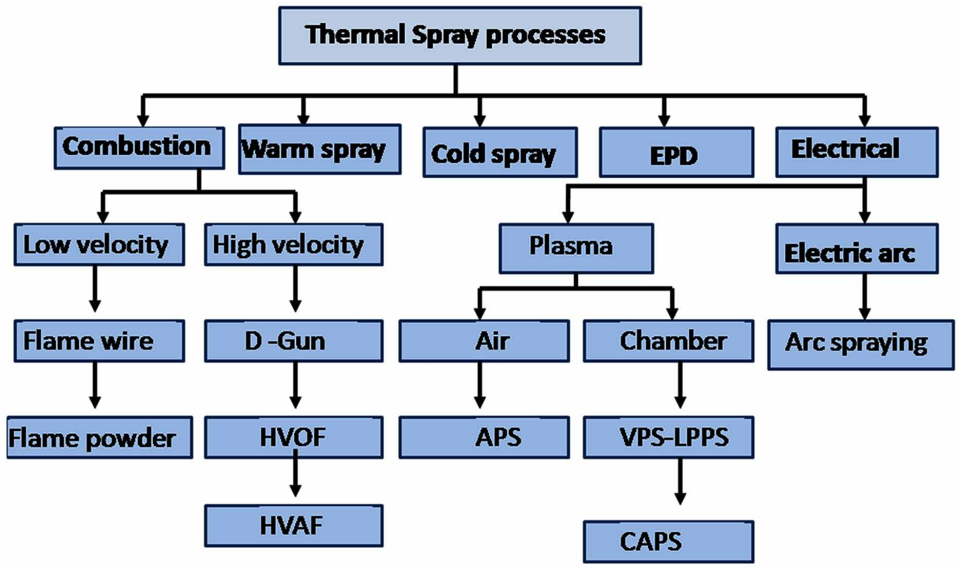
Preface

Thermal spray is a generic term (Pawlowski, 1995) for a group of coating processes where the coating is deposited on a substrate by applying a stream of particles, metallic, or ceramic materials, which flatten more or less forming platelets, called splats. Several layers of these splats form the coating. Upon impact, a bond forms with the surface, with subsequent particles causing a build-up of the coating to its final thickness. Since 1910, when Dr. Schoop for the first time conceived thermal spraying, a large development has taken place. A device to spray metal wires was made available in 1912. This technique is known as flame spraying. Later on, in 1930, new technique for thermal spraying known as flame spraying process was introduced. Subsequently, in 1958, Union Carbide developed detonation spraying. Atmospheric plasma spraying was introduced in 1960. This was followed by development of Vacuum Plasma Spraying (VPS) and Low-Pressure Plasma Spraying (LPPS) in late 1970 and 1980. In the year 1980, High Velocity Oxy Fuel (HVOF) technique was invented. James A Browning developed liquid fuel based coating gun "Jet-Kote" in 1982. The most important technology cold spraying was developed in 1990. The first literature on warm spraying was available in 2006. The classification of various thermal spray processes is summarized in Figure 1. Over last several decades, large developments in thermal spraying have made these techniques as an invaluable tool for engineering applications.

There has been an increased dependence of industrial sectors on thermal spraying technologies, not only for key operational purposes but also for gaining strategic advantage. Thermal spraying is a dynamic process and a rapidly changing field, which is used in a wide range of industries to solve increasingly challenging problems. These techniques are used for performance enhancement and extension of life of industrial components, which are subjected to wear, corrosion, etc., and also to meet numerous other practical solutions. As the application for thermal spraying is expanding to performance-critical applications, it has become mandatory to ascertain how the coating affects mechanical properties of the substrate. It is critical to

Figure 1. Classification of various thermal spray processes



establish standard method and matrix for evaluation of effect of coatings on the substrate. This has resulted in establishing a standard test method for evaluation and comparison.

There are several emerging trends in thermal spraying. Nanostructured coatings by Hypersonic Plasma Particle Deposition (HPPD) have been established (Heberlein, Rao, Neuman, Blum, Tymiak, McMurry, & Girshick, 1997). In this process, vapour phase precursors are injected in to a plasma stream generated by a DC arc. The plasma is quenched by supersonic expansion through a nozzle into a vacuum deposition chamber. Ultrafine particles nucleated in the nozzle are accelerated in the hypersonic free jet downstream of the nozzle and inertially deposited on the substrate. The short transit times between the nozzle and the substrate prevent in-flight agglomeration, while the high particle velocity results in formation of consolidated coatings.

