Review

Porosity and Its Significance in Plasma-Sprayed Coatings

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Abstract: Porosity in plasma-sprayed coatings is vital for most engineering applications. Porosity has its merits and demerits depending on the functionality of the coating and the immediate working environment. Consequently, the formation mechanisms and development of porosity have been extensively explored to find out modes of controlling porosity in plasma-sprayed coatings. In this work, a comprehensive review of porosity on plasma-sprayed coatings is established. The formation and development of porosity on plasma-sprayed coatings are governed by set spraying parameters. Optimized set spraying parameters have been used to achieve the most favorable coatings with minimum defects. Even with the optimized set spraying parameters, defects like porosity still occur. Here, we discuss other ways that can be used to control porosity in plasma-sprayed coating with emphasis to atmospheric plasma-sprayed chromium oxide coatings. Techniques like multilayer coatings, nanostructured coatings, doping with rare earth elements, laser surface re-melting and a combination of the above methods have been suggested in adjusting porosity. The influences of porosity on microstructure, properties of plasma-sprayed coatings and the measurement methods of porosity have also been reviewed.

Keywords: porosity; atmospheric plasma-spraying; chromium oxide; porosity measurement; multi-layer coatings; nano-coatings

1. Introduction

The plasma-spray coating technique has been widely used in surface engineering to ensure efficient processing and reduced cost of operation and maintenance in many industries. Surface coating is ever increasing in transportation industries (ship building and marine structures, automotive and aeronautical fields), mechanical manufacturing and tooling, chemical processing and biomedical industries etc. Coatings have a vital role in engineering by providing protection against wear, friction and corrosion. They are also used for thermal protection in high-temperature environments. Most products are confronted with harsh, corrosive and high-temperature environment during their service life [1,2]. Therefore, it is essential that protection is provided from any deterioration thus enhancing reliability and superior performance of engineering components. Any flaw on the plasma-sprayed coatings is thus abated so that the intended purposes of the coatings are realized. Typically, the intrinsic defects of plasma-sprayed coatings, such as pores (porosity), un-molten or partially melted particles and cracks have adverse effects on the mechanical, physical and chemical properties of the coatings. The porosity is one of the typical features of plasma-sprayed coating, can deteriorate the protective performances of the coatings in harsh working environments [3]. In this work, porosity development

in plasma-sprayed coatings and the impacts of varying set spraying parameters on porosity were studied. Characterization and porosity measurement techniques of porosity in coatings have been summarized based on the related literature. A review of the current processes used in controlling porosity in plasma-sprayed coatings has been studied with the aim of coming up with methods to regulate porosity levels on plasma-sprayed chromium oxide coatings.

1.1. Plasma-Spraying

The plasma-spraying process involves melting of the feedstock at high-temperature, in the presence of a primary carrier gas usually argon or argon/hydrogen mixture which impels the molten and semi-molten particles onto the already prepared substrate surface [4]. The plasma stream generated ranges in temperature up to and above 8000 K at atmospheric pressure, which is sufficient for melting refractory materials or any material (metallic or non-metallic) with high melting point [5]. The process can also be customized for high-added-value coatings in atmospheric air or constrained environment. Plasma-spraying is categorized as direct current (DC) arcs or radio frequency (RF) discharges-generated plasmas. Additionally, other thermal spraying processes in use for coating are wire arcs, flames, high-velocity oxy-fuel flames (HVOF), high-velocity air-fuel flames (HVAF) and detonation guns (D-gun) [6]. Table 1 presents a summary of the various thermal spray methods, the feedstock used in the spraying processes and the quality of coating as related to porosity and adhesion [7–10]. The spray material is in the form of powder, ceramic rods, wire or molten materials.

Conventionally, most thermal spraying processes including plasma-spraying use finely divided powder in the micrometer-sized range. With the development of coating processes and with the need to improve the features of the coatings, the study of nanometer-sized particles injection has grown in interest over the past [11]. The main challenge encountered with nanometer-sized particles is the injection techniques into the center of the plasma jet since they are small in sizes and are easily swept away [8]. The following methods have been developed to solve the problem: (1) agglomeration of nanosized powders to micrometer sizes with adjustments on the spraying equipment, (2) forming amorphous coating by complex alloys with low critical cooling rates for metallic glass formation. These coatings when heated after spraying are recrystallized to the nanosized structure. (3) A suspension of nanometer-sized particles, with the carrier gas replaced by a liquid (“suspension thermal spraying” (STP)). Lastly, (4) precursors in a solution that will form in-flight nanometer-sized particles (“solution precursor thermal spraying” (SPTS)). All these methods have been detailed in other literature outlining the merits of application for each [12].

