CHAPTER 1

INTRODUCTION

Market forecasts of global metal valve manufacturing industries indicate the long term industry outlook and future growth trends (Source: 2016 market research report on metal valve manufacturing industry). Metal valve castings used in petrochemical, chemical and pharmaceutical industries are predominantly used to transfer fluids having different properties that are non-corrosive in steam, water, gas and air. These valves are designed specifically to withstand very high pressure and temperature. Metals with coatings are to be tailored to the operating conditions with bubble-tight shut-off on small molecule gases like hydrogen, helium, nitrogen and oxygen with metal salts.

Valve performance will also be affected by solids for which special internal configurations are to be provided for slurry service. In certain conditions, the valve is to be designed for elevated temperatures even up to 760°C. The rapid thermal flux designs in nickel and cobalt alloys can solve these problems. The design should replace the actuation systems without removing the valves from the system. A design is preferred which warrants the replacement of actuation systems only without the replacement of the entire valve from the system. Generally industrial valves may fail due to tear in the elastomers and seat on continuous operation, difference in designed operating conditions between internal and external pressure, temperatures and unexpected pressure spikes in the pipeline, foreign or abrasive debris in the pipeline, material incompatibility during transmission of fluids, incorrect
assembly, installation, or maintenance procedures. For eliminating these failures, studies had been conducted on valve seat materials of globe valve for industrial applications. A globe valve is shown in Figure 1.1 with major components and material specifications are indicated in Table 1.1. The failure occurs in the seat ring and the seat is indicated in Figure 1.2. The difficulties encountered in this portion is the deposition of carbon, slurry and alkalis formed at the junction of the valve seat due to the impinging velocity of fluids. This restricts the flow of the fluids and also the formation of pitting corrosion on the valve body. The American Petrochemical Industries (API) recommended hardfacing techniques to eliminate the failure of valve components. The hardfacing involves cladding of the base substrate to certain thickness and machined to 2.0 mm thickness. The materials to be hard-faced are to be selected based on the requirement of corrosion and wear properties. Nickel based alloys and cobalt based alloys are commonly used to improve these cited properties. Hardfacing become the most common process in valve industries for improving the tribo-corrosion properties of valve seat materials used for high temperature applications.

Figure 1.1  Typical globe valve with seat
<table>
<thead>
<tr>
<th>S.No</th>
<th>Component Description</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Body</td>
<td>A216 Gr.WCB</td>
</tr>
<tr>
<td>2</td>
<td>Ball</td>
<td>ASTM A351 Gr.CF8M / ASTM A216 WCB / WC9 + St. (Hard faced)</td>
</tr>
<tr>
<td>3</td>
<td>Seat</td>
<td>ASTM A479 Type 316 / ASTM A216 WCB / WC9 + St. (Hard faced)</td>
</tr>
<tr>
<td>4</td>
<td>Seat seal</td>
<td>Graphite</td>
</tr>
<tr>
<td>5</td>
<td>Connector gasket</td>
<td>Graphite</td>
</tr>
<tr>
<td>6</td>
<td>Connector</td>
<td>A216 Gr.WCB</td>
</tr>
<tr>
<td>7</td>
<td>Stud</td>
<td>A193Gr.B7</td>
</tr>
<tr>
<td>8</td>
<td>Heavy Hex Nut</td>
<td>A194Gr.2H</td>
</tr>
<tr>
<td>9</td>
<td>Stem</td>
<td>A564 Type 630</td>
</tr>
<tr>
<td>10</td>
<td>Stem thrust seal</td>
<td>Carbon filled PTFE</td>
</tr>
<tr>
<td>11</td>
<td>Stem packing</td>
<td>Graphite</td>
</tr>
<tr>
<td>12</td>
<td>Identification plate</td>
<td>Stainless steel</td>
</tr>
</tbody>
</table>
1.1.1 Hard facing

The base materials A216-WCB (casting) and A216-WC9 (forging) commonly used in metal valve industries for their strength and low affinity to carbon deposition and oxidization at high temperatures will have the maximum carbon content of 0.25% by weight and their operating conditions are indicated in Table 1.2. When these materials are subjected to high pressure steam, reactive chemical gases and slurries will prone to the formation of cavities and pitting corrosion due to low carbon content. As per the periodic table element 26, a transition metal has to be welded with another transition metal to get the improved version of the existing materials, for which either cobalt, element 27, for wear resistance, or nickel, element 28 for corrosion resistance are to be selected for cladding on the surfaces. The difficulties associated with the building of materials between two transitional materials are improper bond, dilution and penetration. A method can be adopted to
avoid these problems wherein the base materials are preheated and overlay the surface with hard facing.

**Table 1.2 Operating conditions**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Physical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>A216-WCB</td>
<td>Operating temp: -28 °C to 500 °C Max 425°C continuous usage; Pressure:52 kg/cm² to 3.5 kg/cm²</td>
</tr>
<tr>
<td>A216-WC9</td>
<td>Operating temp: -28 °C to 565°C; Pressure:52 kg/cm² to 7.5 kg/cm²</td>
</tr>
</tbody>
</table>

The conventional hard-facing alloys used are cobalt based alloys and one such alloy is stellite 6 whose chemical composition is given in Table 1.3 which is commercially available in the form of rods, wires and powders.

**Table 1.3 Chemical composition of Stellite 6 alloys**

<table>
<thead>
<tr>
<th>Co</th>
<th>Cr</th>
<th>W</th>
<th>C</th>
<th>Others</th>
<th>Hardness</th>
<th>Density</th>
<th>Melting Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>27-32</td>
<td>4-6</td>
<td>0.9</td>
<td>- 1.4 Ni, Fe, Si, Mn, Mo</td>
<td>36-45 HRC</td>
<td>8.44 g/cm³</td>
<td>1285-1410 °C</td>
</tr>
</tbody>
</table>

These alloys exhibit high wear resistance and corrosion resistance. They retain a reasonable level of hardness up to 500°C (930°F). It also has good resistance to impact and cavitation erosion, however, St 6 corrodes primarily by a pitting mechanism and its mass loss in sea water and chlorine solution is below 0.05mm per year at 22°C.
The other common hard facing alloys are Ni based alloys Inconel 600, 718, 800, Hastealloy C-276, Monel 400 etc., which are good in corrosion resistance. The chemical composition of Inconel 600 is presented in Table 1.4. Inconel 600 and Monel 900 alloys are used to withstand wear and corrosion whereas Hast alloys and molybdenum is used to have hydrophobic properties.

Table 1.4   Inconel 600 alloys chemical composition

<table>
<thead>
<tr>
<th></th>
<th>Ni + Co</th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>Si</th>
<th>Cu</th>
<th>T</th>
<th>At °C</th>
<th>430</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>72.0 min</td>
<td>14.0-17.0</td>
<td>6.0-10.0</td>
<td>.15 max</td>
<td>1.00 max</td>
<td>.015 max</td>
<td>.50 max</td>
<td>.50 max</td>
<td>1093</td>
<td>130 BHN</td>
<td></td>
</tr>
</tbody>
</table>

Numerous researches have been conducted to identify the appropriate process to hardface the above alloys which are presented in Table 1.5. The Table is presented based on the practical difficulties faced by the industries. It involves the hard-faced condition, machining time, machining cost and replacement of parts during the service.
The researchers indicate that the MIG welding process as shown in Figure 1.3 is preferred due to optimum cost, but the fumage during the process results in hydrogen induced cracking and porosity due to which a large amount of material is required for hard facing.
In the current research, flux cored stellite 6 wire, nickel based alloys FW2 and FW3 were used with controlled process parameters to avoid the cited problem.

1.1.2 Thermal coating

The presence of heat affected zone (HAZ) and other defects in hardfacing technologies can be overcome by coating tungsten carbide, zirconium, molybdenum and titanium on the substrate using a suitable thermal spray coating like plasma spray coating and lacer coating. The controlled atmosphere is required and the shielding gases are used in plasma spray coating.

