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Performance of Plasma Sprayed Nanostructured and Conventional Coatings

Vikas Chawla [1*], Buta Singh Sidhu [2], D. Puri[1] and S. Prakash[1]

1 Metallurgical & Materials Engineering Department, I.I.T. Roorkee, India.
2 Mechanical Engineering Department, G.Z.S.C.E.T., Bathinda, Panjab, India.

Email: edwalesir@rediff.com

Abstract

This review is based essentially on the results in the field of synthesis and characterization of plasma sprayed nanostructured coatings. Nanostructured ceramic coatings produced by plasma spray process are being developed for a wide variety of applications that require resistance to wear, erosion, cracking and spallation. It is anticipated that, if properly deposited, nanostructured ceramic coatings could also provide improved properties for variety of applications, including wear resistance and thermal barrier coatings. These results clearly demonstrate that the significant improvement in coating performance can be achieved by utilizing proper nanostructured coatings. Plasma sprayed nanostructured coatings shows improvement of resistance to wear, erosion, corrosion and mechanical properties are also improved as compare to their conventional counterparts. The purpose of this paper is to review: (a) the synthesis and characterization of nanostructured feedstock powders; (b) the agglomeration of these powders for use in coatings; (c) the processing of nanostructured plasma spray conditions.

KEYWORDS: Plasma spraying, nanostructured coatings, Feedstock material, Spallation, Erosion, Wear resistance, Corrosion resistance, Ball milling.

INTRODUCTION

Thermal spraying is an effective and low cost method to apply thick coatings to change surface properties of the component [1]. Coatings are used in a wide range of applications including automotive systems, boiler components, and power generation equipment, chemical process equipment, aircraft engines, pulp and paper processing equipment, bridges, rollers and concrete reinforcements, orthopedics and dental, land-based and marine turbines, ships [1]. Plasma spraying has been around for more then four decades and has been used to deposit a wide range of metals, ceramics and even composite materials for many different applications [2]. Despite this long and successful history, there has still been a great interest among the engineers and scientists in developing new coating materials and researching phenomenon associated with the formation and application of coatings.

Oxide ceramics such as alumina, zirconia, titania, chromia, silica and yttria have been used widely as surface coating materials to improve wear, erosion, cavitations, fretting and corrosion resistance [3]. In the past decade, attractive properties associated with a nanostructure have been documented for bulk materials, where most of the research in the field of nanomaterials has been focused. In recent years, there has been a growing interest for engineered coatings, in particular for manufacturing and deposition of nanoscale powders [3]. Bulk nanostructured materials (in general referring to a grain size smaller then 100nm) have exhibited outstanding mechanical properties such as exceptional hardness, yield strength and wear resistance [4]. Such outstanding properties have also been observed in thermal-sprayed coatings derived from nanostructured powders [4].

For example, nanostructured cermet materials such as Cr_3C_2/NiCr and WC/Co coatings have been shown to have higher hardness, strength and corrosion resistance then the corresponding conventional coatings [5].
Exceptional properties can be obtained if the nanocrystalline structure of the starting material is preserved during spraying and reproduced in the coating [3]. Thermal spraying is a technique well suited for such a deposition, as the processing time of the sprayed powders at high temperature is very short. However, spraying conditions must be carefully adjusted to minimize the coarsening, or alteration of the nanograins and to control the chemical reactions and phase stability of the materials [3].

The purpose of this paper is to present the development status of the plasma sprayed nanostructured coatings. In order to highlight the specific advantages of the nano coatings deposited by Plasma spraying process, these are compared with their conventional counterparts.

THERMAL SPRAYING

Thermal spraying has emerged as an important tool of increasingly sophisticated surface engineering technology. The different functions of the coating, such as wear and corrosion resistance, thermal or electrical insulation can be achieved using different coating techniques and coating materials [7]. Thermal spraying has grown into a well accepted industrial technology. Today turbine blades and other components of aircraft engines are coated with corrosion and temperature resistant coatings but the science base for this technology is still poorly established and for certain aspects virtually non-existent. More than 35 years ago, plasma spraying was established as a commercial process, but only recently some serious attempts have been reported to establish a solid scientific base for this technology [8-9]. Thermal spraying is the application of a material (the consumable) to a substrate by melting the material into droplets and impinging the softened or molten droplets on a substrate to form a continuous coating. Most thermal spray processes

FUNDAMENTALS OF PLASMA SPRAY

Spray torch and in most cases (99%) plasma spraying is achieved by using plasma torches [13 & 14]. A high intensity arc is operated between a stick-type cathode and nozzle-shaped water-cooled anode.

