This thesis deals with modeling and analysis of a manufacturing process, namely plasma spraying. Plasma spraying is a thermal spraying technique, which comes under surface modification technologies. In this chapter, the basics of thermal spraying and plasma spray coating process have been introduced first, followed by an extensive survey of the literature on analytical, statistical and soft computing-based modeling of the plasma spraying process. This is followed by framing of the aims and objectives for this thesis work based on the literature survey. The contributions made by the author and the layout of the thesis are reported at the end of this chapter.

## **1.1 Introduction to Plasma Spray Coating Process**

Thermal spray processing is a very rapidly expanding field of surface engineering. It is the generic category of material processing technology that uses consumables in the form of a finely divided molten or semi-molten droplets to produce a coating onto the substrate kept in front of a high velocity impinging jet, which carries the particles. The melting of the consumables may be accomplished in a number of ways, and the consumable can be introduced into the heat source in either wire or powder form.

Such coatings provide a wide range of applications, e.g., resistance to wear, corrosion, high temperature and oxidation, electrical insulation, etc. Compared to thin films, thermal spraying ususally produces much thicker coatings. The thickness can range from 25  $\mu$ m to a few mm, 300  $\mu$ m being a typical thickness. Using this process, it is possible to coat over an area extending to several square meters and with a high deposition rate, where consumables of the order of several kgs per hour can be deposited. Thermal spraying repesents a group of versatile processes, where it is possible to deposite metals and alloy, ceramics and polymeric materials.

Thermal spray processes can be classified as follows:

- flame spraying,
- wire arc spraying,
- high-velocity oxy-fuel spraying (HVOF),
- plasma spraying,

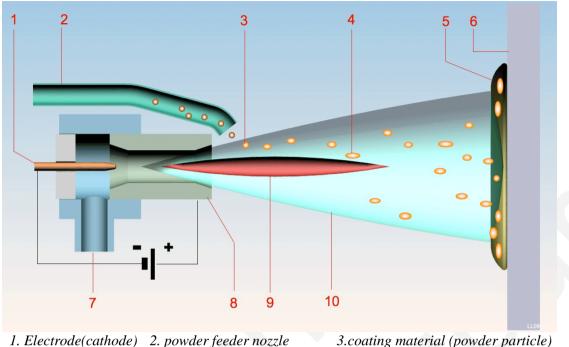
2

- detonation spraying,
- cold gas dynamic spraying or Cold spraying.

Plasma spraying is a well-known thermal spraying process, where the heat source is constituted by a plasma. The schematic of the process is shown in Figure 1.1. An arc is created between a bullet shaped tungsten tipped copper cathode and an hollow copper anode (both water cooled). Plasma generating gas is forced through the annular space between the electrodes. During the passage through the arc, the gas undergoes ionization in the high temperature environment producing plasma. The ionization is achieved by collisions of electrons of the arc with the neutral molecules of the gas. The plasma protrudes out of the electrode encasement in the form of a flame. The consumable material, in the powdered form, is poured into the flame in metered quantity. The powders melt immediately, and absorb the momentum of the expanding gas and rush towards the target to form a thin deposited layer. The next layer deposits onto the first immediately after and thus the coating builds up layer by layer (Heimann, 1996; Budinski, 1988; Powloski, 1995). Sometimes consumables in wire shape can also be used (Pfender, 1999).

The Plasma Spray Process has the ability to produce metallic, ceramic and polymeric coatings. The quality of coating depends on the process parameters. This process involves a large number of such parameters. Examples of major process variables are arc power, plasma gas composition, pressure, flow rate, powder injection details, carrier gas flow, torch-substrate (stand-off) distance, and others.

Plasma spraying has emerged as an important tool of increasingly sophisticated surface engineering technology. It caters to the components belonging to aerospace, energy, oil and gas, automotive, computer and telecommunication industries. The particularly important segment of biomedical coatings for implant is today served by a variety of coating technologies with plasma spraying as the leading contender. This process can also be used to produce free standing part for various shapes and sizes.



1. Electrode(cathode)2. powder feeder nozzle3. coating material (powder particle)4. molten particle5. coating6. Substrate7. plasma gas8. plasma gun nozzle(anode)9. Plasma plume10. spray stream

Figure 1.1: Plasma Spray Coating Process (Courtesy: nl.wikipedia.org)

#### **Need for Input-Output Modeling**

Production of reliable coatings depends on:

- selection of the correct coating materials,
- use of the correct coating process,
- proper surface preparation,
- operating parameters,
- process automation (Grainger and Blunt, 1998).