Figure 1.3 Automatic MIG welding setup for the current research with controlled wire feed rate and current

(Source: https://paulleadingham.wordpress.com)
The plasma spraying process involves the latent heat of ionized inert gas which is known as plasma used to be the heat source. The most common gas used to create the plasma is argon which is referred to as the primary gas. Argon flows between the electrode and nozzle. A high frequency alternating electric arc is struck between the nozzle and the electrode, which ionizes the gas stream. By increasing the arc current, the arc thickens and increases the degree of ionization. This has the effect of increasing the power and also due to the expansion of gas, an increase in the velocity of the gas stream. With a plasma created by argon only requires a very large arc current in the order of typically 800 to 1000 amps to create sufficient power to melt most of the materials. This is generally done by adding a secondary shielding gas to the plasma gas stream once the appropriate gas stream has been established for the material being sprayed. The feed stock, commonly in the form of powder is injected into the gas stream.

The plasma spray process is the most commonly used in normal atmospheric condition and referred to as Atmospheric Plasma Spray (APS). Plasma spray is conducted in protective environment also using vacuum chambers normally back filled with a protective gas at low pressure, which is referred as a Vacuum Plasma Spray coating (VPS) or Low Pressure Plasma Spray (LPPS).

Plasma spraying has the advantage that it can spray materials having a high melting point such as refractory like tungsten and ceramic like Zirconia. Plasma sprayed coatings are generally much denser, stronger and cleaner than the other thermal spray processes with the exception of HVOF (High Velocity Oxygen Fuel) and detonation processes.
1.1.3 Nano Coating

Nano coating is the process of making the solid materials to coat over the base material for preventing from corrosion, wear and rust. The precursors are used to separate the particles and are coated by different processes.

The sol-gel dip coating process is a commonly used method for producing solid materials from small molecules. The method is used for the fabrication of metal oxides, especially the oxides of silicon and titanium. The process involves conversion of monomers into a colloidal solution which is known as sol that acts as the precursor for an integrated network of either discrete particles or network polymers. Typical precursors are metal alkoxides.

The coating of materials through Electrophoretic Deposition (EPD) has started gaining more attention. It is a technique where the charged particles (colloidal particles from suspended liquid) move towards oppositely charged electrons. In general the method can be applied to any solid with particle size of less than 30 microns. Many researches have been carried out on the kinetic electrophoretic deposition process and chemical equations are formulated. Thus EPD plays a significant role in cost effective coatings of various conductive and ceramic materials.

1.2 LITERATURE SURVEY

1.2.1 Introduction

It is desired to undertake the research in the field of surface coating for valve application. Hence a detailed literature survey has been undertaken to appraise the research findings and possible improvement in coating process appropriate for valve applications. The widely employed
surfacing processes like hardfacing, plasma spray process and nano coating are considered for the study. The process parameters used and its limitations are carefully studied to identify the scope for improving the suitable processes. The findings on various process, influencing parameters and outcomes are presented in the following sections.

**Key words:** Hardfacing, cladding, nano-coating, Sol gel, Electrophoretic processes, CVD, PVD, Plasma spray coating.

### 1.2.2 Study on conventional Hard facing Techniques

Foroulis (1984) focused on the evaluation of the sliding wear characteristics of commercially used hardfacing alloys. The author compared wear and corrosion properties of Fe-Cr-Ni alloys which also contain small amounts of cobalt, three classes of alloys; cobalt base alloys, nickel base alloys and Tribo alloys. The results indicated that alloys T – 400 and ST – 6 exhibited excellent galling resistance in addition to good wear resistance and very good corrosion resistance in a variety of environments but Nickel based alloys had inferior galling resistance.

Grainger (1989) presented the history, composition and properties, deposition of hardfacing, hardfacing applications and problems in hardfacing of cobalt based alloys. He also reported that the 62Co_{27}Cr_{4}W alloys and stainless steel are non-toxic and are safe to be used by food processing industries. Wu et al. (1994) examined the microstructural features and wear properties of these families of hardfacing alloys with an objective of choosing the right alloy for the job. Various cobalt and nickel alloys, their commercially available forms and the corresponding hardfacing methods were reviewed in this paper.
Nadkarni (1996) stated that nickel base alloys rods can be easily deposited on substrate materials by oxyacetylene or gas metal arc welding but the clad materials have inferior galling resistance properties. Wu et al. (1999) reviewed about various cobalt and nickel alloys, their available product forms and the corresponding hardfacing methods. Studies also indicated that tungsten is indispensable and ensures that the alloys can retain high hardness at elevated temperatures. The tungsten addition must be higher in high carbon alloys than in low carbon ones, since any carbon that does not combine with the chromium will combine with some of the tungsten and cobalt in the solid solution to form carbides of the $\text{f}_1\text{-Co}_3\text{W}_3\text{C}$ type. It is the tungsten that remains in solid solution, which appears to be responsible for the high temperature properties of the alloys.

Ningaoh et al. (1999) investigated the wear characteristics of cobalt base alloys deposited through plasma-transferred arc welding. In addition to that, Pin-on-disk wear tests were conducted under various conditions to study the effect of oxidation on wear behavior. Wear mechanisms were evaluated through the wear volumes and scanning electron microscopy SEM analysis. It has been asserted that the $62\text{Co}_{27}\text{Cr}_4\text{W}$ with an approximate composition of Co-28Cr-4.3W1.1 (wt %) is widely used because of its good wear and corrosion resistance along with good weldability with different steels. The authors predicted that carbon had the significant influence on the microstructure of $62\text{Co}_{27}\text{Cr}_4\text{W}$. It combines with chromium to form very hard carbides, which are responsible for the high hardness at room temperature. Tungsten ensures that the alloys retain high hardness at elevated temperatures.

Shanmugam and Murugan (2004) developed a methodology for understanding relationship between the principal factors such as normal load, sliding velocity, track radius and wear. The authors also developed the
mathematical model for studying the wear behaviors. The objective of the first part of this study is to find the optimal wear for the hardfaced valve seat rings and the interaction effects are presented in the graphical form for ready reference. The competency of the model proved through F-test and plotting scatter diagram. The author also conducted sensitivity analysis for identifying the critical parameters and ranked them by their order of importance. The author concluded the sensitivity results with wear parameters in the graphical form.

Murugan and Gunaraj (2005) attempted to provide a view to develop mathematical models, statistically designed experiments based on factorial techniques with the use of full replication to obtain the required information about the direct and interaction effects on the response parameters provided. The authors provided detailed literature on mathematical modeling of five level factorial techniques to predict three critical dimensions of the weld bead geometry and shape relationships for ESAB SA1, 3.15mm diameter on IS 2062 steel. The wire feed rate had a positive effect and welding speed had a negative effect on most of the bead parameters. The interaction effects of wire feed rate and welding speed were similar for most of the parameters. Penetration, width, penetration size factor and reinforcement form factor increased with the increase in the wire feed rate for all values of welding speed but these bead parameters decrease with increase in welding speed.

Nouri et al. (2007) experimented the cladding of X65 pipeline steel with 316L stainless steel using pulsed GMAW techniques. The author produced a mathematical model using a full factorial approach to identify the effect of wire feed rate and other parameters on dilution and weld bead geometry. The results indicate that the dilution of weld metal and its dimension i.e. Width, height and depth increases with the feed rate, but the contact angle of the bead decreases first and then increases. It is also observed
that the clad materials require a minimum of 5 mm thickness including penetration for effective hardfacing with lower feed rate of 4.5 m/min and speed of 0.3 m/min. However, considerable consumption of time and the loss of huge materials was observed.

Ghosh et al. (2007) viewed that SAW process is one of the major fabrication processes in the industry because of its inherent advantages, including deep penetration and smooth bead. This model was useful for selecting correct process parameters to predict the desired weld bead parameters. This model facilitated for optimization of the process through sensitivity analysis. Further the authors studied the effect of process parameters on bead quality and the interaction effect of bead parameters focused on getting quality weld joints at cost competitive. It has been observed that the penetration increases with an increase in the current, the reinforcement also increases marginally with an increase in the current but the width decreases i.e. It has a negative effect. It is also observed that as the arc voltage increases, the weld bead becomes wider and flatter while the penetration decreases.

Klaric et al. (2008) experimented MAG processes for hardfacing and provided the guidelines for the selection of shielding gas, welding speed and heat input for hardfacing. The author also indicated there exists a relationship between the heat input in form of weld speed and gas flow on the weld bead width. The authors experimented with dual filler material and shielding gases for obtaining the better reinforcement.