In thermal spraying, feedstock materials in the form of powder or wire are fed into a heat source of spray equipment, where they are fully or partially melted and accelerated in a gas stream toward a substrate to be coated [6]. The high-temperature exposure and the following rapid quenching, which intrinsically involved in thermal spraying, can either improve or deteriorate the nanoscale microstructure of the coatings. Therefore, several challenges still remain in terms of feedstock preparation and processing itself. In order to produce a coating with desired properties, e.g. with high fracture strength, it is not sufficient to control only material structure inside one lamella. Interaction between lamellae, stress stages of the final coating, adhesion to the substrate and cracking must be also controlled [1].
require abrasive blasting or a bond coat to optimize the coating adhesion [10]. There are many thermal spray coating deposition techniques available, and choosing the best process depends on the functional requirements, adaptability of the coating material to the technique intended, level of adhesion required, (size, shape, and metallurgy of the substrate), and availability and cost of the equipment [11].
Heath et al (1997) [12] has summarized the thermal spray processes that have been considered to deposit the coatings, are enlisted below:
(1) Flame spraying with a powder or wire, (2) □Electric arc wire spraying, (3) □Plasma spraying, (4) □Spray and fuse, (5) □High Velocity Oxy-fuel (HVOF) spraying, (6) □Detonation Gun.

PLASMA SPRAY COATINGS

The demand for protective coatings has increased recently for almost all types of super alloys with improved strength, since high-temperature corrosion problem become much more significant for these alloys with increasing operating temperatures of modern heat engines. Among the different kinds of coating technologies, plasma spray coating should be one of the most promising.

Plasma gas, introduced along the cathode, is heated by arc to plasma temperatures, leaving the anode nozzle as a plasma jet or plasma flame. Fine powder suspended in a carrier gas is injected into the plasma jet where the powder particles are accelerated and heated. As the molten powder particles impinge with high velocities on substrate, they form a more or less dense coating [14].

PLASMA GENERATION AND FORMATION

The arc is initiated between the tip of the cathode (typically thoriated tungsten) and the water cooled anode nozzle. The working gas is introduced either axially or with an additional swirl component. The latter improves arc stability in the vicinity of the cathode and rotates the anode arc root which may be desirable for reducing anode erosion. The gas heated by the arc emanates as a plasma jet from the torch orifice. For typical plasma spray applications, the gas flow rate is sufficiently high to ensure a highly turbulent jet with a visible length of several centimeters.

Argon and mixtures of argon with other noble (He) or molecular gases (H_2, N_2, O_2 etc.) are frequently used for plasma spraying. The addition of He and in particular of molecular gases results in a drastic increase in the enthalpy of the plasma, which may be important for complete particle melting [14]. The maximum temperature in the plasma jet is a function of the design and of the operating parameters.

SYNTHESIS OF NANOSTRUCTURED FEEDSTOCK POWDERS

Preparation of nanostructured feedstock powders is the first step for synthesis of nanostructured coatings. A number of techniques that are capable of producing nanostructured materials include gas condensation, mechanical alloying/milling, crystallization of amorphous alloys, thermo-chemical method, spray conversion processing , vapour deposition, sputtering , electro-deposition, and sol-gel processing techniques [15]. Of these techniques, only mechanical alloying/milling and thermo-chemical techniques have been used to produce large quantities of nanostructured materials for possible commercial use.

Mechanical Alloying (MA) is a process, which is routinely used in Powder metallurgy and mineral processing industries. In this process, mixtures of elemental or pre-alloyed powders are subjected to grinding under protective atmosphere in equipment capable of high-energy compressive impact forces such as attrition or shaker mills. Historically, this technique was developed around 1966 by Benjamin and his co-workers at the Inco Paul D. Merica Research laboratory as a part of the program to produce oxide dispersion strengthened (ODS) Ni-base super alloys for gas turbine applications [16]. Such a process was known 40 years earlier from the work of Hoyt, who reported coating of WC with Co by ball milling. In 1966, attention was turned by high Benjamin's group to the production of alloys by high energy ball-milling. The process was initially referred to as milling/mixing. The term 'mechanical alloying' (MA) was actually coined by Ewan C. Mcqueen, a patent attorney for Inco [16].

Mechanical alloying/milling is usually carried out in high-energy mills. A variety of ball mills have been developed for different purposes including tumbler mills, attrition mills, shaker mills, vibratory mills, planetary mills, etc [17]. Powders with typical particle diameters of about 50µm are placed together with a number of hardened steel or tungsten carbide (WC) coated balls in a sealed container, which is shaken or violently agitated. The energy transferred to the powder particles in these mills takes place by a shearing action of impact of the high velocity balls with the powder [17].

