Review

Porosity and Its Significance in Plasma Sprayed Coating: A Review

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Abstract: Porosity in plasma sprayed coatings is vital for most engineering applications. It is either advantageous or disadvantageous depending on the functionality of the coating and the immediate working environment. Consequently, the formation mechanisms and development of porosity has 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 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

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1. Introduction

Plasma spray coating techniques has been widely used in surface engineering to ensure efficient processing and reduced cost of operation and maintenance in many engineering 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 vital role in engineering by providing protection against wear and reducing friction. 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 these coatings are protected from any deterioration to ensure enhanced reliability and uphold 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 being one of the features that plasma sprayed coating has, can deteriorate the protective performances of the coatings in harsh working environments, and the set spraying parameters is one of the influencing factors [3]. In this work, porosity development in plasma sprayed coatings and the impacts of varying

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

2. Applications of plasma spray coatings

Plasma sprayed coatings play important roles on the applications of industrial products in harsh environments by increasing the resistances of products to corrosion, oxidation and wear. Plasma sprayed coatings play important roles of protection against corrosion, friction and wear, thermal and oxidation to many industrial products that are used in harsh environmental conditions. During service life, a product can be exposed to a combination of environmental conditions such as abrasive wear combined with high thermal stress as in turbines, corrosive marine environment and high temperatures as in the case of offshore mining. In other cases, corrosive marine environment with biofouling microorganisms for ocean going vessels and offshore platforms and rigs. Also, for oil and gas transportation and power generation plants (geothermal plants) corrosive gases accompanied with high temperature. The products mentioned above require protection to ensure their functionality. The presence of pores on plasma sprayed coatings is inevitable and so its control is necessary depending with the area of product application. The next section outlines engineering fields where plasma sprayed coatings are used.

2.1. Applications of plasma spray coatings

Plasma spray coating have been widely used for corrosion and wear protection. The function of the coatings is to protect components surfaces from corrosion and erosion during service life. Corrosion and erosion has led to degradation and eventual total failure of industrial components hence a lot of money lost during repairs and also down times. Each design is usually different depending on the immediate environment where the particular component is used. In the design, the thickness of the coating, the surface defects and the feedstock will determine the efficiency of protection. Corrosion protection can be achieved by two kinds of designs, sacrificial coating and non-sacrificial coatings. In both cases, atmospheric plasma spraying has be used [4]. For sacrificial coating, the amount of porosity in the coating does not affect the functionality of the base metal. Any corrosion activities will occur on the metal being sacrificed since such coatings must have a cathodic behaviour comparatively to the ions of the metal to be protected. For the case of non-sacrificial coating, the presence of porosity will affect the base metal especially the interconnected pores. This is remedied by always minimizing porosity in these kinds of coating. Exchange of corrosive media to the base metal is limited by designing a protective bond coat that separates the base metal and the top coat or having a dense protective coat. Moreover, sealing methods can be provided for the coating. This ensures that any pores are filled by a suitable sealant and hence no interaction of corrosive media with the substrate.

Plasma spraying coating has also been used for wear protection [5-7]. Wear associated challenges have been minimized by either using sturdy and abrasion resistant alloys or by surface modification via choosing a suitable coating material which is hard enough to resist any further frictional damages and is also relatively cheaper than the high cost wear resistant alloys. It is recommended that low cost metals which possess same mechanical and physical characteristics as the high cost wear resistant counterparts be used with a wear protective coat. hardness and adhesion strength are two vital properties of a coating that need consideration when it comes to wear resistance[8]. Hard ceramic like chromium oxide, does not abrade easily. Moreover, when bonded perfectly onto a substrate the component can have a longer service life.

Novel valves for high pressure acid-leach services have been coated with a blend of chromium oxide top and titanium oxide bond coat[9]. The method of spray was APS. The hard chromium oxide surface coating is a good abrasion resistant and for its good tribological behaviour even in high temperature regions and was found to have superior performance on these titanium base metal ball

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valves in terms of hardness, adhesion on the bond coat and corrosion resistance. Fuel cladding in nuclear power station- against corrosion resistance and neutron irradiation resistance. In their study to improve the safety of nuclear facilities, Wang et al. [10] coated Accident Tolerant Fuel (ATF) using Cr and FeCrAl using APS because of its suitability in high temperature regions to improve oxidation resistance of Zircaloy-4 cladding substrates.

Thermal barrier coatings of ceramic (TBCs) can be fabricated by plasma spray technique with the appreciable mechanical property, thermal barrier property and oxidation resistances in high temperature environments. During plasma spraying of the TBCs, several processing steps are usually taken i.e. sprayed metallic bond coating and subsequent sprayed ceramic protective coating, in which metallic bond coating for the good adhesive strength between base materials with coatings and ceramic coating for the protective roles at high temperature as shown in Fig. 1.