Bellet et al. (2009) addressed three issues that often constitute bottlenecks for the finite element simulation of welding processes, modelling of material deposited, control of the mesh, inverse modelling for identification of thermal sources. The Lagrangian method was found to be efficient when associated with adaptive remeshing. It provides a good and convenient
alternative to classic element activation techniques, but is limited when simulating multipass and effective assembly of parts. Despite the need of meshing the air phase, the interface tracking method offers significant advantages. The authors concluded that in future finite element analysis would be the effective method to determine the welding energy inputs.

Siva et al. (2009) carried out experiments on depositing Colmonoy 5 over Stainless steel 316L plates of size 150 mm x 90 mm x 30 mm. The experiments were based on the central composite rotatable design matrix. Regression analysis was developed to model the hardfacing methodology. The authors optimized the process parameters for achieving minimum penetration, maximum reinforcement, maximum bead width and minimum dilution using Microsoft Excel Solver [16]. As the amount of data generated in the iterative process for optimization was enormous and each design cycle required number of calculations, software like solver has been used.

Thao et al. (2009) developed the simple and accurate interaction model to apply real-time control for bead geometry in GMA welding process. To achieve this goal, interaction model based on 25 full factorial design has been developed. The SPSS for Windows was utilized in this study to develop a linear, curvilinear and interaction models. The models were developed and checked the fitting by variance test. The predicted bead geometry given by these developed models were compared with the experimental results based on the additional experiments. Also, graphics display the effects of process parameters and interaction of CTWD and welding angle on bead geometry as welding quality.

Esme et al. (2009) investigated the multi-response optimization of tungsten inert gas welding (TIG) welding process for an optimal parametric combination to yield favorable bead geometry of welded joints using the Grey
Relational analysis and Taguchi method. Sixteen experimental runs based on an orthogonal array of Taguchi method were performed to derive objective functions to be optimized within the experimental domain. The objective functions have been selected in relation to parameters of TIG welding bead geometry; bead width, bead height, penetration, area of penetration as well as width of heat affected zone and tensile load. The Taguchi approach followed by Grey relational analysis to solve the multi-response optimization problem. The significance of the factors on overall quality characteristics of the weldment has also been evaluated quantitatively by the analysis of variance method (ANOVA). Optimal results have been verified through additional experiments. This shows application feasibility of the Grey relation analysis in combination with Taguchi technique for continuous improvement in product quality in manufacturing industry.

Ghazvinloo et al. (2010) attempted to study the effect of process parameters on bead penetration of joints produced through robotic GMA welding. Specimens used in this investigation were extracted from single butt-welded joints. The authors applied robotic GMA welding to HQ130 steel sheet having 5mm thickness and determined that the depth of penetration increased from 3.81 to 7.5 mm with increasing the electrode to work angle between 65° to 85°. The depth of penetration decreased from 6.36 to 4 mm with increasing the filler diameter between 0.8 mm to 1.2 mm among carbon dioxide, helium, argon were used as shielding gas in this research, the deepest and lowest penetration values were 6.13 mm and 3.69 mm. The output parameters bead width as measured for any given welding condition. The author concluded that the bead width is increased when the is increase in welding current from 330 to 370 Ampere and similarly the increasing the arc voltage from 22 to 30 V, weld bead width increased which this manner was similar to welding current effect, but the arc voltage effect on weld bead width was stronger and increasing the welding speed from 32 to 72 cm/min, the weld bead width
decreased thus the correlation between welding speed and weld bead width is an inverse trend.

Kumari et al. (2011) statistically designed experiments based on the full factorial technique to reduce the cost and the time involved in obtaining the required information about the direct and interaction effects on the response parameters. Automatic MIG surfacing was carried out by depositing MW1 welding wire onto structural steel IS2062 (%C-0.23, %Si-0.4, %Mn-1.5, %S-0.05, %P-0.05) plate of 5mm thickness, the observed data were utilized to develop the mathematical models. The controllable process parameters were kept in the optimum region for achieving the acceptable quality. The quality of the surfaced layer depends upon the dimensions of the weld bead and consequently upon the dilution. The paper presents mathematical models developed for predicting the main and the interaction effects of MIG process variables for MW1 surfaced on dilution and bead geometry from the experimental data obtained.

Eremin et al. (2015) described a new flux cored wire that deposited metal of high chromium steel of Fe–Cr–Ni–Mo–Mn–Si–Nb–Ti–B alloying system. The effect of the boride compounds on the structure and service properties of the high-chromium corrosion-resisting steel produced by hardfacing was examined and it was determined that Hardfacing with this wire greatly increases the efficiency and reliability of sealing sections of the stop valves.

Kimapong et al. (2016) studied the effects of hardfacing welding layer on microstructure and mechanical properties of weld metal on JIS-50C carbon steel. He found that there is an increase of hardfacing layer that attributed to the increase in hardness of the layer. The increase of the phase that contained higher chromium, manganese and molybdenum increased the hardness and wear resistance of the weld metal and the buffering layer would
produce a sound weld and might not be suited for the hardfacing welding of the medium carbon steel that deteriorated the mechanical properties.

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Singla et al. (2017) studied the four different rare earth (RE) additive iron-based hardfacing alloys by the shielded metal arc welding process with pre-placement technique to study the effect of dry sliding wear parameters and to develop a statistical regression model using full factorial approach. Results indicated that the microstructure was refined at first and then coarsened with the increase of RE additions. The optimal amount of RE was found to be 4 wt%.

Yang et al. (2017) aimed to achieve maximum benefit from the Ti and Nb due to their carbide forming ability that assists in the strengthening of these hardfacing alloys. The results portray that, the carbide precipitation of the Fe-Cr13-C-Nb hardfacing alloy was determined. Fe-Cr13-C-Nb hardfacing alloy with titanium addition exhibited better wear resistance. The precipitation reaction of carbides of Ti and Nb was obviously promoted that resulted in higher toughness because the hardfacing alloy can form dispersive carbides and tough martensite matrix. The wear resistance of the hardfacing alloys significantly increased due to the strengthening and protecting effect of the carbide precipitates.
1.2.3 Survey on Zirconium coating

Yoganandan et al. (2006) developed a chromate free zirconium-cerium conversion coating on AA2024 specimens to investigate their variation in surface and corrosion resistance properties before and after 1 week Clion exposure in salt bath. Field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray analysis (EDAX) and X-ray photoelectron spectroscopy (XPS) have been employed to study the morphology, elemental analysis and oxidation states of elements respectively. The electrochemical behavior, long term corrosion behavior and self-healing ability of the developed coatings have been studied through electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), simulated scratch cell test (SSC) and damage tolerance test (DTT). Neutral salt spray (NSS) test has also been carried out as an industrial practice and the obtained result after 168 hours of exposure is compared with conventional methods.

Pilloud et al. (2008) studied the influence of the substrate bias voltage on some characteristics of reactively sputtered zirconium nitride coatings. The authors investigated the effect of bias voltage on the properties of zirconium nitride films such as structure, morphology, hardness, internal stresses, optical constants and electrical resistivity. Coatings is deposited on steel and silicon substrates by magnetron sputtering of a zirconium target in reactive Ar–N₂ mixture. If a bias voltage is applied to the substrate holder, the film texture changes into a [1 1 1] lattice. It is observed that at the negative bias voltage of −110 V, the lattice constant decreases and porosities are also observed on the surface of the film. These porosities result from a resputtering phenomenon that occur only at high values of negative bias voltage.

Xing et al. (2008) introduced a synergistic agent, OZrP into UV curable systems and studied the synergic effect in flame retarded coatings. The thermal properties and fire retardancy of nanocomposite coatings were
evaluated by thermogravimetric analysis, thermogravimetric analysis/infrared spectrometry and microscale combustion calorimeter. The enhancement of thermal stability and the improvement of flame retardancy were observed. The charring structure was further characterized by scanning electron microscopy and Laser Raman spectroscopy. The results showed that the peak heat release rate and total heat of combustion of coatings with OZrP were significantly reduced.

