of a grain boundary glassy phase, explaining the reason for the high temperature creep performance of mullite.

1.5.6 Limitations of Mullite

Mullite like other ceramics is brittle and has poor fracture toughness. But its brittleness can be controlled to some extent during synthesis and also by controlling the process parameters during coating. Also methods are available to reduce the brittleness of as coated layers, without sacrificing other properties.

1.5.7 Mullite Synthesis

The preparation methods can be classified into three different preparation routes as follows (Juliana Anggono 2005):

1. Sinter mullite
2. Fused mullite
3. Chemical mullite (high purity mullite)

1.5.7.1 Sinter Mullite

Mullite prepared by a conventional process, i.e. mixing powdered raw materials, and sintering was designated “sinter mullite”. Oxides, hydroxides, salts and silicates were used as starting materials. Mullitization (blending of the constituent powders and densification in a furnace) takes place by solid – solid or transient liquid phase reactions of the starting
materials by aluminum, silicon and oxygen atom interdiffusion. The mullitization temperature is controlled by the particle size of starting powders.

The starting materials of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ are usually of micrometer size and are not small enough to accomplish complete mullitization at relatively low firing temperatures within a reasonable duration of time. For example, the mullitization temperature was reported to be higher than 1400°C when quartz particles below 2µm in size and $\text{Al}_2\text{O}_3$ particles with the average particle size of 0.3 – 0.5 µm were used (Hamano 1986).

1.5.7.2 Fused – Mullite

The term fused mullite describes mullites which have been produced either by melting the raw materials in an electric furnace above 2000°C with subsequent crystallization of mullite during cooling of the bath, or by Czochralski crystal growth techniques (Guse and Mateika 1974). The aluminum silicate melt obtained is then cast into ingot molds and cooled to room temperature. Raw materials for fused –mullite ceramics and refractories are alumina, quartz sand, rock crystals and fused silica. The impurity level of the raw materials is relatively low.

1.5.7.3 Chemical Mullite

Mullite powders prepared by advanced processing, eg.sol-gel (The sol-gel process, also known as chemical solution deposition, is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (or sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers), spray pyrolysis (a method in which a thin film is deposited by spraying a solution on a heated surface, where the constituents react to form a chemical compound), chemical vapor deposition (CVD) techniques are designated ‘Chemical Mullite’. The general approach to
powder processing involves mixing of the $\text{Al}^{3+}$ and $\text{Si}^{4+}$ on scales ranging from the atomic to the micron level (Okada and Otsuka 1990).

### 1.5.8 Mullite phase diagram

The phase diagram of mullite is shown in Figure 1.1 (Kolomeitsev et al 1992).

![Figure 1.1 Mullite phase diagram](image)

The composition of mullite is commonly denoted as $3\text{Al}_2\text{O}_3 - 2\text{SiO}_2$ (71.83 wt. % of $\text{Al}_2\text{O}_3$). The phase diagram shows stoichiometric ($3\text{Al}_2\text{O}_3 - 2\text{SiO}_2$) mullite which can be produced without a glassy grain boundary phase resulting in high strength being maintained at high temperatures. As the composition moves away from stoichiometry a glassy grain boundary phase forms, reducing the material’s strength, and lowering the maximum use temperatures. The melting point of mullite is above 1810°C.

### 1.5.9 Industrial uses of Mullite Ceramics

The industrial uses of mullite are given below (Schneider et al 1994)

- Refractory materials in the metallurgical industries for electric furnace roofs, hot metal mixers and low frequency induction furnaces
- Heat resisting materials
- Engineering materials for heat exchangers
- Electronic packaging materials
- Optical applications
- Matrix material for high temperature composite development
- Substrate in multilayer packaging
- Protective coatings
- Turbine engine components
- Infrared-transparent window especially for high-temperature applications
- In the glass industries, these refractories are employed in the upper structure of the tank in which the glass is melted
- Kiln setting slabs and posts for firing ceramic ware as well as for the linings of high-temperature reactors.