A controlled milling environment is introduced into the tank for the following reasons: (1) to decrease contamination of powder caused by air; (2) to control powder temperature because milling causes an increase in temperature of the powders; (3) to introduce a reactive solvent to form the expected phase; and (4) to control powder particle size and morphology [15]. The milling environment used for these purposes can be; (a) gaseous environment (i.e. argon, nitrogen and hydrogen); (b) liquid environment (such as liquid nitrogen, methanol, acetone and hexane); and (c) solid environment (i.e. stearic acid). Argon, dry nitrogen, methanol, acetone and hexane are used for reducing the contamination of the powder from the atmosphere and controlling the temperature. Hydrogen is used to form hydrides. Liquid nitrogen reduces contamination of the powders and provides control of the temperature, but also works as a reactive solvent to form nitrides that facilitates in retarding grain growth of the synthesized powder during thermal exposure [15]. The oxygen-rich stearic acid is used to reduce powder particle size through a reduction in the extent of welding between powder particles.

SPRAY POWDER PREPARATION FOR PLASMA SPRAYING

Plasma spraying of micrometer-sized powder is a well established process [18-19]. In the plasma spraying process , particles typically of 10-100µm in size are injected into the plasma jet and are rapidly melted and accelerated to produce a stream of molten particles that are projected onto the substrate. Using nano sized powder as feedstock to generate nanostructured coatings presents new challenges as well as new opportunities [20]. The first challenge is that individual nanoparticles cannot be thermally sprayed because of their low mass and the resultant inability to be carried in a moving gas stream and deposited on a substrate. To overcome this reconstitution of individual nanoparticles into spherical micrometer-sized granules is necessary. The second challenge is to retain grain sizes at the nanometer regime in the coating [20].

The simplest and quickest way to obtain nanostructured coating by thermal spraying technique is to utilize a nano-type of feedstock material [5].

Storz et al. [21] reported that plasma sprayed Ti_nO_{2n-1} (Magneli-phase) coatings, by using the spraying powder obtained from reducing of TiO_2 powder in the furnace, can modify the tribological properties of coatings. In this study , metal Al particles, which have a low melting temperature and higher reactivity, were added for the production of the TiO_2-Al composite spraying powder, and the unique composition of TiO_2-Al composite powders were utilize to increase the spraying efficiency and investigate the possibility of byproduct from the reaction of TiO2 and Al.

Sang Ok Chwa et al.[5] has reported plasma sprayed nanostructured TiO_2-Al composite coatings. In their study the authors had used TiO_2 powders with an average particle size 7nm, which cannot be directly utilized for thermal spraying because of their inability to be carried in a standard powder feeding system. In order to prepare spherical micrometer sized self-standing granules for thermal spraying, spray drying was carried out using vinyl alcohol as an organic binder. Aluminum powders with an average particle size of 6μm were also added to prepare agglomerated nanostructured composites (TiO_2-Al) of feedstock material. Then the prepared nanostructured composites (TiO_2-Al) powders were plasma sprayed on the substrate.

Leon L. Shaw et al. [20] have investigated plasma sprayed nanostructured Al_2O_3 -TiO_2 coatings for improved wear resistance. Nanosized Al_2O_3 and TiO_2 powders used had a mean particle diameter of 50nm and 70nm, respectively. These powders were mixed to produce a powder mixture that had an equivalent composition as Metco 130 (i.e. 87 wt % Al_2O_3 and 13 wt % TiO_2). The slurry prepared from this powder was then spray dried to form micrometer-sized granules (20-100μm). The granules so obtained were subsequently subjected to a heat treatment to burn out the binder used in the spray drying. Then the thermal spraying of the reconstituted granules was carried out.

Bo Liang et al. [22] have reported the plasma sprayed nanostructure zirconia coatings. The nanosized yttria stabilized zirconia powders prepared via chemistry co-precipitation process, with particle sizes of 50-80nm, were reconstituted into spherical micrometer-sized granules (typical size range in 30-50μm) by spray-drying process before plasma spraying.

E. Irissou et al. [23] have studied plasma sprayed nanocrystalline Ti-Ru-Fe-O coatings. Nanocrystalline Ti-Ru-Fe-O (2-1-1-2) powder was prepared by high energy ball milling using a ZOZ attritor apparatus. Then, an agglomeration process was developed to increase the average particle size for plasma spraying. This process involves the mixing of the powder with polyvinyl alcohol (PVA) polymer. In first step, PVA was dissolved with acetic acid and mixed with the nanocrystalline powder. Then, acetic acid was evaporated (90°C for 12 hrs), leading to the formation of very large particles. Then the plasma spraying process was carried out and during the deposition PVA is evaporated.