Cheng et al. (2008) examined the silicate and aluminate electrolytes that revealed significantly different behaviors in the growth kinetics and properties of the coatings. Coatings were thickened continuously in the silicate electrolyte, while in the aluminate electrolyte, the thickness reaches a relatively constant value. The latter coincides with changing appearances of discharges and detachment of an outer coating layer. Dissolution of zirconium is faster in the silicate electrolyte in the early stage of PEO, but is faster in the aluminate electrolyte following coating breakdown. The pre-spallation coating formed in the aluminate electrolyte shows superior wear resistance, which can be ascribed to its relative compactness, associated with the presence of tetragonal zirconia stabilized by aluminium species.

Cubillos et al. (2013) describes the synthesis of zirconium oxynitrides (ZrOxNy) through unbalanced magnetron sputtering (UBM) using standardized conditions for films of transition metal nitrides. Due to the ceramic nature of the material, these transition metal nitrides corrosion resistance increases. A structural characterization based on the time of film deposition and the morphological changes of the surface was performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). The results indicated that oxidation occurs for few nanometers to zirconia directly on the surface, but its composition from the surface to the substrate is homogeneous and consists of a mixture of ZrO0.8N0.2 and amorphous ZrO2 phases. The
results indicate that the coatings deposited with a deposition time of 30 min are crystalline, homogeneous, and exhibit good adhesion to the substrate, low roughness, and a small particle.

Wang et al. (2013) produced zirconium oxide coatings on Zr–2.5 wt.% Nb alloy by a plasma electrolytic oxidation (PEO) process using a pulsed DC power source with various frequencies 1000, 2000 and 4000 Hz. It was observed that the thickness of the coatings was in a range of 7–15 μm and also the treatment time to reach the preset voltage was less than 5 min when a relatively low termination voltage of 400 V is applied. The coatings, phase structure, tribological and corrosion properties were characterized by X-ray diffraction (XRD), pin-on-plate sliding wear test and potentiodynamic polarization corrosion test. The results indicated that the increase in silicon content decreased the graphite elements present in coatings and increase in ZrB₂. Besides these some residual silicon was identified in ZS50 because of the highest silicon content in pack powders. Compared to other coatings, residual silicon in ZS50 coating played a beneficial role for dense structure of the coating and excellent anti-oxidation resistance.

Calderon et al. (2013) produced zirconium carbonitride coatings with silver nanoparticles by DC unbalanced dual magnetron sputtering system, using two targets, Zr and Zr/Ag in an Ar, C₂H₂ and N₂ atmosphere. The researchers' work was based on the production of ZrC₁–xNx films with embedded silver nanoparticles deposited onto SS316L by dual magnetron sputtering. Evaluation of the silver ion release and corrosion resistance of the system was performed. Systematic study about several parameters such as nitrogen and carbon content, deposition rate and substrate holder rotation and a stability of these variables along with the substrate holder was performed. Electrochemical measurements revealed an improvement in the corrosion behavior of the coated steel compared with the bare steel. Results also showed that the silver introduction did not affect the corrosion resistance of the
coatings nonetheless, the film microstructure has been found to play a significant role related to the film corrosion resistance since factors such as grain size and columnar growth could reduce this property in the system.

Jimenez O et al. (2015) deposited hard, partly amorphous, ZrTiB(N) coatings by Physical Vapour Deposition (PVD) onto (111) silicon wafers at low substrate temperatures of 85 and 110 °C using Closed Field Unbalanced Magnetron Sputtering. The deposition and study of multicomponent coatings with a combination of structural and mechanical properties were made. Also, the influence of alloying elements on the properties like surface, cross-sectional morphology and the possibility to form amorphous and/or nanostructured coatings were explored. The deposition rate and thickness of coatings deposited remained fairly constant for the bias conditions. The resulting surface roughness were very low due to densification and high mobility. A featureless, dense and homogeneous morphology, free of macro defects was the result of ion bombardment and grain refinement due to boron. Coatings without nitrogen resulted softer than their nitrogen-containing counterparts, due to hard ceramic phase formation with the elastic modulus following a similar trend.

Wang Pen et al. (2015) suggested four ZrB2–SiC/SiC dual-layer coatings to be prepared on the surface of graphite matrix by pack cementation to improve the oxidation and thermal shock resistance of graphite. The crystalline structure and morphology as well as the resistance to oxidation and thermal shock of these coatings were investigated. Improving the oxidation resistance of graphite heater and electrode, four ZrB2–SiC coatings were prepared by pack cementation on SiC-coated graphite. The microstructures of the prepared coatings were analyzed. The oxidation resistance at 1500° C and thermal shock properties between 1500° C and room temperature (RT) were investigated. The increase of the thickness of coatings and weight gain of outer coating during oxidation may lead to better oxidation resistance of (ZrB2–SiC)
/SiC coatings. The gas formed during oxidation process, such as CO₂ and CO, could damage the coating leading to severe oxidation and rapid weight loss. In contrast, the weight of ZS50 coated graphite has a slight decline to 97.1% after oxidation for 19 hours. The surface of ZS50 coating was still dense with little pores and no cracks. The dense surface structure is beneficial to oxidation resistance, which can block oxygen penetrating into the coating and oxidizing graphite substrate. With the increasing silicon in pack powders, some residual silicon appeared in ZS50 coating, which was considered to be beneficial to oxidation resistance and thermal shock resistance because it can improve the density of the coating and the SiO₂ formed by oxidation of residual Si can heal the micro cracks at high temperature.

1.2.4 Survey on Molybdenum coating

Molybdenum thin films and coatings can be grown with many different techniques like electron beam evaporation, sputtering processes and electro deposition. They are used in different technological and industrial applications as in large-scale and very large-scale integrated circuits for back contact in advanced solar cell assemblies, electrode materials and more recently using monolayer of MoS₂ for non-linear optics applications by the enhanced properties of bi-dimensional, atomically thick coatings. Moreover, a high-conductivity metallic coating made with Mo is also an interesting option for high performance accelerator components.

Laribi et al. (2006) discussed the relationship between deposition and post-deposition conditions, adherence and wear resistance of molybdenum and Cr–Ni–Mn alloyed steel coatings thermally sprayed on a 35CrMo4 steel substrate. The adherence to steel substrate was determined using a four-point by delaminating Q test bend and the tribological behavior of coatings was studied using a simple ball-on-plate tribometer. The study also focused on the influence of a post-annealing at 850°C for 1 h in vacuum followed by air
cooling on the adherence of the two different coatings on the steel substrate and on their wear resistance under specific wear and lubrication conditions. Flame sprayed molybdenum showed high tribological behavior and strong adhesion in relation with its metallurgical nature and the substrate surface preparation. Post annealing and lubrication are rather beneficial for electric arc sprayed steel coating. The first one improved its adhesion to substrate and the second decreased its friction coefficient against a hardened 100Cr6 steel ball.

Laribi et al. (2007) discussed that surface treatments and coatings are used to extend the life of components and structures, especially if the surface is the most solicited part of the considered engineering component. The authors studied the influence of post-thermal spraying parameters on the metallurgical and mechanical behavior of molybdenum coatings produced by flame spraying on a 35CrMo4 steel substrate. These post-deposition parameters concern the influence of annealing at 850°C for 1 h in vacuum followed by air cooling. The very good friction behavior of thermally sprayed molybdenum is in accordance with its metallurgical nature and mechanical properties. It is characterized by a friction coefficient of about 0.07 in dry conditions and about 0.06 when the friction testing is operated with oil lubrication. Impact test showed a good fatigue resistance to normal impact solicitations, but oil lubrication is not always beneficial so that can severely alter wear and fatigue behavior of such materials.