1.5.10 Coating of Mullite

Mullite can be coated on metallic surfaces by atmospheric plasma spraying, and laser techniques. Coatings of mullite applied by atmospheric plasma spraying (APS) to SiC ceramic matrix composites provides some degree of corrosion resistance to corrosive industrial environments (Basu et al 2007). Another method of coating is the formation of mullite coatings on SiC substrates from colloidal suspension. Colloidal processing of ceramic suspensions offers a low cost alternative approach for producing uniform, thick ceramic coatings on complex -shaped components via a simple dip coating process (Beth Armstrong).
Densification of bulk mullite takes place above 1600°C and in the plasma spray process temperatures of 10,000°C is encountered, resulting in thick, dense and crack free coatings.

Dense, crystalline mullite coatings of uniform thickness have been deposited by chemical vapor deposition (CVD) on SiC substrates (Basu et al. 2007). A graded coating composition has been achieved in the coatings, with the Al/Si ratio being stoichiometric at the coating substrate interface, and increasing monotonically towards the outer coating surface. The coatings should have a close coefficient of thermal expansion (CTE) match with the substrate to minimize thermal stresses during temperature cycling. The coating should have a good chemical compatibility with the substrate for adherent bonding at the interface. Mullite is a promising coating material for silicon based ceramics due to its excellent corrosion resistance, creep resistance and high temperature strength. Mullite has a much better CTE match with the Si-based ceramics than alumina and zirconia, thereby minimizing the thermal stresses during temperature cycling. Plasma sprayed mullite based EBC’s (Environment based coatings) have been deposited on SiC substrates for hot corrosion protection (Lee 1995). In this study, mullite EBC’s have been deposited by the CVD technique, which lends itself readily for control of coating microstructure, uniformity and thickness, even in complex parts with edges, corners and curvatures. In addition, the CVD process leads to coatings that have substantially lower residual stresses due to the lack of rapid quenching inherent to the plasma spray process, thereby avoiding porosity and micro cracks.

It is most important to plasma spray a layer of bond coat of nickel chromium (NiCr) on the aluminum substrate to a thickness of 100 to 150 μm before applying the top coat of mullite to improve the adhesion of the coating to the substrate. This is due to the wide mismatch in the young’s modulus and
the thermal expansion coefficients’ of the substrate material and the mullite ceramic. The bond coat will reduce this mismatch and hence reduce the residual stresses in the coating and enhance the adhesive strength of the coating.

1.6 THERMAL SPRAYING

Thermal spray is the name of a category of coating deposition techniques which use thermal energy to melt and/or pyrolyze the precursor (powder, solution or wire) and accelerate it towards the substrate. At the substrate, the individual molten particles flatten and solidify. A popular method of thermal spray technique is air plasma spray (APS), in which a DC arc is formed between an anode and cathode, which generates plasma. The precursors are injected into the high temperature plasma and accelerated towards the substrate as a result of the high velocity gas flow. Due to the high temperatures attained, plasma spray is a good application method for ceramic coatings, as it can ensure that the precursors have been melted before hitting the substrate. Plasma spray process parameters govern the resulting coating characteristics and when changing these parameters (gas flow rate, current, standoff distance, feeding rate, etc.), coating characteristics change. Thus, we need to optimize the plasma parameters to have a coating with the desired characteristics.

The temperature drop across the ceramic coating is inversely proportional to the thermal conductivity of the ceramic. Therefore, the lower the thermal conductivity of the ceramic layer, the cooler the metallic surface will be. The temperature drop is proportional to the thickness of the coating. Thus, a thicker TBC is preferable. However, an unlimited increase of the thickness is not beneficial for three reasons. First, it adds weight to the part, which is detrimental to rotating components such as turbine blades. Second,
thickness increases residual stress and total strain energy, making the ceramic coating prone to failure. Third, the more insulating the ceramic layer, the higher its surface temperature, leading to the possibility of sintering and associated structural and thermal problems.