STUDIES RELATED TO PLASMA SPRAYED NANO COATINGS

Pavitra Bansal et al. [24] have characterized the interfacial microstructure, toughness, and failute modes in “conventional” and “nano” Al_2O_3-13wt% TiO_2 plasma sprayed coatings. The interfacial toughness of the “conventional” and the “nano” Al_2O_3-13wt% TiO_2 plasma sprayed ceramic coatings on steel substrate , as measured using the Rockwell indentation method, was found to be 22 and 45 Jm^{-2}, respectively. The microstructure of the “conventional” coating consists primarily of fully-molten (FM) and solidified “splats”. The “nano” coating microstructure is bimodal in nature and consists of regions of FM “splats”, interspersed with partially-molten (PM) rounded micro-structural features. The FM/steel interfaces in both the “conventional” and the “nano” coatings are found to be spontaneously cracked (before mechanical testing), whereas the PM/steel interfaces in the “nano” coating are found to be adherent. Under the three-point bending, the failure in the “conventional” coating is dominated by a single vertical crack in the coating, and an interfacial crack along the ceramic/metal interface. In the “nano” coating, there are multiple vertical cracks, and the interfacial crack is primarily within the coating near the ceramic/metal interface.

The weaker FM/steel interface results in the interfacial fracture in the “conventional” coating, whereas in “nano” coating, the strongly adherent PM/steel interface interrupts the interfacial cracks.

Leon L. Shaw et al. [20] have investigated the feasibility of using nanosized Al_2O_3 - 13 wt% TiO_2 powders to generate nanostructured coatings with plasma spraying process. Authors successfully developed the coatings and found the coatings produced from nanopowder feedstock could have better wear resistance then the coatings produced using commercial coarse-grained powders. Chuanxian Ding et al. [2] have investigated the plasma sprayed nanostructured zirconia coatings for wear resistance. The plasma sprayed nanostructured zirconia coatings reported possess a higher wear resistance then their conventional counter parts. The higher wear resistance of the nanostructured coatings is attributed to their optimized microstructure and improved micro-hardness.

L. Leblanc [3] has evaluated micro-structural as well as abrasion and sliding wear properties of APS (Atmospheric plasma spraying) and VPS (Vacuum plasma spraying) sprayed Al_2O_3-13TiO_2, Cr_2O_3-5SiO_2-3TiO_2, and TiO_2 coatings from micro-structured and nanostructured powders. Performance and characteristics of VPS-applied coatings are generally superior or equal to those of APS-applied coatings. Nanostructured powders are found to be more sensitive to the thermal spray process used, as compared to conventional micro-structured powders. VPS provide a better environment for applying nanostructured oxide ceramic materials, as compared to APS. The superior properties of coatings applied from nanostructured powders seem to be associated with coatings that have retained a nanostructure, i.e. a bimodal structure composed of partially or unmolten particles, combined with fully molten regions.

Nanostructured alumina-titania coatings were produced by plasma spray of reconstituted nanostructured powders, using optimized processes, defined by a critical plasma spray parameter [25]. Physical and mechanical properties, including density, hardness, indentation crack growth resistance, adhesive strength, spallation resistance in bend and cup tests and resistance to abrasive and sliding wear. These properties were also examined as a function of critical plasma spray parameter (CPSP) and compared with the Mtco-130 (conventional) coating. Superior properties of nano coatings are reported as compared to their conventional counter parts. The superior properties are associated with coatings that have a retained nanostructure, especially with partial melting of the nanostructured powders.

Jin-hong Kim et al [6] have successfully developed thermal sprayed nanostructured WC-Co wear resistant coatings and the resultant coatings showed significant improvement of wear resistance in comparison with the conventional counterparts. Micro structural in homogeneity of the conventional Cr_2O_3 based solid-lubricant coatings was successfully solved by utilizing nanostructured feedstock powder developed.

Nanostructured and conventional zirconia coatings were deposited by atmospheric plasma spraying and the thermal shock resistance of as-sprayed coatings was investigated by the water quenching method [22]. The results showed that the nanostructured as-sprayed coatings possessed better thermal shock resistance then the conventional coating. This phenomenon is explained in terms of the difference in microstructure and micro-structural changes occurring during thermal shock cycling. During the thermal shock cycling, the formation of vertical cracks, inter-granular fracture as well as the tetragonal to monoclinic transformation which occurred on the coating surface also make a contribution to the better thermal shock resistance of the nanostructured zirconia coatings.