Guo Jin et al. (2007) described the metallurgical and the mechanical properties of the electro-thermal explosion directionally sprayed molybdenum coatings that were determined by means of SEM, XRD and micro hardness tester. The coatings were given on stainless steel (AISI 420) specimens through EEDS and HVAS. The microstructure, composition, distribution, phase constitution, nano-mechanical properties and wear resistance were investigated. Experiments on the tribological property of the coatings were performed using a ring-on-block type wear tester. Results showed that the
Molybdenum coatings were characterized by compact microstructure, high bonding strength and high wear resistance. The applied loads and the counterpart's hardness have an obvious influence on the tribological properties of the coatings. The microstructure and sliding wear behaviors of stainless steel (AISI 420) coatings prepared by electro-thermal explosion directional spraying (EEDS) and high velocity arc spraying (HVAS) are also investigated for comparison. The debris broken off from the coatings usually lie between the ring and block and they act as abrasive particles that will accelerate the wearing processed. Results showed that the EEDS coatings possessed more compact microstructure, higher nano-hardness and nano-elastic modulus, finer bond and better wear resistance than the HVAS coatings. The dominant wear mechanism of EEDS coatings is slight furrow and that of HVAS coatings is serious furrow and delaminating.

Zhu et al. (2013) synthesized Molybdenum nitride coatings by ion-beam-assisted-deposition (IBAD). The effects of nitrogen partial pressure and bombarding ion energy on the phase formation were investigated. The coefficient of friction and wear resistance of the coatings in different environments were studied. The roles of main deposition parameters, essentially the ratio of nitrogen partial pressure of argon and the bombarding ion energy on the phase compositions were investigated. There was a remarkable decrease in hardness as the oxygen content in the coating increased and induced the appearance of MoO$_3$ phases. The stoichiometric ratio of nitrogen to Mo of the molybdenum nitride phases increased with the nitrogen partial pressure. The hardness, coefficient of friction, wear and oxidation resistance of MoN were superior to that of Mo$_2$N coating.

Rhushikesh et al. (2013) used a new approach for synthesis of high quality faceted microcrystalline coatings of molybdenum (Mo), tungsten (W), their carbides and composites. These studies were carried out using Hot Filament Chemical Vapor Deposition (HF-CVD) method wherein parent
materials (Mo and/or W) were taken in the form of wires (dia~0.5 mm) and are heated to a high temperature (TF ~ 1500 – 2000°C), in an ambient of “oxygen (O₂) diluted hydrogen (H₂) gas”. Due to high filament temperature, a series of pyrolytic reactions take place. Firstly, the gasification of wire material (Mo and/or W) occurs in the form of its oxide. Amongst different process parameters, the filament temperature and the composition of chamber gas are of more importance, which sensitively affect the nature of the morphology and thickness of the resulting coatings. The morphological details of coating depend upon the type of the substrate. The growth of Mo particles was found to be of hexagonal shaped, while the growth of W particles is found to have three/four sided pyramidal shaped geometries. In situ carburization of pure metal coatings lead to the formation of carbides. The Composites of Mo-W could also be fabricated by simultaneous use of both types of filaments.

Marcelli et al. (2015) explained the electrical resistivity measurements with frequency that were performed on two molybdenum coatings grown by RF magnetron sputtering technique on a sapphire substrate at room temperature and annealed at different temperatures. The results confirm that Mo coatings with an electrical conductivity comparable to that of copper can be obtained by optimizing the thickness and the post-deposition annealing process. A comparison of the difference among spectra of the two samples with the Mo metal indicated at the edge an intense positive peak, that independent of the treatment, was roughly two times more intense in the thicker sample (BrN₂) than in the thinner (BrN₁) film, which exhibited the highest conductivity. Morphological and structural investigations on Mo coatings were performed before and after annealing by synchrotron radiation X-ray diffraction and X-ray absorption spectroscopy to identify the chemical status of Mo, to probe the presence of different oxides and to control the multiphase nature of these metallic films.
1.2.4 Literature Survey on Plasma Spray Coating

Tucker Robert (1994) stated that the thermal spray was a generic term for a group of processes in which metallic, ceramic, cermet, and any polymeric materials in the form of powder, wire, or rod are fed to a torch or gun with which they were heated to near or somewhat above their melting point. The resulting molten or nearly molten droplets of material were accelerated in a gas stream and projected against the surface to be coated (i.e., the substrate). On impact, the droplets flow into thin lamellar particles adhering to the surface, overlapping and interlocking as they solidify. The total coating thickness was usually generated in multiple passes of the coating device. A gas, usually argon, but occasionally nitrogen, hydrogen, or helium, was allowed to flow between a tungsten cathode and a water-cooled copper anode. An electric arc was initiated between the two electrodes using a high frequency discharge and then sustained using do power. The arc ionizes the gas, creating high-pressure gas plasma, which result in an increase of gas temperature exceeds 30,000 °C and in turn increases the volume of the gas and, hence, its pressure and velocity at the exit nozzle.

Looney and Stokes (2004) explained about the residual stress in thick deposits. Due to the nature of the high velocity oxy-fuel thermal spray process, residual stress built up in thick deposits is a significant and a limited problem. Application of analytical technique to calculate residual stress in thermally sprayed deposits based on geometric properties was performed. Residual stress resulted for WC–Co (tungsten carbide–cobalt) samples are compared to experimental results (X-ray diffraction and hole-drilling method). A change in deposit stress-state from tensile to compressive stress with deposit thickness was analyzed in terms of quenching and cooling stresses. The combination of the quenching and cooling stresses calculated also identify a near-zero residual stress in the deposit at 1.2 mm.
Ibrahim et al. (2009) discussed the surface modification of engineering materials to produce superior products in terms of reduced wear, increased corrosion resistance, better biocompatibility and improved optical and altered electrical/electronic properties. Excimer laser annealing provided a rapid and efficient means for surface alloying and modification of ceramic materials. In this study, alumina–13% titanium coatings were sprayed with a water-stabilized plasma spray gun. The coated surface was treated by excimer laser having a wavelength of 248 nm and pulse duration of 24 ns. The surface structure of the treated coating was examined by field emission Scanning Electron Microscope (SEM) and X-ray diffraction (XRD). A detailed parametric study was performed to investigate the effects of different parameters such as laser energy density (flounce), pulse repetition rate (PRR), number of pulses on the mechanical properties, surface morphology and microstructure of the coatings. The study revealed that the laser flounce played a major role in modifying the surface morphology of the coating, followed by the pulse repetition rate. SEM and XRD observations showed that microstructure of laser treated was composed mainly of nano-sized $\gamma$-Al$_2$O$_3$. Therefore, the intense and extremely short pulse of the excimer laser resulted in grain refinement and microstructural modification.

1.2.5 Literature Survey on SEM Analysis of coated samples

Rochat et al. (2003) studied the mechanical properties of ultrathin oxide coatings on polymer substrates by scanning electron microscope and stated that uniaxial fragmentation tests were carried out in situ in a scanning electron microscope (SEM) on 10-nm-thick silicon oxide coatings deposited by plasma enhanced chemical vapour deposition on polyethylene terephthalate. In order to prevent charging effects due to the isolating nature of the oxide surface, an additional conductive gold layer was sputtered onto the coating prior to its tensile loading in the SEM chamber. It was nevertheless
possible to analyze the damage mechanisms of the thin coating without a gold layer due to sufficient crack opening. The coating cohesive strength was found to be equal to 5.1 GPa and the coating polymer interfacial strength was found to be equal to 84 MPa using a Weibull size-dependent probability of failure for the oxide, and assuming a perfectly plastic stress transfer between the different layers.