1.7 PLASMA SPRAYING TECHNIQUE

1.7.1 Introduction

A brief description of the various features of plasma spray technique is highlighted (Smart and Catherall 1972). Plasma spray deposits can vary in thickness from 0.10 – 0.60 mm. Due to the high particle temperatures and the rapid impingement on the target, the coatings are usually dense and adherent—porosities as low as 1% being common, while the presence of an inert atmosphere during spraying minimize oxidation of the coating.

Plasma coatings are being increasingly used for wear and abrasion resistance, electrical conduction, thermal and electrical resistance, reclamation of worn parts; repair of wrongly machined components and in certain cases, corrosion resistance. Some of the features of plasma spraying are

1. Impingement speed/sec : 150
2. Approximate temperature, °C : 20,000
3. Typical deposit porosity, % : 1-10
4. Typical adherence, MPa : 30

Some of the advantages are low porosity, good adhesion, versatility, cool substrate and low contamination.
1.7.2 Plasma Spraying Features

As discussed earlier, plasma spraying is a suitable method for applying ceramic coatings. Due to the high temperature, most ceramic materials can be sprayed using this method. However, to have satisfactory deposition efficiency, the melting temperature should be at least 300K (27°C), lower than the vaporization or decomposition temperature (Heimann 1996). There are some unique features in plasma spraying such as (Pawlowski 1995).

1. A wide range of materials can be deposited, from polymers to metals to ceramics and their combinations.
2. Combinations of ceramics and alloys having different vapor pressure can be deposited without significant changes in final composition.
3. Homogenous coatings can be produced with no significant difference in composition through the thickness parallel to spray direction.
4. Fine, equiaxed grains without columnar defects can be produced.
5. Functionally graded coatings can be generated.
6. High deposition rates of the order of mm.s⁻¹ are achievable.
7. Near-net shape free-standing thick coatings can be sprayed.
8. The process can be carried out in different environments such as air, reduced pressure, controlled atmosphere, and underwater.

1.7.3 Process Parameters

A common way to achieve a satisfactory deposit is to apply a design of experiment (DOE) to find a combination of process parameters that
produce acceptable coating properties (Sampath et al 2003). Understanding the relationships between the process parameters, plasma characteristics, and the in-flight particle characteristics is vital to assure reproducible, high-quality coatings. In plasma spraying, the relationship between the processing variables and the resulting plasma and particle characteristics is complex because of the large number of processing parameters, including plasma current, plasma gas composition and flow rate, powder size, powder feed rate, carrier gas flow rate, standoff distance, and plasma gun traverse speed (Zhao et al 2000). For example, Zhao et al (2000) tried to interpret plasma characteristics in an A2000 vacuum plasma spray system (Sulzer Metco AG, Winterthur, Switzerland) by modeling the influence of different plasma parameters on the energy balance of the jet.

1.7.4  Steps in the Successful Plasma Spraying Process

The METCO ROBOT plasma spraying equipment used to fabricate the specimens in this study consists of a control system, a spray gun, a powder feeder, a cooling water pump and connecting hoses. The primary plasma gas is argon and the secondary gas is hydrogen, and the powder carrier gas is argon. Coatings were applied using optimized spray parameters. Figure 1.2 shows the plasma spraying process. The steps in plasma spraying are given below.

Figure 1.2 Plasma spraying process
1. **Clean**: Remove paint, corrosion products, dirt, and grease.

2. **Grit blast**: To finish cleaning and provide rough, high activity surface

3. **Spray**: Deposit coating

4. **Finish machine**: Buff, turn, mill, grind.

The steps are detailed below

1. **Substrate preparation**: To obtain optimum adhesion, the surface of the part to be sprayed is cleaned to remove dirt, grease or oil. Paint and loose rust are removed by pickling, scraping or wire brushing. Vapour degreasing or liquid degreasing is then performed in trichloroethylene. Following degreasing, handling of the work piece is minimized.