Table 1. Summary of thermal spray methods and nature of feedstock used.

Method	Description	Nature of Feedstock	Qualities of Coating
DC plasma torches	An electric arc is generated between electrodes and the thermal plasma is formed from the continual input of carrier gas and feedstock, projecting outward as a plasma jet/flame.	Mostly solid feedstock, recently using suspensions and solutions Commonly used to spray ceramic oxides	Porosity ranges between 3%–8% Good adhesion of > 40–50 MPa Deposition efficiency 50%
Wire arc spraying	Here two continuously advancing consumable wires are independently fed into the spray gun. Arcs are generated which melts the conductive wires. The molten feedstock is then deposited with the help of compressed air. Uses oxyacetylene gas mixtures	Mostly conductive wires Wires are made of ductile material or of a ductile envelope filled with a non-ductile or ceramic material.	Porosity level is well over 10% Medium adhesion of 40 MPa range Deposition efficiency 80%
Flame Spray torches	achieving combustion temperatures up to about 3000 K, with sprayed materials are introduced axially into the spray torch. Usually have high porosity that can be corrected by post treatment. They are characterized by supersonic speeds of gas flow. Combustion of hydrocarbon either as gas or liquid is achieved at lower pressures of 0.24 and 0.82 Mpa with specialized guns. Powder which can be injected radially, axially or both depending on gun design.	Feedstock is in the form of powder, rods or cords Mostly metals and polymers	High porosity of >10% Low adhesion of <30 MPa Deposition efficiency of 50% High oxide content of 6%–12%
High-velocity Oxy-fuel Flame (HVOF) and high-velocity air-fuel flame (HVOF)	The detonation is mainly generated in acetylene- or hydrogen oxygen mixtures (with some nitrogen to modify the detonation parameters) contained in a tube closed at one of its ends. The shock wave created by the combustion in the highly compressed explosive medium results in a high-pressure wave (about 2 MPa) pushing particles heated by the combustion gases.	Mostly for powder Suitable for metals alloys and cermets Recently liquid feedstock injection was developed for axial injection (solution and suspension)	Good adhesion of about 60–80 MPa Deposition efficiency of 70% Low porosity level Low oxygen content of about 0.5%
Detonation gun (D-gun)		Mainly powders of metals, alloys and cermets; some oxides can be sprayed but with particle sizes in the 20 µm range or below Feedstock and gases are fed in cycles	Porosity level is below 1% Low oxygen content of 0.1%–0.5% Deposition efficiency of 90% Tightly and highly bonded coatings

1.2. Applications of Plasma-Spray Coatings

For general application, plasma-spray coatings like the other thermal spray coatings can be used for corrosion protection, wear protection and for refurbishment and salvage of worn out parts and poorly machined parts [13]. Corrosion protection can be achieved in three ways using plasma-spray coatings i.e., anodic coating (sacrificial protection/cathodic protection), cathodic coating and neutral coating. Corrosion protection can be achieved in three ways using plasma-spray coatings i.e., anodic coating (sacrificial protection/cathodic protection), cathodic coating and neutral coating [6]. Plasma-spraying coating can also be used for wear protection. In engineering materials used in the industry, wear fall in four categories, i.e., erosive wear, fretting wear, adhesive wear/sliding wear and abrasive wear [14].

Plasma-spray coatings are also applied in metal manufacturing industries on tooling parts and dies thereby reducing the cost of replacing when damaged. Novel valves for high-pressure acid-leach services have been coated with a blend of chromium oxide top and titanium oxide bond coat [15]. The hard chromium oxide surface coating is a good abrasion resistant and for its good tribological behavior even in high-temperature regions and was found to have superior performance on these titanium base metal ball valves in terms of hardness, adhesion on the bond coat and corrosion resistance. In their study to improve the safety of nuclear facilities, Wang et al. [16] coated accident tolerant fuel (ATF) using Cr and FeCrAl using atmospheric plasma spraying (APS) because of its suitability in high-temperature regions to improve the oxidation resistance of Zircaloy-4 cladding substrates. On a broader view, APS has been used for high-temperature coatings in metal processing industries, chemical industries, electrical utilities, ceramic and glass manufacturing, aerospace, land-based turbines. It has also been used to provide protection against combined corrosive and erosive wears [17–19].