R. Soltani et al. [26] have successfully deposit nanostructured coatings of Y2O3-PSZ (partially stabilized zirconia) from nano-particulate powder feedstock. Wear testing of nanostructured and conventional coatings showed that the nanostructured coating had a lower coefficient of friction and had lower wear loss under discontinuous testing conditions.

Xinhua Lin et al. [27] have studied the effects of temperature on tribological properties of nanostructured and conventional Al_2O_3-3 wt % TiO_2 coatings deposit by atmosphere plasma spraying. The tribological properties of both coatings against silicon nitride ball were examined in the temperature range from room temperature to 600°C. The wear resistance of the nanostructured coating was found better at high temperature as compared to their conventional counterpart.

Lima et al. [28] have studied thermal spray nanostructured and conventional zirconia–8 wt% yttria (YSZ) deposits, which have been employed as thermal barrier coatings (TBCs). Despite some

initial positive research results, there are still fundamental questions to be answered on the applicability of nanostructured YSZ coatings as TBCs. These questions are related to sintering effects, which could significantly increase the thermal diffusivity/conductivity and elastic modulus values of these types of coatings in high temperature environments. In this study, nanostructured and conventional YSZ coatings were heat-treated at 1400 ◦C for 1, 5 and 20 h. It was observed that the nanostructured coatings counteract sintering effects, due to the presence of a bimodal microstructure exhibiting regions with different sintering rates: (i) matrix (low rate) and (ii) nanozones (high rate).
Important sintering-affected properties, like thermal diffusivity and elastic modulus were studied.

The thermal diffusivity and elastic modulus values of the nanostructured YSZ coatings were significantly lower than those of conventional YSZ coatings, even after an exposure to a temperature of 1400 ◦C for 20 h. This study demonstrates that nanostructured YSZ coatings can be engineered to counteract sintering effects and exhibit significantly lower increases in thermal diffusivity and elastic modulus values in high temperature environments when compared to those of conventional YSZ coatings.

The fatigue and mechanical properties of HVOF-sprayed nanostructured and APS conventional titania (TiO_2) coatings were investigated by Lima et al. [29]. The fatigue strength of coatings deposited onto low-carbon steel (AISI 1018) showed that the nanostructured titania coated specimens exhibited significantly higher fatigue strength compared to the conventionally sprayed titania. The strain–time curve of AISI 1018 coated with TiO_2 indicated that the strain amplitude of the HVOF-sprayed nanostructured TiO_2 coating was much lower than the corresponding data of APS conventional TiO_2.

Lima et al. [30] have investigated process-property-performance relationship for titanium dioxide coatings engineered from nanostructured and conventional powders. In their study, Nanostructured (Nano), fused and crushed (F&C) and plasma-fused (PF) titania (TiO_2) powder particles were thermally sprayed via flame spray (FS), air plasma spray (APS) and high velocity oxy-fuel (HVOF) on low carbon steel substrates. Flame spray processing, although widely employed industrially, generally has received very limited attention in academic papers. However, the results of this research have demonstrated that a FS Nano titania coating was the best performing among all coatings tested, exhibiting no measurable signs of mass/volume loss after dry-sliding wear testing (ball-on-disk) and the highest deposition efficiency (DE) level. This is regarded as an important result, considering the fact that among these three processing techniques FS is the least expensive, the most portable and exhibits the lowest energy consumption levels. In addition, scanning electron microscopy (SEM) analysis demonstrated that the sliding wear scars of the FS and HVOF-sprayed Nano coatings were smooth, without significant irreversible deformation or formation of ridges. These characteristics are not typical of ceramic materials. It is hypothesized that this plastic-like behaviour and resilience exhibited by FS and HVOF-sprayed Nano coatings explain their improved performance under dry-sliding wear.

CONCLUSIONS

1. Plasma sprayed ceramic coatings using nanostructured powder feed have also exhibit exceptional properties.
2. Nanostructured ceramic coatings produced by plasma spray process are being developed for a wide variety of applications that require resistance to wear, erosion, cracking and spallation.
3. If properly deposited, nanostructured ceramic coatings could also provide improved properties for variety of applications, including wear resistant and thermal barrier coatings.
4. The published results show that mechanical milling can be effectively used to synthesize nanostructured powders. Using nanostructured powders as feedstock powders, various nanostructured coatings with improved performance can be developed.
5. Nanostructured coatings have strong technological potential, and rapid industrial growth is expected over the next decade.

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