In order to automate a manufacturing process, its input-output relationships in both forward and reverse directions must be known beforehand. Plasma spraying is a relatively straight forward in concept but rather complex in function. Practical difficulties are often encountered arising from the use of the system under nonoptimal conditions. Functionally, the plasma spraying process is governed by a number of variables, of which many are interrelated. Accurate and comprehensive insitu measurements of the plasma spray process are difficult and sometimes impossible. Hence, process modeling is a prerequisite to automation.

### **1.2 Literature Review**

Plasma spray coating process had drawn the interest of the researchers across the globe to understand and model the inherent complex physics underlying the process. A considerable amount of research work had been carried out for modeling of plasma spray coating process, which involved mathematical and thermal analysis, statistical regression analysis, and in recent years, soft computing-based approaches. Fisher (1972) put an insight on the variables influencing the characteristics of plasma spray coating. In his extensive review on plasma spraying process, approximately 150 variables could be identified, of which many are interrelated and this makes exact analysis of the system very difficult.

#### **1.2.1 Mathematical and Thermal Modeling Based on Experiments**

The problem of optimizing the coating process calls for mathematical models of such processes. Once constituted, such models can be utilized to solve the problems of thermal spraying processes in the rational regimes and it is expected that such models would serve to obtain coatings with improved properties.

Garvis and Shevchuk (1991) proposed a generalized mathematical model of thermal spraying in order to compute the radiation energy, effects of turbulent flow of the gas jet, spraying distance and required degree of preheating of the substrate, keeping in mind the thermal processes that come into play during coating. Micro-structure, composition and property relationships of plasma sprayed thermal barrier coatings had been analyzed by Taylor and Brandon (1992). They measured the phases, microstructure, mechanical properties, thermo-physical properties like thermal diffusivity and thermal expansion coefficient and annealing behavior of partially stabilized zirconia coatings on nickel-based super-alloy substrates.

Fluid dynamic analysis of temperature, velocity, and concentration distribution in plasma jets was performed by Pfender (1994). The behavior of a typical plasma spray jet was discussed, including turbulence, gas entrainment, jet instabilities, demixing effects and the associated problems of measuring temperature and velocity fields using spectroscopy and enthalpy probes. Moreover, particle behavior in a plasma jet,

including particle trajectories, particle velocities, and their heating histories were analysed. Plasma jets used for plasma spraying showed strong fluctuations owing to fluid dynamic effects as well as instabilities induced by the arc motion in the anode nozzle. Modeling of the arc root motion was in qualitative agreement with experimental findings. Entrainment of the surrounding cold gas into the plasma jet was found to be detrimental in terms of both particle heating as well as particle acceleration.

A one dimensional mathematical model was developed by Das et al. (1995) relating the effects of parameters on temperature and velocity of particles, and on the void content of coating. Ahmed and Bergman (1999) developed a two-dimensional model of the heat transfer process using enthalpy-based control volume formulation. This model had been used for predicting the thermal history of nano-structured ceramic coatings during deposition. Wan et al. (2001) also had presented a model, which subsequently had been tried for improving the spray conditions of functionally graded materials. They applied computational fluid dynamics concept to model the plasma gas flow.

Zagorski and Stadelmaier (2001) reported a full-scale model of a thermal spray process through comprehensive simulation. Simulation results were compared with experimental data in respect of the influence of particle size, temperature, speed, spraying angle and stand-off distance on coating structure and surface texture.

Influence of process parameters on the deposition foot print in plasma spraying had been modeled by Ramesh et al. (2003). This report dealt with spatial distribution of particle parameters, such as temperature, velocity, and size in the plasma plume and their comparison with experimental measurements. The authors compared their simulation predictions with a well-documented experimental measurement of in-flight particle temperatures, size, and velocities published by Kucuk et al. (2001).

Ghafouri et al. (2003) developed a stochastic model to simulate the formation of a thermally sprayed coating to predict porosity, thickness, roughness and their variation with particle speed, particle size and gun traverse speed. A model of High Velocity

6

Oxy-fuel (HVOF) spray coating process involving process parameters like particle size, temperature, velocity on splat geometry and coating microstructure had been presented by Mostaghimi et al. (2003). They applied gas dynamics and heat transfer concepts in their analysis.