2. Since the bond in a plasma sprayed deposit is predominantly mechanical, the surface to be sprayed is roughened by sand blasting; this produces a rough, clean, high activity surface. Gas pressures of 0.2 to 0.6 MN/m² are used. Areas not requiring spraying are covered by PVC tape.

3. **Plasma spraying**: The work piece is setup in the handling equipment, a lathe and the gun traverse limits are set. Cooling jets are arranged for substrate cooling. The deposition parameters are set and trial run conducted. Apart from the nature of the arc/powder gas and the powder itself, the variable in the plasma spraying process include power input, spraying distance and angle, arc and powder gas flow rates and hopper setting. After the calculated number of passes, the work piece geometry is checked to determine whether further
passes are required. When the required coating thickness has been attained, the part is removed from the handling equipment and inspected. Prior to the finishing operations, the part is cleaned and the protective tape is removed.

4. Finish machining: For smooth finish (70 µm CLA), finish machining is required. Ceramics are generally diamond ground.

1.7.5 Testing and Quality Control of Deposits

1.7.5.1 Introduction

The testing of deposits is an essential part of any coating development and is a routine feature of all quality control. It is generally necessary to use laboratory tests for assessment purposes. The routine tests used for evaluation are tensile tests, adhesion test, corrosion resistance, wear rate, thermal stability or thermal shock resistance, chemical composition analysis, micro structural analysis and service simulation tests.

1.7.5.2 Powder evaluation

Successful plasma deposition depends upon the use of the correct feed material, and powder evaluation is widely practiced; normal powder metallurgy tests are suitable for this purpose. Chemical analysis, powder size, shape and area, powder density and flow rate are generally measured. Standard chemical analysis techniques are used. The apparent density of the powder is measured in a flow meter and calibrated cup, the weight of dry powder to fill the cup being used to determine density. The time for a standard amount of powder to pass through the flow meter gives the flow rate. The particle size characteristics are measured by normal sieving, using automatic agitation of the sieves. Particle shape is assessed by examining the
powder under a low power microscope, the shape being reported as acicular, irregular, spherical, etc. Surface area is determined by surface adsorption of nitrogen.

1.7.5.3 Deposition efficiency

The efficiency of deposition is taken as the ratio of the weight of material deposited to the weight of powder used, expressed as a percentage. Using such deposition tests, the spraying parameters are optimized for any given powder; however, it is also necessary to check coating structure, bond quality and porosity level (by metallographic examination) to ensure that spraying efficiency is not improved at the expense of deposit quality.

1.7.5.4 Metallographic examination and porosity measurement

The coating generally consists of a heterogeneous mixture of sprayed material, oxide and pores. Shrinkage and degassing after deposition are the principle causes of porosity, but under suitable conditions, the latter can be kept to as little as 1 % of the bulk density of the coating material. In general, the porosity is in the range 1 -10%. The level can be decreased by subsequent infiltration or heat treatment. Oxide inclusions arise either from pickup during spraying or from excessive surface oxide on the starting powder. The former can be controlled by using a shroud gas, while the latter requires attention to powder quality and particle size. The particles undergo rapid cooling on the substrate and there is insufficient time for significant diffusion. Because of the high cooling rates, non-equilibrium structures result, this can have interesting properties. These can be subsequently sintered to stable structures if required. A common structural feature of poor coatings is the presence of unmelted particles, which indicates incorrect powder quality or spraying conditions. The need for a reasonable temperature interval between the melting and boiling points of the sprayed material is a must; if
this does not exist; excessive vaporization can occur leading to sooty loosely bonded deposits. The composition of the coating should correspond to that of the original powders, but it can differ because of decomposition of the material, reaction with the arc gas, oxidation and possibly electrode contamination. These are controlled by paying attention to spraying conditions.

Metallographic examination of polished sections of the deposit and substrate plays a major part in the evaluation procedure for general coating quality and integrity, porosity, inclusion content, etc. Quantitative metallographic techniques have been developed for the reliable measurement of porosity.