Suspension thermal spraying in which fine powders suspended in suitable liquid phase are sprayed (Bouyer, Gitzhofer, & Boulos, 1997). Suspensions exceeding 50 wt % solid phase content is successfully injected into inductively coupled plasma. Coating is deposited successfully by a novel radio frequency – Suspension Plasma Spraying (RF-SPS). However, this approach still relies on the use of expensive nano/ultra-fine powder feedstock. Difficulties in suspending the particles in a stable manner and maintaining homogeneity also exist. Alternately, a single-step coating process involving *in situ* synthesis of nanoparticles and their subsequent consolidation into an adherent deposit through solution precursor spraying appears promising. Some preliminary reports on High-Velocity Oxy-Fuel (HVOF) spraying of solution precursors is also available (Ma, Roth, Gandy, & Frederick, 2006).

A new electromagnetic powder deposition technique that employs electromagnetic force can accelerate powder particles up to 2 km/sec as opposed to 1km/sec obtained by conventional thermal spray process has been developed (Bacon, Davis, Polizzi, Sledge, Uglum, & Zowarka, 1997). Particles travelling with this velocity have sufficient kinetic energy to melt their own mass and equivalent mass of the substrate on impact. In this technology, argon gas and high-energy electrical pulse provided by a capacitor bank drives the gas to a very high velocity, which ultimately allows the particles to travel at the velocity of 4 km/sec.

Cold Gas Dynamic Spray (CGDS) is a process where coating is deposited by high-velocity jet of solid phase particles, which has been accelerated by a supersonic gas jet at a temperature much lower than the melting and softening temperature of the coating materials (Bhagat, Amateau, Papyrin, Conway, Stutzman, & Jones, 1997). The warm spray process (Kuroda, Watanabe, Kim, & Katanoda, 2011) is based on high velocity impact bonding of powder particles, which is similar to cold spraying, but the temperature of the particles at impact is significantly higher and often very close to the melting point of the material. Therefore, warm spray may be regarded as a process to fill the gap between HVOF and CS.

Considerable effort will be diverted for further development of functionally graded thermal sprayed coatings. A functionally graded coating can be defined as a series of the coating having continuously changing composition from substrate to the surface to achieve combinations of properties (Kawasaki & Watanabe, 1997; Krumova, Klingshirn, Haupert, & Friedrich, 2001). These advanced coatings with gradient in composition, structure/specific properties in the preferred direction/orientation are superior to homogeneous materials composed of similar constituents. Functionally graded coating offers several advantages over conventional monolithic coating system, such as reduction of in-plane and through-the-thickness transverse stresses, improved thermal properties, high toughness, etc. Functionally graded coatings consisting of metallic and ceramic components are established to enhance the properties of thermal-barrier systems by making smooth transition of the properties with depth-leading enhancement of adhesion characteristics of the coating.

Smart thermal sprayed coatings, which respond in a selective way to external factors such as stress, temperature, etc., are another important recent development (Fasching, Prinz, & Weiss, 1995). With the help of thermal spraying, it is possible to deposit novel smart coatings with embedded sprayed sensors by combining coating and shaping methodologies. Various sensor materials can be selectively sprayed and shaped using masking techniques (Weiss, Prinz, Adams, & Siewiorek, 1992). Discreet shapes can be formed with appropriately shaped masks. Sprayed sensors, such as thermocouple, humidity sensor, etc., have been manufactured and performance evaluated successfully. In addition, sensors, like strain gauges, antennas, pressure sensors, etc., have been developed. There are several important properties with sprayed sensors that cannot be easily achieved by other conventional methods. It is possible to have sprayed sensor conforming to complex surface shapes with optimal surface contact by flexible masking. For a given application, the shape of the sensor and its interconnection can be separately designed. Production of sensor array is straightforward, as coating and sensor are deposited simultaneously. Sensors can be protected against the environment by depositing another coating. It is also possible to incorporate new materials for sensor technology by using multi-component powder.