Finite element analysis of layer-wise deposition, heat transfer and process cooling of thermally sprayed coating on light metal substrates had been performed by Wenzelburger et al. (2004) for the purpose of layer growth and residual stress modeling. In this case, spraying on the internal surface of a cylinder liner was considered. The effect of various simultaneous cooling techniques on the heat transfer was also analyzed.

Mariaux and Vardelle (2005) developed a three-dimensional model of plasma spray process that could provide a useful insight in the time-evolution of the performance of the process. The effect of the transient behavior of the arc on the gas flow had been modeled with a time dependent heat source. This heat source was located inside the plasma gun nozzle and it evolved with the arc voltage.

A hybrid (deterministic and stochastic) model of the HVOF process had been proposed by Li and Christofied (2005). The model included continuum type differential equations that described the evolution of gas and particle temperature and velocity, and a rule-based stochastic simulator that predicted the evolution of the coating microstructure. Dyshlovenko et al. (2006) carried out numerical simulations of different parametric conditions like career gas flow rate and standoff distance to model plasma particle interactions and coating growth during plasma spraying of hydroxyapatite.

The analytical approaches for the modeling of both thermal as well as plasma spraying processes undertaken by various researchers have been discussed above. However, it was found to be difficult to obtain any ready-to-use model for obtaining input-output relationships of these processes owing to their inherent complexity.

## **1.2.2 Statistical Regression Analysis on Plasma Spray Coating Process**

Plasma spraying is a complicated process involving a large number of process parameters and comprising of various phenomena, all of which may not be understood completely. Thus, it may not be always possible to develop an appropriate differential equation of the said process. In such situations, models are made from the outcomes of experiments performed according to some statistical designs and then, analyzed by regression methods to predict the required output. Several attempts had been made to carry out statistical regression analysis for determining input-output relationships of thermal spray coating process. A brief description of some of the major studies is given below.

Lovelock et al. (1998) worked on the optimization of process parameters of atmospheric plasma spray (APS) and high velocity oxy-fuel (HVOF) spraying deposited WC-Co coatings using Taguchi method. Preliminary work using Taguchi's statistical experimental design was not so useful, since the variations in measured properties were too small to be correlated with the changes in the levels of spray parameters. The application of Taguchi method would have been more effective over a much wider parameter space than that was used originally.

Kingswell et al. (1993) investigated vacuum plasma spray deposition of metal, ceramic and cermet coatings using full and fractional factorial designs of experiments. Experiments were conducted considering six process parameters, namely gun current, flow rates of plasma gases, flow rate of powder carrier gas, chamber pressure and spray distance, and their effects on particle melting and spray efficiency were analyzed. It was found that the processing of an alumina powder was very sensitive to the variations in deposition conditions, particularly injection velocity of the powder and plasma gas composition. In comparison, a nickel-based alloy metal powder and WC-Co were less sensitive to the processing conditions.

The influences of process parameters of the HVOF process on the microstructure and oxygen content of MCrAlY coatings were discussed by Lugscheider et al. (1998). The authors used a two-level factorial plan of  $2^{(4-1)}$  type experiment, considering four parameters, namely fuel/oxygen ratio, spray distance, powder feed rate and powder

carrier gas flow rate. It was found that the spray distance, fuel/oxygen ratio and powder feed rate exerted a major influence on the microstructure and oxygen content, whereas the effect of carrier gas flow rate was not so significant.

Saravanan et al. (2001) carried out experimental investigations to produce highquality alumina coatings by optimizing the detonation spray process parameters following a  $(L16-2^4)$  factorial design approach. The process parameters considered were fuel ratio, carrier gas flow rate, frequency of detonations and spray distance. The corresponding responses were roughness, hardness and porosity of the coating. The performance of the coating was evaluated on the basis of erosion, abrasion and sliding wear testing. Fuel ratio, spray distance and carrier gas flow rate were the three major controlling parameters identified for almost all the coating properties studied. Furthermore, frequency of detonations was found to have no significant influence on the coating attributes. However, it was the only dominant factor influencing surface roughness. The results of their study clearly indicated that a higher fuel ratio, a lower spray distance and a lower carrier gas flow rate would result in improved particle melting and higher particle velocity, which, in turn, could produce coatings with a lower porosity, a higher hardness and an improved wear resistance. An optimal combination of detonation spray parameters for the selected spray-grade of  $Al_2O_3$ powder had been identified with a reduced number of experiments by utilizing a fractional-factorial design.