Cheang et al. (2005) discussed the thermal sprayed tungsten carbide (WC) cobalt (Co) coatings. It was extensively employed as abrasion/wear protective layers. However, carbon loss (decarburization) of WC–Co powders during thermal spraying, reduced the efficiency of the coatings against abrasive wear. Post-spray treatment with spark plasma sintering (SPS) technique was conducted on plasma-sprayed WC–Co coatings in the present study with the aim to compensate the lost carbon in the coatings. X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and transmission electron microscope (TEM) was utilized to characterize the microstructure and phase changes in the coatings brought about through the SPS treatment. Results showed that the rapid SPS technique was successful in supplying superfluous carbon for the restoration of WC in the coating through phase transformation from W2C or reaction with W. The predominant presence of WC was revealed in the coatings treated with SPS at 800 °C up to 6 min. Furthermore, changes in microstructure, e.g. grain size growth, redistribution of various indigenous phases, were revealed within the coatings after the SPS treatment. It was found that the SPS-induced WC reconstruction will be achieved within the coating surface with limited thickness. Transmission electron microscopy (TEM) results also showed the evidence of supplementary reaction between Co and WC/W2C to form Co3W3C during the SPS processing. Micro-hardness values obtained on the surface of SPS-treated coating proved 40% enhancement over as-sprayed surface.
Mikowski et al. (2010) stated that hardness for rough surfaces will be obtained by instrumented indentation data using two different methods: the Oliver and Pharr method and the one proposed by Malz binder which was based on mechanical energies involved at the tip surface contact. This method was based on energy appeared as promising to evaluate hardness of rough surfaces, since the energy variations are less influenced by the initial contact with the asperities. The methods were compared using data from a reference material (soda-lime glass) and then applied to a rough titanium surface obtained by glow discharge nitriding. Indentation hardness values were also corrected by a method previously developed, which was based on stiffness analysis at the contact, and the results compared for both described. The reinforcement properties of bacterial cellulose nano fibers were considerably enhanced by an enzyme treatment. The enzymatic treatment also had the advantage of causing less material loss in comparison to other nano fiber production processes, such as acid hydrolysis or mechanical fibrillation. The increased reinforcement capacity of the enzyme treated fibres was related to two different mechanisms. The first was the elimination of less organized regions between the fibers that entangled them to each other in the original material, thus allowing a much better dispersion of the reinforcing agent into the starch matrix. The second was the reduction of defects in the surface of the fibers that could act as crack propagators.

1.2.6 Literature Survey on X-Ray Diffraction particle synthesis

Chiaramonte et al. (2006) produced TiO$_2$ and TiNxOy thin films by low pressure metal-organic chemical vapour deposition (LP-MOCVD) on top of Si (001) substrate and the coatings were characterized by X-ray multiple diffraction. X-ray reflectivity analysis of TiO$_2$ [110] and TiNO [100] polycrystalline layers allowed to determine the growth rate (80 Å/min) of TiO$_2$ and (40 Å/min) of TiNO films. X-ray multiple diffraction through the
Renninger scans, i.e., f-scans for (0 0 2)Si substrate primary reflection is used as a non-conventional method to obtain the substrate lattice parameter distortion due to the thin film conventional deposition, from where the information on film strain type can be obtained. For both films the surface mosaic spread increases with the thickness so that, imperfection on the substrate surface (interface film/substrate) increases for thinner films and stabilizes itself around 65 s for films thicker than 150 Å.

Gou et al. (2011) discussed about the stress measurement based on the importance and complex working environment of X70 pipelines. Analyses were performed on an in-service process pipe, an anamorphic pipe in tunnel and three new welded pipes. Stresses in both the inner and outer walls of the pipes were measured by X-ray diffraction and thus the components of complex stress, internal pressure working stress, welding residual stress (WRS) and bending stress were obtained by comparative analysis on stresses of various pipes. The results indicated that the maximum WRS occurred in the heat affected zone on inner wall, and its orientation is parallel to the weld seam. These maximum WRSs in various measured spots are mostly more than 0.80σ.2 and up to 1.05σ.2. However, on outer wall the stresses are less than 0.40σ.2, and WRS appears in the weld area of 40mm wide. Maximum axial and circumference stresses for the tunnel pipeline were up to 0.93σ.2 and 0.80σ.2 respectively. High WRS and other additional stress may lead to stress corrosion and corrosion fatigue in natural gas transmission pipeline. The HAZ is the weakest position of the pipeline and should be monitored and controlled carefully. The maximum principal stress of WRS is parallel to the weld and the high WRS occurs in the zone of 40 mm wide around the weld.
1.2.7 Literature Survey on Wear Test of coated specimens

Yan et al. (2003) studied of sliding wear caused by pin-on-disc test apparatus. The proposed framework indicates the wear rate in the plane strain region can be determined from a two dimensional idealization of the contact problem and three dimensional contact analyses. Periodic unit cell techniques are used in conjunction with a ratcheting based failure criterion to predict the wear rate in the central plane strain region. The approach is used to predict pin-on-disc test data from an Al–Si coating using a tungsten carbide pin. The predicted results are found to be consistent with measured data. Numerical results indicate that z-pins can greatly increase mode current delamination toughness of composite laminates. Parametric study showed that increasing the pullout peak force through improving z-pinning technique can greatly improve the delamination toughness of z-pinned laminates.

Venkateshwarlu et al. (2003) worked on the dry sliding wear tests on specimens of mild steel (MS) and WC coated mild steel (MSC). The specimens were performed against hardened EN32 steel and a WC coated EN32 steel disc. Four different combinations of specimen and counter surface were tested under dry sliding conditions. Results showed that wear mechanisms differ depending on the combination of materials under the sliding contact of MS specimen suffered high wear loss, but the MSC specimen showed interesting results. MSC specimens showed negative wear results against EN32 disc, whereas positive wear results occurred against EN32C disc. Steady wear rate was attained after a critical sliding distance. The strength and stability of the transfer film to sustain sliding conditions depends on the ductility of the binder phase, cobalt. Cobalt owing to its appreciable ductility promoted the formation of a dense transfer film, which showed good adherence under dry sliding conditions. It may be concluded that the equilibrium rate of film transfer to the disc may be due to the loss of wear
particles as debris presented during sliding motion. Thus HVOF sprayed dense WC coating may be used for protection against wear under dry sliding conditions.

Rayon et al. (2011) studied on hardness and Young's modulus distributions in atmospheric plasma sprayed WC–Co coatings using nanoindentation. The statistical indentation analysis of WC–Co coatings obtained by atmospheric plasma spray (APS) with two secondary plasma gases, H$_2$ and He, was investigated using an instrumented indentation technique with the aim of correlating the influence of the nano mechanical behavior of each constituent phase with the micromechanical characteristics of these coatings. X-ray diffraction (XRD) and backscattered electron (BSE) analysis showed that H$_2$ gas produced a greater decarburisation of the WC phase. Although this phase was hardened by decarburisation, it caused the WC and W$_2$C measurements to shift to lower values, matching the mean mechanical behavior of the coatings. The carbides measured on Co and Co–W+C softer phases displayed an induced error even at the tested 45 nm penetration depths, making it necessary to revise all the previous data acquired for the WC nanohardness obtained in this composite.

The dissolution and decomposition of the WC phase during the process produced a Co+W+C solid solution as binder phase and the formation of W$_2$C and W as secondary phases. The nanohardness (H) and Young's modulus (E) resulting from a grid of 300 indentations performed at 50 nm in depth identified the characteristics of each phase in the heterogeneous structure produced by decarburisation. A statistical study by a CDF fit and Gaussian simulated distribution showed that the mechanical properties of the coatings were governed by the binder phase content, which decreased the hardening effect of the arising hardest phases (W$_2$C and Co+W+C solid solution).
1.2.8 Literature Survey on Corrosion Test

Spencer et al. (2003) investigated the stress-corrosion cracking and bending tests of 304L stainless steel substrate with a corrosive atmosphere containing magnesium chloride. After 500 hours of exposure to the corrosion environment, closely spaced cracks are seen on the specimens. The results also indicated the threshold stresses of 10 MPa and a threshold humidity of 30%. Cracking rates increased with stress to maximum at plastic strains to the extent of 2%. Examination of cracks by focused ion beam milling and electron diffraction indicated a multi-stage mechanism of propagation of cracks through preferential oxidation of slip planes. The apparent activation energy was 34 kJ mol\(^{-1}\) in the temperature range 333 K–363 K. Corrosion rates were given by the Weibull distribution function, mean and standard deviation wherein the maximum values for corrosion rates are obtained for structural members based on the entire population of the database.

Dubey (2006) studied the importance of corrosion of dental metals and alloys. The author discussed that the better understand on effect of corrosion in the oral problem. Due to wide change in the environmental conditions the generalized conclusions were difficult to arrive, hence the author inhibited the compounds by using electrochemical techniques such with open circuit potential and potentio-dynamic polarization and provided the guidelines for tafel plot based experimentation on corrosion.