Thermal barrier coatings (TBCs) have been extensively used in the aerospace industry in heat insulation, oxidation resistance, clearance control coatings (in cases of abradable coatings) and the following areas combustors, transition ducts, stationary airfoils, rotary airfoils and shrouded casing for abradable porous ceramics [20,21].

TBCs typically consist of three layers: the metal substrate, metallic bond coat and ceramic topcoat. Figure 1 shows a scanning electron microscopy (SEM) images outlining the four constituents of TBCs, before oxidation and after oxidation.

Figure 1. Showing the components of thermal barrier coating (TBC) (a) before oxidation (b) after oxidation with the inclusion of thermally grown oxide (TGO).

The presence of microcracks and interconnected pores in TBC topcoat allows oxygen through to the bond coat at elevated temperatures during operations and oxidation occurs [22]. This leads to the formation of oxidized scale on bond coat known as thermally grown oxide (TGO). TGO is pronounced in any coating with a lot of interconnected porosities and microcracks. TGO contributes to the failure of TBC during cyclic operations in high-temperature places due to the thickening of TGO during oxidation. Any thickening of TGO induces stresses on the bond coat/top coat interface causing delamination of the coatings [23].

Plasma-sprayed ceramic coatings such as calcium phosphate ceramics coatings have been used in medical fields for rehabilitation orthopedics by improving the surface biocompatibility of the feedstock materials like titanium, cobalt and chromium [24,25]. Hydroxyapatite (HA) and double layer HA/Al₂O₃-SiO₂ have also been coated on titanium implants to improve the surface roughness and hydrophilicity of the implants [26].

2. Porosity

Porosity has been categorized differently by various authors. Thirumalaikumarasamy et al. [27] grouped pores depending on their formation mechanisms and sizes as type A and type B. Type A ranged from 0 to 10 µm and type B range from 10 to 25 µm. Type A resulted from the interaction between particles and gaseous medium while type B was formed by splashing on impact with deposited material or voids emanating from deformation of partially molten particles. Others researchers like Ctibor et al. [28] and Konyashin et al. [29] grouped pores as open pores, closed pores and microcracks. They also outlined that pores and microcracks can be formed from different sources such as enclosed gases, partial filling in the solidifying splats and shrinking of splats during fast solidification. In addition, others are classified as globular pores, inter-lamellar flat pores and vertical cracks (micro-cracks). The globular pores are approximately convex in shape. In thermal spraying, the inter-lamellar flat pores are thin voids filling spaces between splats, usually perpendicular to the spraying direction [28,30].

2.1. Formation of Porosity Plasma-Spray Coating

During coating formation, layers of impacted and accelerated particles are formed on top of the previously molten particles which spread and flatten on the substrate surface. The process continues with an increasing number of spray passes. The effectiveness of plasma-sprayed coating depends on the quality of the substrate/coating interface adhesion bond and on the cohesion of buildup layers.

The rough substrate surface (grit blasted) ensures a mechanical cohesion/adhesion bond where molten impacting particles spread out to fill any groove and pits on the substrate surface.

Consequently, inter-diffusion at high-temperatures (local heat transfer) from underlying compacted layers and subsequent solidification leads to the interlocking of layers forming lamella or splats. Formed coating layers sometimes have entrapped air sacks (gasses), voids or unmolten particles which leads to various shapes and sizes of pores [31]. In general, porosity forms from entrapped air sacks and solidification shrinkages [32,33] during solidification of plasma-sprayed coatings. The ultimate flattening and spreading out of particles is controlled by both mechanical and thermal constraints. The thermal constraints control the rate of solidification which depends on splat thickness, thermal conductivity/diffusivity of the sprayed material and the underlying solid layer (bond coat) and the quality of contact between the previously sprayed layers and the compacting particles on top. Porosity is generated if the space between the arched splats is not overlaid by the subsequent compacting deposits of particles.

Coating formation and hence porosity is linked to the nature of the raw powder properties in terms of its size (diameter and morphology), specific density and purity which affects flight particles. Good powder flowability is needed to achieve the correct deposition efficiency which subsequently affects the kind of coating. Different powder preparation techniques have been studied and are found to work well in for certain work than others hence ensuring a quality and reliable coating. The techniques include atomization, agglomeration by spray-drying, melting and grinding, wet particle coating, sintering etc. [34].