Mawdsley et al. (2001) conducted statistically designed experiments and multiple regression analysis to determine the effects of process parameters on the following properties of plasma sprayed alumina coatings: permeability, hardness and thickness. The parameters, viz., powder injection angle, powder injection offset, plasma gun power, plasma gas flow rate, percent of hydrogen in plasma gas flow and spray distance had been used in a 2-level fractional factorial design of experiments. Additionally, the following parameters were considered in a separately conducted 3-level D-optimal design of experiments: carrier gas flow rate, spray distance, arc power and plasma gas flow rate. It was found that plasma sprayed alumina could provide good corrosion protection against salt water solutions. However, the coating hardness could not be optimized under the same conditions. The conditions that yielded coatings impermeable to salt solutions were those that imparted somewhat low

particle velocities and temperatures. On the other hand, conditions promoting high coating hardness were high particle temperatures and velocities. Finally, the conditions of high particle temperatures with low particle velocities yielded the thickest coatings.

A full-factorial design with three factors, each set at two levels was performed by Burlacov et al. (2006) to determine the dependence of photocatalytic activity of titania coatings on processing parameters like plasma power, carrier gas flow rate and powder feed rate. The concentration of rutile, anatase and oxygen deficient phases were found to depend upon the career and plasma gas flow rates. Rodriguez et al. (2003) conducted an experimental study of the wear performance of NiCrBSi thermal spray coatings using a  $2^4$  factorial design.

A full-factorial design of experiments had been utilized by Jandin and his associates (2003) to analyze the correlation between operating conditions, microstructure and mechanical properties of twin wire arc sprayed steel coatings using two different atomizing gases: air and nitrogen. Nitrogen lowered the oxide content in the coating compared to that for air. The oxygen content was found to reduce with a higher nitrogen or lower air flow rate. A higher oxide content, in turn, yields a higher hardness of the coating. Young's modulus of the coatings was assessed using a single point cantilever beam measurement technique supplemented by finite element calculation. Splat thickness and oxide content, which are dependent on the spraying conditions, influenced the elastic modulus significantly. A similar work on the mechanical properties of suspension plasma sprayed  $TiO_2$  coatings was reported by Jaworski et al. (2008).

Li et al. (2003) investigated on plasma sprayed titanium-nitride coatings using a uniform design method, wherein third-order polynomial equations of the process parameters were formulated. In a subsequent study, Li et al. (2005) applied the same technique on yttria stabilized zirconia coatings. The third-order regression equations obtained from the analysis were found to be the most appropriate to identify the influences of primary and secondary gas flow rate, arc current, powder feed rate on deposition efficiency, porosity and oxide content.

A D-optimal experimental design had been used by Azarmi et al. (2008) to characterize the effects of some process parameters (powder size, spray distance, feed rate, arc current, plasma gas flow rates) on in-flight particle temperature and velocity, and also on the oxide content and porosity in a plasma sprayed nickel-based superalloy coating. Wang and Coyle (2008) performed the optimization of solution precursor plasma spray process through a central composite design, investigating the effects of process parameters (Hydrogen flow rate, arc power, solute flow rate, solute concentration, standoff distance, etc.) on coating porosity and deposition efficiency.

The above studies provided more or less satisfactory results in predicting the responses (one at a time) from process parameters. However, all the responses are to be modeled simultaneously in order to capture the dynamics of a manufacturing process completely. Statistical regression analysis helps to determine the responses for a set of input parameters. However, the reverse modeling, that is, predicting the process parameters in order to ensure a set of responses, may not be always possible to implement, particularly when the transformation matrix representing input-output relationships becomes non-square.

# **1.2.3 Soft Computing-based Modeling of Plasma Spray Coating Process**

The responses of coating properties to variations in input parameters are complex and in most of the cases strongly nonlinear. Accordingly, in order to recognize the interactions, correlations, and individual effect of parameters on coating properties, a robust methodology is required. Such a methodology should also take equipment and economic constraints into account. Soft computing-based approaches have such kind of flexibility. Complex theoretical models relying on evolutionary algorithms, application of artificial neural networks and fuzzy logic control are the potential tools to estimate the behavior of complex plasma spray environment through validation either by key experiments or first-principle calculations.