Baorong et al. (2007) investigated the effect of UV illumination on the NaCl-induced atmospheric corrosion of 09CuPCrNi weathering steel (WS) qualitatively and quantitatively. UV illumination strongly affects the NaCl-induced atmospheric corrosion process of 09CuPCrNi-WS substrate mainly through the photovoltaic effect of the corrosion products with semiconductor properties. The photogenerated electrons and holes can directly participate in the cathodic and anodic reactions and thus directly affect the
atmospheric corrosion rate of 09CuPCrNi WS. Meanwhile, the photogenerated electrons and holes can directly involve in the corrosion product formation process and therefore affect the performance of the corrosion product layer formed under UV illumination. Triazole derivatives show excellent inhibition properties for the corrosion of mild steel in 1 M HCl solution, and the inhibition efficiency increases with increasing the concentration of the inhibitors. The values of free energy of adsorption and the calculated quantum chemical suggest that the inhibition behavior of these triazole derivatives involves two types of interaction, chemisorption and physisorption.

Maggiolino (2008) compared the corrosion properties of Aluminium samples made out of friction stir welding process and the metal inert gas welding (MIG). Welding of aluminium is a critical operation due to its complexity and the high level of defects that can be produced in the joints. The factors that promote defects in the aluminium metal are high thermal conductivity, high chemical reactivity with oxygen and high hydrogen solubility at high temperature. The analysis was conducted on welded and polished samples in an acid salt solution. Sample sheets of two aluminium alloys with two different thicknesses were considered for welding both via MIG and FW techniques. In MIG welding AA6082 T6 sheet has been used with same metal as the filler metal while AA6060 T5 sheet was used in FW. Results indicated that the FW sample has better corrosion resistance than the MIG samples.

Xiaogang and Liang (2009) studied the influence of various AC current densities on stress corrosion cracking behavior and mechanism of X80 pipeline steel in carbonate/bicarbonate solution by polarization curves and slow strain rate tensile tests. Results indicated that with the increasing AC current density, the SCC susceptibility of the steel increases, especially at high AC current density. The significant difference in the SCC behavior and
mechanism was found for the steels with or without application of AC current. In the absence of AC current, the fracture mode is inter-granular and the mechanism was attributed to anodic dissolution. Under AC current application, the cracks propagation is trans-granular, and the mechanism is controlled by both anodic dissolution and hydrogen embrittlement.

Marimuthu (2010) introduced optoelectronic instrument for measuring corrosion of metal surfaces. Here, the measurement is done using the scattering pattern. The instrument consists of a thin beam light emitting diode (LED) and an array of photodiodes spread over a hemispherical structure covering. The light from the LED illuminates a tiny spot of light on the metal surface and the photodiode records the light scattering pattern. Using this scattered pattern a mathematical model is developed which defines how the corrosion factor is correlated with the light scattering pattern. The temporal behavior of corrosion of stainless steel samples immersed in nitric acid of various concentrations was analyzed. Traditional light scattering based experiments has limitations such as poor sensitivity of the sensors, and size of the laser that restrict the portability of the instrument. The proposed instrument overcomes these limitations with its simple, quick and online applications. The major limitation is that this instrument is suitable for measuring the initial stages of corrosion until a thin film of corrosion covers the entire surface.

Qiao (2010) presented a sensor based detection method for the identification of corrosion in reinforced concrete structures. The sensor used here is based on the electrochemical techniques. A half-cell potential map and guard ring techniques are applied as typical qualitative and quantitative methods to access the corrosion status, respectively. The experimental setup consists of an RC panel which is provided with pressure piping that injects typical NaCl solution at the measuring points. After 30 days, the corrosion rate and the half-cell potential of concrete panel were measured by the Gcorr
system and copper sulphate electrode. The data were collected before and after the NaCl solution application. It is found that probability corrosion is less than 10% before and 90% more after the NaCl application.

Samuel (2011) studied the corrosion behavior, particularly in saline as well as acidic environment along with its effect on mechanical properties of pearlitic rail steel. The cases of corrosion of rail under Indian environment were studied. It has been determined that in marine environment, both the yield strength and tensile strength decreased with increasing corrosion rate. In an acidic environment, yield strength increased with increasing corrosion rate, although the tensile strength decreased with increasing corrosion rate. The author suggested that in highly aggressive corrosion zones like the sea coast areas and wide underground tunnels, the rail tracks made of pearlitic steel may be replaced with bainitic rail steel which is expected to have higher mechanical properties than pearlitic rail steels.

Roqueta (2011) proposed the non-destructive corrosion damage detection method for reinforced concrete structures based on the analysis of the electromagnetic signature of the steel rebar corrosion. Electrochemical measurement techniques require partial exposure of steel reinforcement which makes it not suitable for all situations and nondestructive evaluation (NDE) methods using ground penetrating radar under traditional operation mode (100 MHz to 3 GHz) as it results in blurred image which is not sufficient for proper analysis. An optimized system consists of electromagnetic reflections capable of detecting and quantifying the steel corrosion at any stage of the corrosion process can be developed for use. Here measurements are taken on 12 reinforced concrete samples using three different antenna setups for different frequency ranges.

Jun (2012) dealt with the corrosion analysis in semiconductor devices. Since such devices have very small dimensions, they are very much
prone to airborne molecular contamination. During wafer preparation many acids such as HF, HCl and Sox are used which will create an acidic environment which in turn causes the corrosion of the metals in the semiconductor device application. In a real fab environment, metal corrosion defects were found with HCl concentration at 2.9–4.2 ppbv during 10 minutes of short exposure test. This result shows that the pattern wafer exposure time can be shortened from 1 hour to 10 minutes for a real 150 mm fab. The metal corrosion in semiconductor devices is mainly caused by either HCl induced corrosion or local induced meal corrosion. The factors which promote this metal corrosion are Al grain size, metal film thickness, backside conditions of the wafers, metal etching process parameters and lithography pattern density. Analysis indicated that among these factors chlorine ion contamination is more significant. Al-Cu pattern wafer was employed in a simulated chlorine contaminated environment and monitored using IC analyzer.

Fahimpour et al. (2012) presented the corrosion behaviour of the aluminum alloys, mainly aluminum 6061 and its welding behaviour. Depending on the specific application, corrosion behaviour is a significant factor of a welded joint. It is noted that the welded zones of most joints are susceptible to corrosion. Factors which promote the corrosion in this region are porosity, crack, residual stress, wrongly selected filler and incorrect design of the edges. Here wrought 6061-T6 aluminum sheets having a 13mm thickness were welded together by friction stir welding (FW) and gas tungsten arc welding (GTAW) methods. Aluminum 4043 alloy was used as the metallic filler in GTAW. It is found out that the FW joints having a higher resistance to corrosion than GTAW joints. Its microstructural changes are studied using Tafel polarization cell using 3.5wt% NaCl solution.

Alamin et al. (2012) studied the non-destructive evaluation method which was applied to a set of mild steel with varying levels of
corrosion and various surface preparations. The author focused on the characterization of early-stage corrosion with an increase in thickness. Additionally, many steel components include a coating material and corrosion occurs under the coating. Based on these considerations, uncoated and coated steel samples provided by International Paint, with corrosion produced in a marine atmosphere are evaluated. The panels were exposed to outdoors for the same period of time and the surfaces prepared in different ways, resulting in four different corrosion grades in accordance with the surface preparation standards of the society for protective coatings. The responses from PEC testing is a complex mix of factors such as coating thickness variations, electrical conductivity and magnetic permeability changes due to the chemical process of corrosion and surface roughness changes from both corrosion and blistering or delaminating of the coating layer. By using time-frequency domain PCA of PEC responses from a set mild steel set one can differentiate the various corrosion grades easily.

Cranny (2012) dealt with the sensor based diagnosis of corrosion with the nickel-aluminum bronzes (NAB) in marine environments and the detection copper ions during the corrosion process. The author explored the development of voltammetry sensors for the detection of corrosion by-products primarily from copper-nickel alloys used in marine environments. Robust sensors with the minimum of maintenance and capable of sustained operation over long time scales are required considering the nature of these environments and the area of application. Planar screen printed platinum electrodes were developed for use in corrosion monitoring have been evaluated using cyclic differential pulse voltameter and shown to detect cupric ions over a range up to 100 mm in a background of 3.5% by weight sodium chloride solution. The author suggested that in 3.5% NaCl the reduction of Cu$^{2+}$ to metallic copper proceeds as two successive single-electron reactions. It is evident that screen-printed platinum electrodes demonstrate identical
behavior to that of pure platinum under the same conditions, giving confidence in their use as a cheaper alternative electrode material.