2.2. Morphology of Porosity

As has been outlined earlier, the nature of deposition from plasma-spraying exercise is a random one, where molten and semi-molten particles impinge on the prepared substrate and/or earlier deposited layers at high-pressure and temperature, flatten and solidify to form thin splats. The resulting coating

is an anisotropic lamellar structure composed of various pilling defects within the layers such as globular pores which may be or not connected to the upper surface coating to form open pores. In some cases, there are vapors from chemical reactions and atmospheric gases which can be trapped together with inclusions from unmolten, dirt etc. which may coalesce during solidification [35]. These voids and inclusions, in most instances, initiate delamination which may be accompanied with intra-lamellar microscopic cracks. Figure 2 shows a typical morphological representation of the plasma-sprayed coating.

Figure 2. Scanning electron microscopy (SEM) images showing typical atmospheric plasma-sprayed coating morphology for chromium oxide coating on Q235 steel.

The collection of these features gives the pore morphology of a typical plasma-sprayed coating, and by which the quality and hence the functionality of a coating can be derived [36].

2.3. Effects of Porosity on Plasma-Sprayed Coatings

Porosity has a direct impact on the plasma-sprayed coatings. This can be advantageous if incorporated in the design or deleterious if not. Porosity characteristics such as morphology, pore sizes, pore distributions, microcracks sizes and orientations and lamellar splats are governed by spray process parameters. Furthermore, pore distributions are also affected by the nature of elements and the bonding mechanisms [28]. Mozhegov et al. [37], Ghasemi and Hamideh [31], and Jamali et al. [38] noted that splats structure and morphology, crack morphology and size of porosity have a direct effect on adhesion and cohesion strength of plasma-sprayed coatings. Gas entrapments in coating influence thermal behavior in TBC. It was found that nanostructured TBCs had lower diffusivity due to smaller splat sizes and nano-pores existing in this structure compared to the one for conventional TBCs [31]. It has been reported in other pieces of literature [39–43] that the pores in the nano-zone retard the heat transfer in nanostructured TBC. Porosity in Suspension Plasma-sprayed (SPS) topcoats was found to affect not only the thermal conductivity and strain tolerance but also the mechanical properties such as hardness and toughness of the TBC [44–46].

Porosity level in plasma-sprayed coatings significantly affects the density of the segmentation cracks [47,48], it also affects the thermal diffusivity and thermal conductivity [49]. Increasing porosity in TBCs can decrease residual stress from thermal expansion mismatch between the substrate and ceramic [50] Cernuschi et al. [51] argued that thickening of TGO led to crack propagation, which compromised the adhesion bonds between the bond coat and the top ceramic coat.

Porosity has also been found to influence the electrical conductivity of bulk material [52]. Khal et al. [53] found that bulk conductivity depended on the microstructure and the pore volume fractions. They found that porosity affected the electrical responses of porous Lanthanum molybdate ($\text{La}_2\text{Mo}_2\text{O}_9$). Samples which had an identical porosity level but with smaller pore/grain interfaces surface areas possessed lower blocking factor compared to the ones that had larger pore/grain interface surface areas. The above study was similarly established in the investigation of yttria-stabilized zirconia (YSZ) [54] and gadolinia-doped ceria [55]. In other literature, Elshikh [56] and Wu et al. [57] found out that heat treatment of plasma-sprayed YSZ resulted to the densification of the sprayed coating during sintering processes, leading to reduced porosity, reduced resistivity and increased electrical conductivity.