Hybrid thermal spraying will draw a lot of attention in the years to come. Low-pressure plasma spray hybrid system can produce coatings within three distinct regimes. Plasma spray-PVD can produce thick, columnar-structured coatings using high gun enthalpy to vaporize specific types of feedstock materials. Plasma spray-CVD uses modified conventional thermal spray components operated below 0.5 mbar to produce CVD-like coatings at higher deposition rates by using liquid for gaseous precursors as feedstock materials. Plasma spray-thin film can produce thin, dense layers from liquid splats using a classical thermal spray approach but at high velocity and enthalpy.

Another important development for thermal spraying is forming of near-net shape components. Refractory materials have high melting points, high temperature strength, good thermal properties, and high ablation resistance. Parts of near-net shape refractory materials, such as heating element, crucible, and rocket nozzle, etc., have found wide applications in chemical processing, electrical and mechanical engineering, airplane and aerospace industries (French, Hurst, & Marvig, 2001). However, due to their ultra-high melting point and high ductile-to-brittle transition temperature (around room temperature), it is difficult to fabricate large-scale or thin-walled parts with complex shape of these materials by conventional industrial methods such as Powder Metallurgy (PM) and Chemical Vapour Deposition (CVD) (Cockeram, 2006). It has always been intended to develop new and effective fabrication methods to produce refractory metallic parts of desired shapes and density. Capable of making high quality near-net-shape parts, Plasma Spray Forming (PSF) then came into play as one such potential fabrication method of choice for refractory materials. During PSF process, refractory metallic powders are directly fed onto a predesigned mandrel (Park, 1999). Almost any feedstock can be sprayed onto the mandrel in a controllable manner to provide a compact of desired shape and wall thickness with benefits of simplifying fabrication process and cost reduction. Substantial research is expected to be directed in the development of removable mandrel and development of complex shape. A larger variety of coatings for near-net shape tribology-related components and their increased usage is expected to come in the near future.

Over the last decades, various sensors relevant to the thermal spraying process and capable of operating under the harsh environment of spray booths have been developed (Fauchais & Verdelle, 2010). Today, sensors are available to measure trajectories, temperatures, velocities, sizes, and shapes of in-flight particles (Fauchais, 1992; Landes, 2006; Gougeon & Moreau, 1993). Infrared cameras and pyrometers are employed to understand the temperature profile of substrate and coatings during preheating, spray process and cooling down (Matejicek & Sampath, 2003; Clyne & Gill, 1996; Kuroda & Clyne, 1991). Sensors are also developed to measure the stresses within the coatings and evolution of thickness of the coating during spraying (Nadeau, Pouliot, Nadeau, Blain, Berube, Moreau, & Lamontagne, 2006). Further development towards improved precision on measurement is expected. New techniques, such as shadowgraphs and laser, allow precise measurement of particle diameter, which was not hitherto possible. Development of sensors will allow online control of thermal spraying and thus enhance coating quality and reliability.

Over the last several decades, thermal spraying has come a very long way, especially in terms of revolution with regard to automation of process variables and work handling equipment. Process automation has brought about a much higher degree of repeatability and reliability to the thermal sprayed coating process and the coating being produced. As a result, thermal spraying is being considered as a modern and well-respected manufacturing process. The widespread use and growing acceptability of thermal sprayed coating for commercial product is the testimony for that. Although lot of investigation has been carried out and significant information has been generated about the variables involved in the thermal spraying process, much still needs to be learned. Automation has induced more correctness and more adequacies in controlling these variables to a significant extent. Automation has also helped us in mass production of a large number of feasible components.

THE CHALLENGES

It goes without saying that demands for high performance thermal sprayed coatings and coatings with added functionality have been on the increase. And any attempt to deal with the problem demands an adequate understanding of the challenges that exist in the new millennium. Such challenges can be classified into following categories:

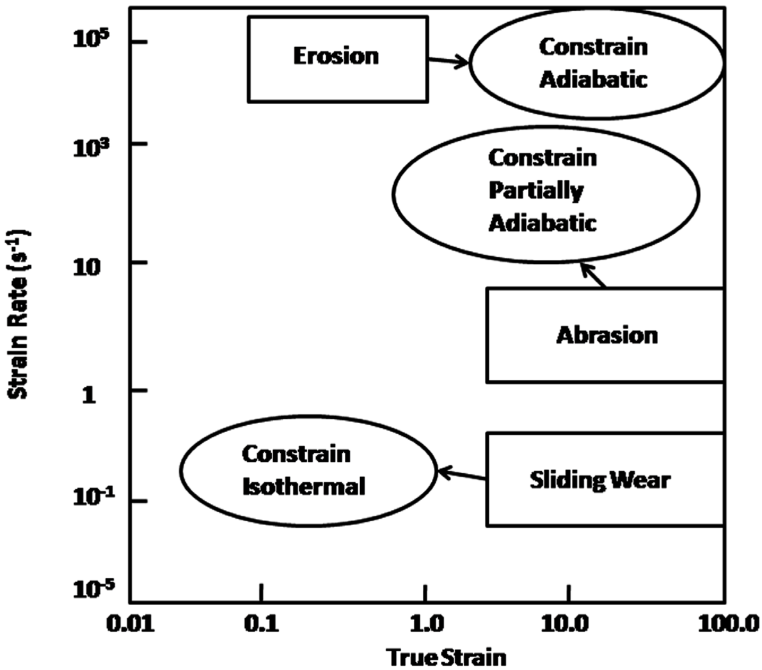
- The challenge of establishing newer techniques giving rise to coatings with improved mechanical properties and performances.

- The challenge of establishing new coatings with new composition and new functionality.
- The challenge of establishing correct processing condition for the existing deposition techniques for existing coating materials.
- The challenge of establishing appropriate spraying technology to meet the challenging demand of modern technology for operation in demanding and harsh environments.
- The challenge of establishing automation for the processing conditions and equipment handling to meet the challenging demand of modern technology.
- The challenge of establishing appropriate spraying technology to meet demand for mass production.

Although thermal sprayed coating has evolved as an important tool for large variety of applications, a significant fraction of thermal sprayed coatings are used for protection against tribology in ambient or in corrosive environments. Tribology, which deals with the science of friction, is an important degradation process, protection against which is essential. Commonly occurring tribology-related degradations are erosive wear, abrasive wear, and sliding wear. Erosive wear can be due to impact by solid particles liquid droplets, or it can also be due to liquid metal or cavitations. Abrasive wear can be defined as material loss when a hard particle is made to slide against a relatively soft material. Sliding wear is essentially degradation when two surfaces are made to rub against each other. Sliding wear can be unidirectional or reciprocating. The strain, strain rate, thermodynamic status of deformation of erosive wear, abrasive wear, and sliding wear differ considerably. The unique features of the deformation conditions pertinent to various degradation conditions, such as erosive wear, abrasive wear, and sliding wear are given in Figure 2. The other variety of tribological degradation process is fretting when rubbing takes place in reciprocating motion with very low amplitude. When tribology-related degradation takes place in the presence of a corrosive medium, degradation is an outcome of synergistic effect of tribology and corrosion such as erosion-corrosion, fretting-corrosion, abrasion-corrosion, etc. When such degradation takes place at elevated temperature, material loss is an outcome of interaction between tribology and oxidation, such as erosion-oxidation, etc. Erosion oxidation interaction map for Ni, for feed rate of 0.2 gm/min is illustrated in Figure 3.

Prevention of tribology-related degradation is an age-old phenomenon. Surface hardening by diffusion of carbonaceous materials has been known since Roman times. Vikings were also famous for embedding the leading edges of their ploughs to resist soil erosion. However, scientific investigation to minimize tribology-related problems started in the last 50 years. To be more precise, enhanced understand-

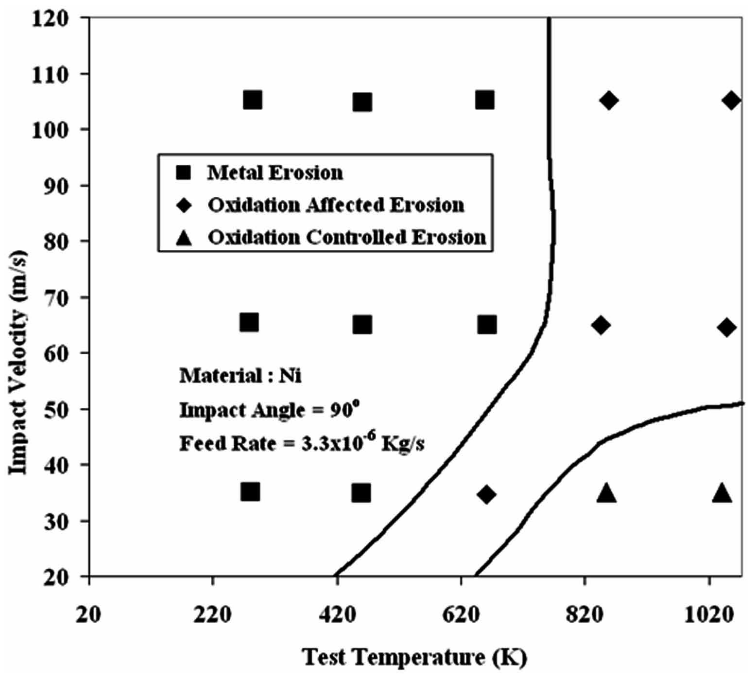
Figure 2. The unique features of the deformation conditions pertinent to various degradation conditions such as erosive wear, abrasive wear and sliding wear (Roy, 2006)