**1.7.5.5 Mechanical properties**

The adhesion (or bond strength) of the coating /substrate interface and the hardness of the deposit are the mechanical properties most usually measured; the tensile strength of the coating is also determined. The adhesion test shown in Figure 1.3(a), is widely used as an acceptance test for sprayed coatings, the halves of the specimen being bonded with a suitable resin, normally an epoxy. When a more viscous resin is used the results are more reliable. Such resins are commercially available. Specimen size of 20 mm diameter and 40 mm length with 100 µm thick coatings are generally used.

It is possible to determine whether the test has been valid by examining the fracture. Separation at the coating/substrate boundary, or failure wholly within the coating, indicates a reliable test; a mixed fracture, partly in the deposit and partly in the bulk material, is considered invalid.

A simple and fairly reliable test for coating strength is based upon two tubes, of the same diameter and accurately machined to give mating faces. Refer to Figure 1.3(b). The tubes are mounted on a mandrel and sprayed along their length. The ends of the tubes are threaded to fit a tensile
testing machine and after removal of the mandrel, the coating may be pulled to failure. Subsequent diffusion either by torch fusing or by post sintering improves the bond strength.

**Figure 1.3  Test arrangements for plasma sprayed coatings (Smart and Catherall 1972)**

The hardness of individual layers in a coating is best measurement by micro hardness indentations on transverse sections of the particle/layer. The micro hardness is measured by Vickers’s hardness tester or Knoop hardness tester. The presence of porosity lowers the bulk hardness and care must therefore be exercised to ensure that a representative hardness value is obtained.

1.7.5.6  **Residual stress**

In common with other deposition processes, plasma sprayed coatings may contain residual stresses. These arise from contraction during cooling and they can cause surface cracking or fracture of individual particles. The magnitude of the stresses, therefore, depends upon the thermal expansion coefficient of the coating material; and its difference with that of the bulk material. For thermal cycling applications, similar thermal expansion
coefficients in the substrate and the coating are desirable. In thin coatings, stresses are rarely sufficient to cause trouble but thick coatings may become detached in service. When difficulty is expected, post heat treatment may be used to relieve the stresses.

1.7.5.7 Wear properties

One very important use of plasma coatings is in tribological applications. Ceramic coatings on aluminum can play a major role in enhancing the wear resistance of aluminum under elevated temperature conditions in applications like auto engines, jet engines, aerospace engines, brake shoes/drums and sleeve bearings. Aluminum has the advantage of low density, but performs poorly in wear resistant applications. The problem is aggravated when components are exposed to elevated temperatures. Hence suitable ceramic coating plasma sprayed on aluminum would improve the elevated temperature wear resistance of aluminum cast or wrought. The pin on disc method is a popular method of testing the wear properties of coatings.

1.7.6 IC Engine Application of Plasma Spraying

Pistons can also increase their performance characteristics with ceramic coatings. Coating the piston's crown and top will cause heat reflectivity, driving a percentage of any detonation energy back into the fuel burn zone, to increase fuel burn efficiency. It will also lower carbon buildup, which reduces detonation quality, as it builds up on the piston's crown and increases the risk of detonation damage to the piston crown surface. By protecting the crown and land diameter surfaces, it will allow for a leaner fuel mixture.

Piston skirts can be coated to create an excellent dry sliding surface during engine start-up and will help eliminate skirt slap during initial engine
run-in. Ceramic coatings can also be applied over the piston ring contact, which provides lowering friction between the ring face and cylinder inner bore surface scuffing, and also improves wear resistance.

1.8 AIM AND SCOPE OF THE PRESENT THESIS

1.8.1 Aim

- To design and fabricate a relatively low cost duplex (bond coat and top coat) ceramic, thick thermal barrier system, which is physically and chemically stable under the operating conditions typical of a petrol engine, which could minimize the internal stress experienced when subjected to a thermal gradient typical of that experienced in service.

- To evaluate the mechanical performance characteristics, thermal, wear, and corrosion characteristics of mullite coated cast aluminum samples and to study the microstructure, SEM/EDS/XRD, of the above samples.