2.4. Inter-Correlation of Porosity and Residual Stresses in Plasma-Sprayed Coatings

The longevity of any plasma-sprayed coatings will depend on the environmental conditions it faces during its service life, for instance, harsh corrosive media, abrasive contacting surfaces or high cyclic temperatures which induce stresses in the coating [58]. During coating formation, the pilling-up of individual splats dictates the kind of microstructure, consequently the quality of the coating [59]. It has been noted that residual stresses originate fundamentally during coating formation, and they are superimposed through thermal cyclic activities and thermal shock behavior [23]. Residual stresses affect the adhesion bond mechanism between the metallic bond coat/ceramic top coat interface and occasionally the substrate/ceramic topcoat where the metallic bond coat is optional [60,61]. Furthermore, residual stresses have been related to failure resistance on coatings in thermal shock and thermal cyclic behavior [36]. The most common failure modes associated with residual stresses and stresses resulting from cyclic behaviors are cracks and delamination/spallation [59], and poor adhesion bonds [22,62]. It is, therefore, necessary to understand the correlation of porosity (or intrinsic coating defects) and residual stresses on the coating. It is, therefore, necessary to understand the correlation of porosity (or intrinsic coating defects) and residual stresses on the coating. Residual stresses originate basically from two areas that are associated to porosity i.e., during coating manufacture where interlamellar pores and globular pores are formed and during the development of thermally grown oxide at the oxidation stages [62,63]. Firstly, interlamellar pores are formed when there is a rapid solidification process during coating formation leaving behind tiny cavities as a result of incomplete contacts between the deposited layers, or around unmelted particles or of troughs previously due to surface roughness. These sites are prone to further cracks during any thermal stresses or tensile relaxation stresses. A large amount of these kinds of pores leads to increased residual stresses within a coating [61,62,64]. As was mentioned earlier, these kinds of defects are linked to improper localized adhesion and premature failures during thermal cyclic activities. Additionally, these pores are also associated with a reduction in thermal conductivity. Secondly, thermally grown oxides (TGO) are thin films/scale of oxide that is formed between the metallic bond coat and the ceramic top coat when the coating is exposed to elevated temperatures [65]. The oxide scale formed serves as a diffusion shield to the next oxide and commonly formed oxides are Al_2O_3 , Cr_2O_3 , etc., it is reported that a porous coating or a coating with higher percentage porosity will tend to allow thicker growth of TGO, which in this case is detrimental to the integrity of the coating [66]. Any further growth of TGO poses residual stresses to the coating leading to cracks and delamination [67,68]. It is therefore clear that as porosity increases in any plasma-sprayed coating, there is a likelihood that residual stresses are heightened and this compromises on the reliability of coating.

3. Methods of Measuring Porosity

The integrity of any coating can be ascertained by measuring porosity and porosity related features. This is done by considering the following parameters: (a) the percentage porosity (P_m), (b) pore density per unit area (PD_m), (c) maximum pore diameter (D_m), (d) equivalent pore radius (R_m), (e) pore size and pore classification, (f) pore analysis. The above constitutes a pore system.

The models of evaluation and analysis can be broadly classified as the direct and indirect methods. In the direct method, the samples are physically subjected to the measurement process, whereas in indirect methods, it is via imaging analysis of the sample. Most of the methods portrayed in Figure 3 can be applied in varying ranges from the macro to nano levels with others overlapping to complement.

Figure 3. Porosity characterization techniques.

Figure 3 gives a summary of the most common methods used in characterizing porosity on materials. They include image analysis (of micrographs from SEM, atomic force microscopy (AFM) and transmission electron microscopy (TEM)), electrochemical impedance spectroscopy (EIS), Archimedian method, neutron scattering, nondestructive testing method, thermoporometry etc. The method chosen depends on availability, its applicability in the length scale range and the skills. Some need more skill in the analysis than others. In the next section, several methods are discussed outlining their merits and demerits.

3.1. Liquid Intrusion

3.1.1. Mercury Intrusion Porosimetry

Mercury porosimetry can be used both in mesopores and macropores diameter analysis. It has been used for assessing the surface area and particle distribution. Additionally, the information such as pore shape, network effects, skeletal and bulk densities can be obtained by mercury porosimetry. Figure 4 shows the cross-sectional view of a mercury penetrometer. This is commonly used for porous materials. For plasma-sprayed coatings and most of the thermal spray coating, the principle of use is the same.

Figure 4. Cross-sectional view of a mercury penetrometer.

The non-wetting liquid (mercury) requires pressure application to get into the pores and voids. The method can be used to measure pore diameters of up to $0.0070 \mu\text{m}$ [69]. Total porosity is computed by considering the total volume of mercury intruded into the voids in the samples and the bulk volume of the sample. It is taken as a percentage by the following equation [70].

$$\text{Porosity (\%)} = \frac{V_t}{V_b} \times 100 \quad (1)$$

where V_t is the total volume of mercury in the voids and V_b is the bulk volume of the sample. For volumetric distribution of pores, the Washburn equation is used. As mercury pressure is increased, the mercury intrudes into the voids in decreasing order. Hence, if ΔV is the volume intruded between P and $P + \Delta P$, it will equal the volume of pores with radii between r and $r - \Delta r$ related to the following Washburn equation below [71,72]:

$$r = \frac{2\sigma \cos \varphi}{P} \quad (2)$$

where σ is taken as the surface tension of mercury, usually for pure mercury, 484 mN/m and φ the contact angle depends on the material used.

Since mercury poses health and environmental issues, other intrusive liquids with the can be used to substitute use mercury. Other safer metals that can be used are Gallium, Indium, Galinstan (Gallium, Indium and Tin), Wood's metal (Bismuth, Lead, Tin and Cadmium) and Field's metals (eutectic of Bismuth, Indium and Tin) [73].