ing for more complicated problems involving tribology and corrosion interaction is merely a decade old. Most manufacturing industries are forced to overcome a loss of 0.5% of their turnover due to tribology and related problem and this figure should be applicable worldwide. Hence, it is an expensive degradation process and there are enough incentives to minimize it by applying a coating by thermal spraying. Since tribology is mostly a surface-related phenomena, thermal sprayed coatings have been, more often than not, successful in improving the performances. Thermal sprayed coating is one of the most widely and commonly used methods for protection against such degradation.

Because of the requirements for protection against the above-mentioned degradation, demand for thermal sprayed coatings is increasing. The book, *Thermal Sprayed Coatings and their Tribological Performances*, has been planned keeping this important aspect in mind for future research. Research on thermal sprayed coatings has gathered huge momentum across the world as evidenced from the number of research publications in this area in recent times. Today, many spheres of life, which includes energy, oil and gas, mining, transportation, and healthcare sectors,

Figure 3. Erosion oxidation interaction map for Ni, for feed rate of 0.2 gm/min (Roy, 2006)



etc., have problems related to tribology. Over the years, numerous studies, reviews, and special issues and books have been published on thermal sprayed coatings. However, no attempt has ever been made to compile a book addressing exclusively the tribological problem. This is the first attempt to compile a book related to the tribology of thermal sprayed coating.

Because of time constraints, we have missed several areas, like elevated temperature erosion, abrasive wear, etc., of thermal sprayed coating. We have also missed tribology of several emerging thermal sprayed coating processes, such as cold sprayed, electromagnetic deposition process, etc., as the literature in these areas are limited. We hope to have a book with all varieties in future. We think that the chapters are a valuable reference and that many researchers will use them as a useful guide to the state of the art in the field of tribology of thermal sprayed coatings.

ORGANIZATION OF THE BOOK

After this introductory preface, it is pertinent to describe the organization of the book. In this book, we have successfully gotten several leading practitioners who are currently involved in research and development of thermal sprayed coatings for tribological application to contribute. The book is organized into 11 chapters. A brief description of each of the chapters follows:

Chapter 1 discusses the effects of feedstock powder and deposition technique on the hardness and tribological performance of thermal-sprayed WC-Co coatings. It was found that the high-temperature gun produces harder and more wear-resistant coatings than the standard gun. WC-Co Coatings deposited with nanostructured feedstocks are useful in bearings and other machinery with sliding parts because they inflict much less wear on the material on which they slide than conventional coatings. Coatings with micrometer WC grains are suitable for abrasion resistance applications such as earth moving or slurry processing machinery

Chapter 2 identifies tribo-corrosion of thermal sprayed coatings. Tribo-corrosion is material degradation resulting from synergistic action of wear and corrosion and it is prevalent in many engineering applications although the involved mechanisms are still little understood. In this chapter, a brief overview of tribo-corrosion testing techniques followed by issues which have helped in gaining in-depth scientific knowledge of tribo-corrosion has been discussed. The overview is further substantiated by detailed studies and observations on tribo-corrosion of thermal sprayed coatings in recent times.