#### **Fuzzy Logic-based Approaches**

Fuzzy logic control is a knowledge-based methodology that translates human linguistics into an optimized model of controllable reality using a set of fuzzy rules

and membership functions. Fuzzy logic-based systems have demonstrated their ability to solve different kinds of problems in various application domains. Hybrid approaches developed based on various soft computing tools (Pratihar, 2008) have attracted researchers for the purpose of modeling of manufacturing processes. Neurofuzzy systems and genetic-fuzzy systems hybridize the approximate reasoning method of fuzzy systems with the learning capabilities of neural networks and evolutionary algorithms, respectively (Cordon et al. 2004). The neuro-fuzzy systems, for example adaptive neuro-fuzzy inference system (ANFIS) (Jang, 1993), had been applied in many processes to model and predict the behaviors of unknown and complex interactions of parameters based on experimental input-output data.

A few studies have also been reported on fuzzy logic-based analysis related to coating processes. In the recent past, Duan and his associates (2000) attempted to use fuzzy logic-based model showing the effects of operating parameters, namely arc current, gas flow rate, etc., of an argon/helium plasma spraying of yttria-partially stabilized zirconia powder on the coating properties like porosity and deposition efficiency. Warne et al. (2004) developed a hybrid PCA-ANFIS measurement system for monitoring the anchorage of polymeric deposits on substrates. Jean et al. (2006) used fuzzy logic technique to explore functional relationships among variables to determine the effect of operating parameters, and achieve optimal process conditions for reinforced zirconia depositions using plasma spraying. Wang et al. (2006) presented an application of fuzzy logic systems to control a powder deposition process. Their study focused in minimizing waste, reducing the time for selection of parameters and improving savings.

Kanta et al. (2007) intended to develop a model-based estimation for the process parameters in an atmospheric plasma spray process. Their study was based on fuzzy logic and they tried to predict the deposition yield as a function of process parameters of an alumina-titania coating. ANFIS had been applied by Hayati et al. (2011) for the prediction of grain size of nano-crystalline nickel coatings. They considered current density, saccharin concentration and bath temperature as input parameters, and the resulting grain size of the nano-crystalline coating as the output. The results obtained from ANFIS model were compared with that of an artificial neural network model and reported more reliable results than those of the latter. Guo et al. (2011) also applied ANFIS model to predict surface roughness in precision surface grinding of a nano-ceramic coating. Their proposed prediction model was improved by hybrid Taguchi genetic algorithm.

Computational complexity of a fuzzy logic-based system increases with the number of variables and that of linguistic terms used to represent them. Due to the 'curse of dimensionality' problem (Pratihar, 2008), it becomes difficult to develop a suitable fuzzy logic controller for controlling a complex real-world problem involving many variables. The concept of hierarchical fuzzy logic controller (FLC) overcomes this difficulty. The prediction of responses and optimization of different other manufacturing processes had been done by some of the researchers using hierarchical hybrid systems (Peres et al., 1999, Sarah et al., 2000, Lee and Shin, 2004). Hierarchical fuzzy system-based model had not yet been developed for the plasma spraying process studied in this thesis.

#### **Neural Network-based Approaches**

Soft computing-based tools are other potential techniques to tackle the high nonlinearity involved in the plasma spraying process. Guessasma et al. (2003, 2004, 2006) and Guessasma and Coddet (2004, 2005) had worked extensively on the neural network-based approaches to plasma spraying process optimization. They designed an expert system using neural networks to control the plasma spray process (Guessasma et al., 2003). Modeling of the atmospheric plasma spray process including parameter optimization and property prediction had been done using multilayer perceptrons (2004). Guessasma and Coddet (2004) analyzed the microstructure of plasma sprayed alumina-titania coatings using artificial neural network (Guessasma et al., 2004). In addition, they applied neural computation to atmospheric plasma spray process for porosity analysis (Guessasma and Coddet, 2005) also. The neural computation work had been extended to the prediction of wear characteristics of alumina-titania coatings as well (Guessasma et al., 2006, Sahu et al., 2007).

Neural network model had been implemented to predict the rate of coating deposition under various operating conditions by Chaithanya et al. (2006). Back-propagation neural network had been implemented by Wang et al. (2007) to investigate temperature and velocity distribution irregularities of in-flight particles and formulate the nonlinear relationship between spray parameters and coating porosity and hardness. Artificial neural networks had also been applied by Kanta et al. (2009) to predict atmospheric plasma process parameters, namely arc current intensity, plasma gas flow rate, hydrogen content, velocity and temperature of the in-flight particles required in order to deposit a coating with the desired structural characteristics like coating thickness, porosity in coatings.