3.1.2. Water Intrusion Porosimetry

Water intrusion in hydrophobic materials has been suggested. Its use is based on the same principle as that of mercury intrusion [73,74]. This method has been reported by various researchers as a dependable, productive and not time-consuming method. The principle is a very simple one, where samples are submerged in water. If there are pores in the sample, especially the interconnected or networked pores or microcracks, the sample will act like a sponge. As air from the air sacks, pores or microcracks diffuse out, water will diffuse into the samples causing the weight of the samples to increase. The more and larger the number of interconnected pores the more the weight gain in the samples. The weight gain can be taken to be directly proportional to the volume of the pores and hence the apparent porosity of the samples. Enclosed pores cannot be accounted for through this method, although the apparent porosity is usually as close to the total porosity as long as the closed porosity is as small as possible [26].

3.2. Nondestructive Testing (NDT)

Nowadays, NDT methods also have gained ascendancy in evaluating and assessing the extent of porosity in plasma-sprayed coatings. Methods such as magnetic particle testing, dye penetrant and eddy current methods have been used to assess cracks and integrity of materials, especially in the inspections of materials quality and integrity of structures. Nondestructive testing techniques are expedient over the standard destructive methods by being less time consuming, reliable especially with ceramics and their applicability to service parts still in operation. Hence they can be used in inspection to predict any density or thickness variations which might lead to premature failures.

Radiography and ultrasonic testing methods which have also developed with the advancement in technology, are versatile and are applicable to every kind of material. They are both applicable for depth sizing, orientation and volumetric. The specialized and developed techniques, for example, ultrasonic and X-ray testing methods are also in use. These methods are more accurate, provide for repeatability, rapid and easy to use and capable of automation. The ultrasonic method has been in use for the characterization of ceramics and bulk materials and also for plasma-sprayed coatings. Combined laser-ultrasonic techniques have also been employed [75]. This method was merited over the conventional ultrasonic method which is contactless, eliminating all the inconveniences of direct-contact or immersion techniques. Furthermore, it provides for easy control of the generation and detection laser spots hence the accuracy in use.

Parthasarathi et al. [76,77] applied X-ray computed tomography (CT) to investigate density and porosity distribution in plasma-sprayed alumina coatings. The method uses the X-ray attenuation coefficients to reconstruct images of an internal cross-section of a sample. The images obtained can be used to analyze pores sizes, pore shapes and orientations. Farber et al. [78] also found out that even though X-ray computed tomography was less precise in finding the total porosity of granules, it was more suited for morphological information such as pore shape, spatial distribution and connectivity. The technique uses an array of 2D shadow X-ray images of an object to rebuild its 3D structure using mathematical procedures. Additionally, small-angle neutron scattering methods have been utilized in pore morphology and pore size distribution with very large pore length scales of up to 1000 nm or more [79]. It has been reported that it is applicable for even smaller pores and closed pores where mercury porosimetry is inapplicable. Another method that can be used to characterize pore structure from melting or freezing point depression of liquid restrained in pores is thermoporometry. This method total pore volume, specific surface area, pore radius and pores size distributions can be quantified [80].

3.3. Image Analysis -Microscopy

Microscopy provides a more dependable examination of pore geometry and morphology in the mesopores, macropores and nanopores ranges through direct observations of thin cross-section specimens of solid materials. Optical microscopy can be used when not much intricate information is required since the wavelength in optical microscopy has a resolution of 200 nm. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are applicable for micrometric and nanometer scale defects. The samples are prepared in thin sections which allow for the analysis of small components at all depths and levels. Where contrast between the metal matrix and pores is a challenge, various ways are used to improve the contrast such as surface replication, shadowing or impregnation of pores space with fluorescent resin. Moreover, non-conducting samples need coating with thin metallic coatings, for instance, the polymeric membranes [81]. For a comprehensive characterization of pore geometry, pore morphology and size distribution, quite a large number of samples and measurements are required. The micrographs obtained are then analyzed using available commercial imaging software for automatic 2D image processing [71].

Image analysis via microscopy provides direct measurement which does not require models or making additional assumptions. However, it also has its challenges or demerits; it is a destructive method since the sample has to be either a thin plane cross-section in nature or the application of

metallic coating for polymeric membranes is required. Furthermore, the analysis depends entirely on sample preparation and handling which requires skillful workmanship in contrast enhancement (metal coating procedures) and thin sectioning for viewing through microscopy. Another aspect is having the right equipment which will allow the right resolution to be achieved. Lower resolution implies that all the details will be captured [28,82].