- To study the residual stresses present in the coating.

- To apply this coating on a two stroke petrol engine piston and cylinder head and study the performance of the engine for comparison with uncoated engine.

1.8.2 The Scope of the Present Work

1.8.2.1 Characterization studies

- To establish a method to coat mullite on cast aluminum specimens which could be solution heat treated, quenched and artificially aged (T 6 condition), in order to enhance the surface...
properties, like wear resistance, corrosion resistance, thermal shock resistance.

- To strengthen the adhesive bond of the coating so as to prevent delamination.

- To carry out characterization studies to understand the abrasive wear behavior, corrosion behavior, mechanical behavior like tensile strength and adhesive bond strength, thermal shock resistance, micro structural and compositional details.

- To prepare specimens carefully for each study comprising of coating with and without bond coat, soft and T6 treated specimens.

- To study the effect of T6 treatment on the coating properties.

- To conduct wear studies on bare specimens of Al 6063-O and cast Al A 356.0 and compare with the performance of coated specimens.

1.8.2.2 Modeling and simulation studies

To use modeling and simulation techniques to study the tensile strength, the flexural strength and the temperature distribution of the coating system; to study the residual stresses developed in the coating during service.

1.8.2.3 IC engine experiments

To spray mullite coat on a two wheeler IC engine cylinder head and piston outer surfaces, conduct the performance study to evaluate the improvements in torque-speed characteristics, efficiency-speed characteristics, temperature distribution on cylinder head and
body. Also to conduct emission studies on the two wheeler mullite coated IC engine exhaust and uncoated IC engine exhaust to compare the emission characteristics.

1.9 STRUCTURE OF THE THESIS DOCUMENT

Chapter 1 gives an introduction to surface engineering and the surface treatments on aluminum. The ceramic coatings on aluminum and the characteristics and properties of mullite are detailed. The thermal spray process is introduced and the plasma spray method is detailed and the most significant process parameters are described.

Chapter 2 presents a review of the literature on development and characterization of mullite coatings, coatings on aluminum and more specifically ceramic coatings on aluminum, and ceramic coatings on IC engines and the performance studies conducted.

Chapter 3 discusses the selection of materials and methods used for fabrication of the specimens for the various tests. The method of optimizing the process parameters in plasma spraying are also presented.

Chapter 4 discusses the methods and procedures used in the characterization of the mechanical properties of the coating. Tensile strength, micro hardness, adhesion and coating thickness measurements are presented and the results discussed. Experimental set-up for the characterization of various properties and experimental and statistical analysis of the data are presented. This includes modeling and simulation of mechanical behavior of the coating system (tensile strength and flexural strength) and the temperature distribution when the coating is exposed to a heat flux, using finite element analysis.
Chapter 5 discusses the corrosion resistance of the mullite coating on aluminum and describes the experimental setup and the results obtained.

Chapter 6 discusses the wear behavior of the mullite coating. The experimental setup and the details of the observations and the statistical analysis are presented. The results of the wear measurements are presented and discussed.

Chapter 7 discusses the thermal barrier properties of the mullite coating. The experimental set up for the thermal conductivity measurements and thermal shock tests are discussed and the experimental and statistical analysis of the data is presented. The thermal conductivity and shock test results are presented and discussed.

Chapter 8 establishes the microstructure of mullite coatings. This includes characterization of the feedstock powder and deposited coatings. Image analysis of the microstructure of the coatings, porosity, SEM/EDS/XRD studies are included.

Chapter 9 reviews the nature of residual stresses in plasma sprayed mullite coatings. Numerical modeling of the build-up of internal stresses during service, and the associated residual stresses are included in this chapter.

Chapter 10 deals with the performance studies of the IC engine coated with mullite. Performance curves are presented and compared with those of the uncoated engine.

Chapter 11 deals with the further scope in this study. In this chapter, the results of the study are discussed, conclusions drawn, and suggestions for further studies presented.