Chapter 3 specifically focuses on the emergent Solution Precursor Plasma Spray (SPPS) technique that has been the subject of considerable research interest in recent times. A variant of the thermal spray family, the SPPS method offers significant advantages by avoiding use of powder-feedstock that has to meet stringent particle size specifications, permitting better control over coating chemistry and yielding interesting features like vertical cracks, nano-sized pore structure, fine splats, etc. Some illustrative examples of the large variety of coatings that can be realized by adopting the above hybrid route that involves combining the conventional plasma spray and SPPS techniques will be discussed. In an attempt to understand coating formation by the proposed hybrid route, splat formation under varied processing conditions has been comprehensively investigated. The relationship between these splats, the resulting coating microstructure and tribological behaviour of the coatings has also been comprehensively discussed.

Chapter 4 reviews research associated with the development of coatings that are designed to withstand combined abrasive wear and corrosion conditions. Understanding how coatings perform under these tribo-corrosion conditions is essential if the service life of equipment is to be predicted. Therefore, the tribo-corrosion performance of coatings deposited by thermal spray techniques is discussed and the main mechanisms associated with their degradation under combined wear and corrosion highlighted. The importance of post-coating deposition treatments such as laser resurfacing and sealing are also discussed. Interactions between abrasion and corrosion mechanisms are identified along with some models and mapping techniques that aim to inform coating selection and predict performance.

Chapter 5 deals with detailed overviews of the development of functionally graded coating by thermal spray deposition techniques. In addition, the present status of research efforts in development of functionally graded coating for tribological and thermal barrier applications is also elaborated.

Chapter 6 is concerned with elevated temperature sliding wear of various thermal sprayed coating actually meant for high temperature application. After introducing the subject in Chapter 1, a brief outline of various thermal spraying techniques is made in subsequently sliding wear of various thermal sprayed coatings is addressed. High temperature application of thermal spayed coatings and future direction of research for high temperature thermal spray coating are eventually furnished.

Chapter 7 provides a comprehensive overview on the characteristics of various cermets coatings intended for erosion resistant applications. In this chapter, evolution of thermal sprayed coating, erosion testing methods and erosive wear of thermal sprayed coatings are discussed extensively with emphasis on recent developments. It is generally found that erosion of thermal sprayed coatings depends on erosion test conditions, microstructural features and mechanical properties of the coating materials. Most thermal sprayed coatings respond in brittle manner having maximum erosion rate at oblique impact and velocity exponent in excess of 3.0. Erosion rate is also dependent on thermal spraying techniques and post coating treatment. However, little work is done on dependence of erosion rate on coating techniques and coating conditions. Future direction of work has also been reported.

Chapter 8 addresses tribology of thermally sprayed coatings in the Al_2O_3-Cr_2O_3-TiO_2 system. This contribution summarizes some important issues, regarding wear protection applications of coatings in the Al_2O_3-Cr_2O_3-TiO_2 system, the advantage of alloying the individual oxides, the influence of different feedstocks and spray processes.

Chapter 9 reviews slurry erosion of thermal sprayed coatings. This chapter presents basics of slurry erosion phenomenon in its first part. Effect of different parameters on slurry erosion process is also discussed. In the second part of chapter, slurry erosion behavior of several thermal sprayed coatings is presented with the help of some case studies. An attempt has been made to understand the role of different coating compositions and deposition processes to control slurry erosion. Slurry erosion mechanisms for these coatings have also been explained.

Chapter 10 deals with on the tribological characteristics of the detonation sprayed coatings. It provides a comprehensive overview on the characteristics of various cermet coatings generated at varied process conditions and its influence on the tribological properties under abrasive, sliding and erosive wear modes. The aim of this chapter is to provide its readers an opportunity to judicially select the right material composition for the perceived tribological application and also to understand the role of processing conditions to achieve the desired coating properties.

Chapter 11 concludes with an elaborate discussion of some techniques to evaluate and analyze the mechanical and tribological properties of different thermal spray. This chapter is intended to help the reader to firstly understand the basic principle and methods of characterization of thermal spray coatings using instrumented nanoindentation, nanoscratch, abrasive wear testing techniques and secondly to get an idea of the recent techniques and review the research and development in the same field.

This research book can be used as a support book for final undergraduate engineering course (for example, materials, mechanical, manufacturing, etc.) or as a subject on thermal spray at the postgraduate level. In addition, this book can serve as a useful reference for academics, materials researchers, materials, physics, mechanical, and manufacturing engineers, as well as professionals in related industries with thermal spray.

Manish Roy
Defence Metallurgical Research Laboratory, India

J. Paulo Davim
University of Aveiro, Portugal

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