4. Ways of Controlling Porosity in Plasma-Sprayed Coating

As one of the widely used plasma-sprayed coating, chromium oxide coatings have excellent properties such as chemical inertness, high mechanical strength, high hardness and good corrosion and wear resistance [83,84]. Nevertheless, plasma-sprayed chromium oxide coatings also suffer from porosity defects, which are considered to have a negative impact on properties of coatings like hardness, strength, and wear-resistance and corrosion resistance [62]. It is thus necessary to reduce porosity hence improve the service life of chromium oxide coatings.

Porosity in plasma-spray coating can be minimized by optimizing the set spraying parameters, for instance, spraying power, feed gas pressure (for primary gas-argon and the auxiliary gas-He/H), powder feed rate, stand-off distance (SOD), number of spray passes and preheating passes etc. [85,86]. From earlier research over the years, several ways of reducing porosity have been studied and other researches are still ongoing. Ekberg et al. [46] used heat treatment as a post-treatment method to reduce porosity in their work. They found out that fine pores were reduced but coarser ones increased. They agreed that coalescence of pores occurred during the heat treatment for the cases of coarser pores. They also suggested the use of finely-grained feedstock to reduce porosity. Ganvir et al. [49], agreed with Ekberg that heat treatment caused microstructural changes such as densification, coarsening and grain growth. Other researchers [46,49], also used suspension Plasma-spraying as a way of reducing porosity in plasma-sprayed coating. The working principle is to ensure a dense coating with regular packing of splats and minimum voids. The cases that will provide dense lamellae will have the least porosity. This idea has been used experimentally to achieve a coating with the least percentage porosity as possible. In the literature, porosity can be as high as 20% or as low as 3% [87–90] depending on the spraying technique, the material used or the skills of operation.

Currently, many researchers have used following: (i) multilayer coating [33,91] (ii) doping using other elements-co-doping [32,91–94] (iii) nanostructured coating in (multicomponent coating, gradient coating, nanocomposite coating, super-lattice coating, duplex coating, adaptive coating) [42,95–97].

In this work, these methods are proposed and trusted to have the potential of reducing porosity in chromium oxide coating.

4.1. Multilayer Coating

Multilayer coating, as the name suggests is the application of more than one identical or different layers on a substrate. Typically the layers are alternated after the bond coat, as represented in Figure 5. It has been used to reduce residual stresses to a large extent and inhibit the proliferation of cracks across a coating [91]. Multilayer coatings have a reduced grain size. Zhou et al. [98] linked the increased hardness and endurance of multilayer coating to Koehler Hall-Petch effect. The boosted characteristics are accredited to the increased volumetric density as a result of refined grain sizes, which increases the resistance to dislocation movements. The function of the multilayers is to reduce the chances of defects such as microcracks, pinholes or pores propagating to the substrate [99].

The main merits of a multilayered coating come from the kind of layers exhibited by the coating. Multilayer coatings can have various approaches. Interface layers give a transition from the substrate to the following coat, usually providing for better adhesion of a coating to the substrate and ensuring a smoother transition from coating properties to the substrate material at the substrate/coating boundary. The interface layers also act as inhibitors to further reactions besides, they also impart some special wear-protecting layers to the substrate and minimize the chances of microcracks and pinholes extending to the previous layer. The interface layers can consist of a large number of various layers which have

different physical or chemical properties. When various layers combined into a whole interface layer, they can work together and avoid individual disadvantages. Thereby complementing each layer by improving on the stress concentration and reduction of chances of crack propagation through layers.

Figure 5. A representation of a multilayer coating where two different coating materials are alternated.

Another group of multilayered coatings is the diverse property layers. This is unique and is gaining use in the industry where the surfaces can be improved by depositing layers of coating that have a dissimilar effect on the substrate. For example, coatings that are for wear protection coupled with corrosion protection. Another case is thermal insulation coating with electrical conductivity or diffusion barrier with adhesion enhancers to the substrate [100–102]. Examples of elements that can be used in these cases are carbon, silicon and vanadium, which are mostly used for alloying.

4.2. Doping of Chromium Oxide Coating

Doping is the intentional insertion of impurity elements into the main parent element. The impurity elements can change some of the overall physical properties of the established materials such as density, electrical or optical properties of the overall material. Figure 6 shows a schematic representation of the co-doping coating.

Figure 6. Schematic representation of a co-doping coating.