Changfeng et al. (2013) investigated the effect of carbon steel in the aqueous H$_2$S environment. The products, which include mackinawite, cubic FeS, troilite, and pyrite, are characterized through their shapes, chemical compositions and crystal structures. Mackinawite appears with a flake shape, Cubic FeS has a perfect/truncated octahedral shape and pyrite is framboind-shaped. Flower-shaped troilite is developed from beam- or hexagonal wire-shaped grains by electrostatic interactions along a certain lattice plane. The large single beam-shaped troilite has a growth pattern along the c-axis. The corresponding crystal structure micro-morphology and three-dimensional models were generated. The studies indicated the dissolution of the inclusion and the re-passivation of the fresh matrix has important functions in the initiation of pitting corrosion. This pitting corrosion occurs due to oxides of Mg, Al, Ca inclusion because of its lower surface potential.

El Hajj et al. (2013) investigated the carbon steel corrosion in carbon dioxide clay-rich environment for understanding its behavior under geological conditions. The results show the formation of magnetite as the main source of corrosion followed by the formation of different corrosion products with complex mixtures of iron-oxide, hydroxycarbonate, hydroxychloride and sulfide phases. These results strongly contrast with similar experiments conducted under H$_2$ atmosphere where the major corrosion products consisted of iron sulfides. The authors suggested considering all the geochemical parameters including gas composition to study better the corrosion of steel buried in geological formations. The transition from aerobic to anaerobic conditions stimulates SRB activity and hydrogen sulphide production. This results in the transformation of ferric oxyhydroxide, formed during the aerobic
stage, into pyrrhotite and leads to a better protection of steel under anaerobic conditions.

Guilbert et al. (2013) studied the remote measuring of corrosion in places like underwater parts of the ships, pipelines etc. The application of electrochemical phenomenon and the computational aspect of electromagnetic fields were utilized. This new method of measuring corrosion ensures great accuracy in short time. The underwater structures suffer from corrosion mainly due to galvanic coupling. In order to protect the structure from such type of corrosion two methods were used (1) sacrificial anode cathodic protection and (2) impressed current cathodic protection. In these two methods, electromagnetic fields will be produced. By studying these field properties one can diagnose the presence of corrosion in the structures. The authors study was based on electric fields and applied to real measurements on a mock-up, extensively improves a method based on electric potential measurements.

1.3 MOTIVATION OF THE RESEARCH

The literature survey indicated that many researchers have undertaken research on cladding the cobalt based alloys on valves based on conventional hard facing techniques by the TIG welding process on selecting the clad materials in form of uncoated wire and optimizing its bead parameters. The findings indicated the formation of hydrogen induced cracking in hardfaced surface due to thermal barrier between the clad metals and substrate. This research gap leads to the introduction of flux cored stellite 6 wire for further experimentation. It is also absorbed that only few research works focused on thermal spray processes coated on steel substrate and limited researchers focused on Nano-coating of metallic components. The research gap identified from the literature has to be addressed for further improvement in processing techniques, methods and materials to suit the valve industry.
Hardfacing and coating (surface treatment) have become more important because of the increasing demand for low cost industrial valve applications. In most hard facing techniques as indicated in the literature survey, the failure occurs due to weak bond between the substrate and coating materials. It is also unpredictable for identifying the internal defects like porosity, cracks, brittle nature between the coating surface layers. Pre-surface treatment and post surface treatments are proposed technologies for constructing the hard-faced structure. The surface defects present in the hardfaced surface can be minimized with optimum process parameters like wire feed rate and current for controlling the dilution, penetration and bead width. In the proposed system, the surface modifications are done on the primary base element. The optimum parameters are designed by design of experiments software Mini tab and Genetic algorithm for coding. The microstructural analysis were carried out to study the porosity and residual elements present in the coated materials.

Coating of the surface includes thermal spraying techniques in which coating materials are melted or heated and sprayed directly onto a surface. The "feedstock" (coating precursor) is heated by electrical (plasma or arc) or chemical means (combustion flame). Thermal spraying can provide thick coatings (approx. thickness range is 20 micrometers to several mm, depending on the process and feedstock), over a large area at high deposition rate as compared to other coating processes such as electroplating, physical and chemical vapor deposition. Coating materials available for thermal spraying include metals, alloys, ceramics and composites. They are fed in powder or wire form, heated to a molten or semi molten state and accelerated towards substrates in the form of micrometer-size particles. Combustion or electrical arc discharge is commonly used as the source of energy for thermal spraying. Resulting coatings are made by the accumulation of numerous sprayed particles. The surface may not heat up significantly,
allowing the coating of flammable substances. Coating quality is usually assessed by measuring its porosity, SEM analysis, wear testing and corrosion testing. Generally, the coating quality increases with increasing particle velocities.

The problem with the thermal spray coating is physical damage to the base materials and increasing carbon content, insufficient coating and difficulty in masking. In the present work described in this thesis effort has been given to minimizing the HAZ, providing masking on the surface by introducing the sol gel processes and electro phobic process which were earlier used for coating of glass applications.

The objective of this work is to replace the conventional hardfacing techniques with thermal spraying or nano-coating materials. The materials under investigation are ceramic elements like zirconium, titanium, molybdenum, tungsten-cobalt alloys. The results were interpreted for corrosion, wear and SEM analysis were done to confirm the results and prove the concept with hard facing alloys

1.4 RESEARCH OBJECTIVES

The research work aims to develop a suitable surfacing material, methods and processes with minimum cost, maximum corrosion resistance and minimum wear resistance suit high pressure valve applications. The selected base substrate is low carbon steel (ASTM A216) with of less than 0.25% Carbon. The steel specimens are hard-faced, thermally sprayed and nano-coated with the clad materials. The primary objectives of the research work are proposed as below:

i. To conduct experiments on hardfacing of low carbon steel by MIG processes by developing a mathematical model for weld
bead geometry, dilution and penetration and compare their corrosion and wear properties with minimum porosity.

ii. To apply thermal spray coating processes for minimizing the deposition thickness, eliminating the post heat treatment and machining processes with improved corrosion and wear properties.

iii. To introduce nano-coating process with corrosion and wear resistance by enhancing the hydrophobic property of the substrate.

iv. To utilize the nano-coating on substrate for minimizing thermal stress as an alternative for surfacing of the substrate through hardfacing and thermal spray coating.

v. To appraise the results of corrosion, wear and metallurgical studies of hard-faced coating, plasma sprayed coating and nano-coating to infer on the best coating methodology and materials.

Thus, the main focus of this research is to design and analysis of a suitable surfacing material for metal valve applications that would have considerable benefits over the traditional hardfacing methods.

1.5 ORGANISATION OF THE THESIS

The thesis is organized to report the studies of corrosion, wear and metallurgical characteristic of various clad materials and clad techniques and organization of rest of the chapters given below,
Chapter 2 discusses on “Investigation of tribo-corrosion properties of ASTM A216 steel through hard-facing by FCAW processes”, where in the mathematical model developed for hardfaced processes, experiments were conducted for Flux core Stellite wire, FW2 and FW3 by MIG welding processes and the results were validated by conducting corrosion, wear and metallurgical analysis.

Chapter 3 elaborates the methodology for “Investigation of tribo-corrosion properties of ASTM A216 steel through Plasma Spray Process”. The coating materials prepared Tungsten Carbide –Cobalt powder, Zirconium and Molybdenum were subjected to investigations. The corrosion, wear and metallurgical studies were conducted and presented.

Chapter 4 presents the Nano coating on the WCB A216 material with different process like Sol gel and Electrophoretic deposition process with various materials coated like zirconium and molybdenum. The corrosion, wear and metallurgical studies were conducted for validation.

Chapter 5 explains the overall performance of all the processes which are carried in this work. It also gives more knowledge about hard facing, plasma coating and nano-coating processes. The results were compared and discussed in detail.

Chapter 6 concisely gives the conclusions of the research work carried out in this thesis. Possible directions for future research were also highlighted.