Soft computing tools could be used for the modeling of manufacturing processes in both forward and reverse directions. However, they require proper tuning to improve their prediction capability at a low computational load.

## 1.3 Gaps in the Literature

Although a considerable amount of research work had been carried out in the area of thermal spraying, there is no such ready-to-use model for the predictions of input or output parameters of coating process. The following issues led us to conduct the present research work:

- The existing literature related to the topic of present study provides significant information on statistical regression modeling of different thermal spray processes. However, a very few of them addressed the plasma spray process in particular. In most of the cases, factorial design of experiments was followed and the number of experiments conducted was inadequate for capturing the complete dynamics of the process.
- For fuzzy logic-based modeling, in most of the cases focus was on the reduction of rule bases to avoid computational complexity. Accordingly, the numbers of input parameters were less in numbers. Moreover, multiple levels of process parameters were not considered. Hence, earlier studies might have produced some reasonable results in terms of prediction capability, but were not adaptive enough to capture the overall dynamics of the process.
- Multi-layer feed-forward neural networks with back-propagation algorithm were explored in a number of problems related to input-output modeling of plasma spraying process. The selection of number of neurons in the hidden

layer was based on assumptions and experience of the users in most of the cases. No study had been reported on a systematic determination of hidden neurons of the networks.

In this context, radial basis function neural network may be an alternative approach, as it can provide more or less same accuracy in predictions but at a lower computational complexity. The concept of clustering can offer a more logical way to decide the number of hidden neurons.

• No work had been reported on reverse modeling of the process, which is equally necessary in automating the process.

## 1.4 Aims and Objectives

A systematic investigation on plasma spray coating process is required to obtain its input-output relationships. Moreover, the review on existing literatures figures out the shortcomings related to the modeling of plasma spray coating process. Hence, the objectives of the present thesis have been set as follows:

- To conduct well-structured statistically designed elaborate experiments so as to generate a rich database. For this purpose, four inputs, namely primary gas flow rate, stand-off distance, powder flow rate and arc current, and three outputs, such as coating thickness, porosity and hardness of coatings, are considered.
- 2. To perform experimental investigations on coated samples and analysis using statistical regression approach.
- 3. To device a fuzzy logic-based expert system in order to predict the responses under consideration.
- 4. To develop artificial neural network-based and hybrid models for the predictions of both the responses as well as process parameters using forward and reverse modeling techniques.

## 1.5 Contributions made by the Scholar

A systematic analysis on plasma spray coating process has been conducted by the scholar. The combination of input-output parameters considered for this study has not been adopted in any other studies for the same coating process. The surface plots showing the correlations among process parameters and responses are not reported in any other studies.

The hierarchical structure developed for the prediction of outputs is novel. This approach reduces computational complexity for the input-output combinations and levels. For the first time, particle swarm optimization (PSO) has been used to train the developed models for making predictions of the inputs and outputs.

Multi-layer feed-forward neural networks had been used earlier by other researchers in a number of cases, but radial basis function neural networks were not explored to model the plasma spraying process. The scholar has implemented such structures of neural networks and their parameters have been optimized using two evolutionary optimization techniques. In this context, PSO has once again been applied in modeling the process. Another relatively new concept introduced in this thesis is that of the clustering hybridized with neural networks, which had not been used by others for modeling of this process.

Author has developed computer programs in C language on Unix platform for fuzzy logic and artificial neural network-based modeling.

## **1.6 Layout of the Thesis**

This thesis contains seven chapters including this. The remaining chapters describe the topics as follows: Chapter 2 explains the tools and techniques used for modeling of the process. Next, experimental details of plasma spray coating have been described in Chapter 3. The results and discussion part of the thesis spreads over the next three chapters. Chapter 4 deals with statistical regression analysis on the responses of the coating process. Fuzzy logic-based modeling techniques developed in the present thesis are explained in Chapter 5. Finally, Chapter 6 presents the developed artificial neural network-based approaches used for modeling the plasma spray coating process. Concluding remarks and the scope for future study are reported in the last, i.e., 7th chapter.

## 1.7 Summary

Plasma spray coating process has been introduced at the beginning of this chapter. A thorough literature survey has been carried out and the gaps in the literature have been identified. The aims and objectives of the present thesis have been stated. Moreover, the contributions made by the scholar have been described. At the end of this chapter, layout of the thesis has been presented.