Porosity levels of chromium oxide coating can be reduced by doping modification and changing of the microstructural scale. Previously, Yang et al. [103] improved wear resistance of chromium oxide by doping modification and changing the microstructural scale of the coating. They used CeO_2 and Nb_2O_5 which also had improved effects on the porosity of coating. From the above criteria, doping can also be used in the densification of the topcoat by the way of reducing the level of porosity. Yang et al. [96] noted that modification through doping, for instance, Cr_2O_3 -3% TiO_2 and Cr_2O_3 - Al_2O_3 not only improved wear resistance but also reduced porosity significantly. Sadri et al. [104] and

Leclerc [105] in their investigation on self-lubrication by adding solid lubricants such as CaF_2 and nano-Ag respectively, found out that there is a direct relation between improved wear resistance and reduction in porosity. All of them illustrated that the decrease of porosity and the improvement of the hardness are beneficial to the wear resistance of coating [106–108].

The microstructural properties of chromium oxide coating after doping can be improved by post-heating e.g., heat treatment or laser remelting to densify the deposited powder. It has also been found by that chromium vaporization can be reduced by spraying with cobalt-based, manganese-based and spinel coatings, when used for doping [93]. Some of the elements that can be used in doping of chromium oxide are cerium, niobium, silver, calcium, fluorine, titanium etc.

4.3. Nanostructured Coating

The microstructural length scale for nanostructured feedstock falls between 1–200 nm [109]. Nanostructured powder may cause agglomeration before they are used in plasma-spray so not all the particles are molten, which has been proved by the previous studies. Thus, the sprayed coatings are made up of the molten powders and some semi-molten powders. It has been noted that these special structures of sprayed coatings benefit the properties of the nanostructured coating, especially the improvement of denser coating with better hardness surface and better strength [110–112].

From these previous works, it is evident that nanostructured materials produce better coating compared to the conventional ones [96]. From this backdrop, it is evident that nanostructured chromium oxide will have a denser coating and lower porosity level. Nanostructured coatings can be further treated by sintering the topcoat using heat. This has been recorded by Jamali et al. [38] as a viable practice. They also agreed that nanoparticles resulted in a bimodal structure which improved bonding strength together with porosity network. Figure 7 shows a representation of a nanostructured coating. In nanostructured coating, there arise two kinds of powder. One that is fully molten and the other which is partially molten.

Figure 7. Schematic illustration of the nanostructured coating during plasma-spraying of agglomerated nanostructured based powders. (a) Partially molten particles. (b) Fully molten particles.

5. Challenges and Future Research Trends

The proposed methods above are still undergoing research for different applications. Every area of application has its own challenges. Nanostructured coatings have been lauded for their low porosity coating. As nanoscale feedstock has a low mass, they have poor flowability during deposition. They need to be agglomerate before they are feed into the plasma jet for deposition. This increases the operating costs from consumable and machine part configurations. Many research work is still needed to achieve optimal results.

6. Conclusions

In this work, the origin of porosity in plasma-sprayed coatings is comprehensively explained. During fabrication of plasma-sprayed coatings, the molten feedstock powder piles up to form layers, leaving voids at interfaces which might be exaggerated as the lamellae solidify and cool down. In some cases, the porosity is desirably introduced in the design e.g., pharmaceutical products like medicine, whereas the porosity plays deleterious roles in the case of structural materials. Lastly, methods to minimize porosity in chromium oxide have been suggested.

Measurements methods of porosity mainly include water intrusion porosimetry (WIP), mercury intrusion porosimetry (MIP), SEM, AFM, TEM and NDT methods. Each measurement method has its merits and demerits. Application of one could also be influenced by the level of skills needed for the operator. In terms of length scale, for macro and to some extent micro-sized pores, water intrusion porosimetry (WIP) and mercury intrusion porosimetry (MIP) can be applied. For micro to nano-scaled pores SEM, AFM and TEM are suitable for the determination of pore parameters. In addition, advanced NDT methods like X-ray micro-tomography and ultrasonic testing methods can be applied. For most of the laboratory experimental works, SEM can be coupled with energy dispersive spectroscopy (EDS) to achieve so many analysis. The methods that have been suggested for controlling porosity in plasma-sprayed coating which can also be used for chromium oxide coatings are multilayer coating, doping with rare earth elements and using nanostructured feedstock. It has been studied that these methods not only improve on the microstructure of the coating but also reduces porosity and enhance other features like hardness, wear-resistance and adhesion onto the substrate.

This work can enrich the study of plasma-sprayed coatings, guiding the research methods of formation mechanisms, measurements and controlling of the porosity of the coating, which is greatly meaningful and important for the widespread applications of the plasma-sprayed coatings.

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