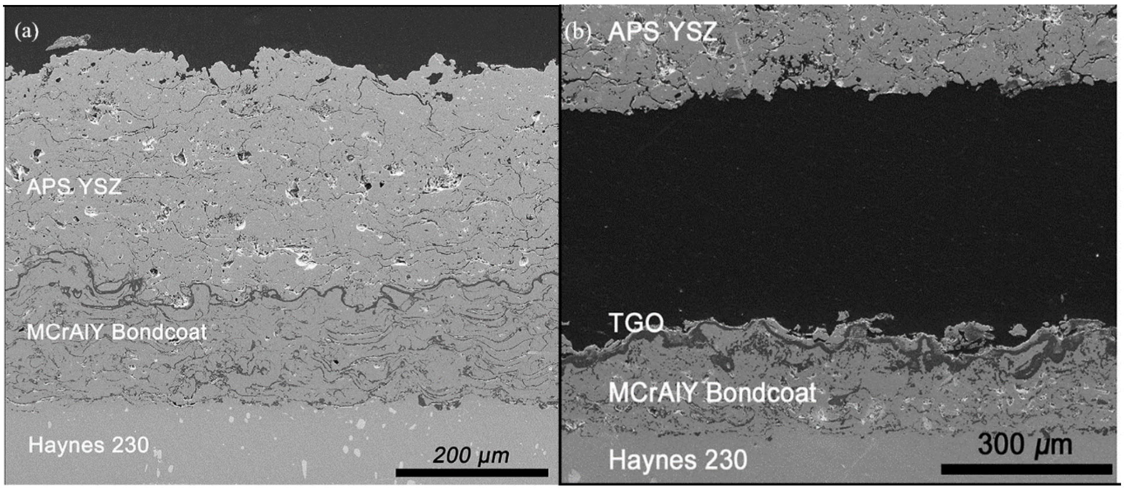

Figure 1 showing the components of TBC (a) before oxidation (b) after oxidation with the inclusion of TBC

TBCs typically consist of three layers: the metal substrate, metallic bond coat and ceramic topcoat. Fig. 1 shows a SEM images outlining the four constituents of TBCs, before oxidation and after oxidation. An effective TBC should be able to have the following qualities: high melting point, no phase transformation between room temperature and operating temperatures, low thermal conductivity, chemical inertness, similar thermal expansion match with the metallic substrate, good adherence to the substrate and low sintering rate for a porous microstructure [11, 12].

TBCs have been widely used in the hot section of aero-turbine engines to protect the base material from severe heat effects or high temperature oxidation [13, 14]. Khan et al. [15]investigated the influence of plasma sprayed on NiCr–Cr2O3 and Al2O3–40% TiO2 (A40T) coatings on Inconel 617 at elevated temperatures. The resulting coating was found to possess superior resistance to hot corrosion and also the thermal effects on the general material was reduced. Nickel based alloys that are frequently used in gas turbine parts in aeronautical and nuclear industries have been modified by doping with rare-earth elements to improve their functionality in harsh conditions to solve hot erosion/corrosion and thermal fatigue problems. A good example is Nd2O3 doped into plasma-sprayed NiCr-Cr2O3 composite coating[16]. Also titanium alloys coated by APS have been used in gas turbine components, especially areas that are prone to hot corrosion. A protective thermal coating has been used to reduce chances of oxidation during the service life of these components. For a period of time, plasma sprayed coatings like calcium phosphate ceramics coatings have been used in fields of rehabilitation orthopedics medicines through improving the surface biocompatibility of the feedstock materials like titanium, cobalt and chromium[17]. HA (hydroxyapatite) and double layer HA/Al2O3-SiO2 have also been coated on titanium implants to improve the surface roughness and hydrophilicity of the implants. APS is one of the techniques that has been customarily used to produce such surfaces. It has been studied that the coatings have enhanced biological behaviour without hampering the fundamental quality of the implants. 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[18].

3. Porosity in plasma sprayed coating

3.1. Formation of porosity in plasma spray coating

Plasma spray process (see Fig. 2) involves melting of the feedstock particles at high temperature, in the presence of a primary gas carrier usually argon or argon/hydrogen mixture, which impel the molten and semi-molten particles onto the substrate surface. Consequently, layers are formed on top of the previously molten particles which spread and flatten on the surface. As this process continues with increasing number of spray passes, a coating is eventually formed. Entrapped air sacks, voids and unmolten particles leads to various sizes and shapes of pores [19]. This is illustrated in fig. 3. The porosity in plasma sprayed coating can also result from both mechanical interlocking and diffusion bonding during spraying process. Interlocking comes to play because of the grit blasted surface. Due to the difference in nature of the particles from the molten powder and the substrate, bonding is required to ensure that a firm coat is formed which does not easily experience spallation. During solidification of the coatings, the pores can be formed by the air sacks and solidification shrinking. Micro-cracks can also be counted as pores since they also compromise the integrity of the coating in similar ways [20, 21].

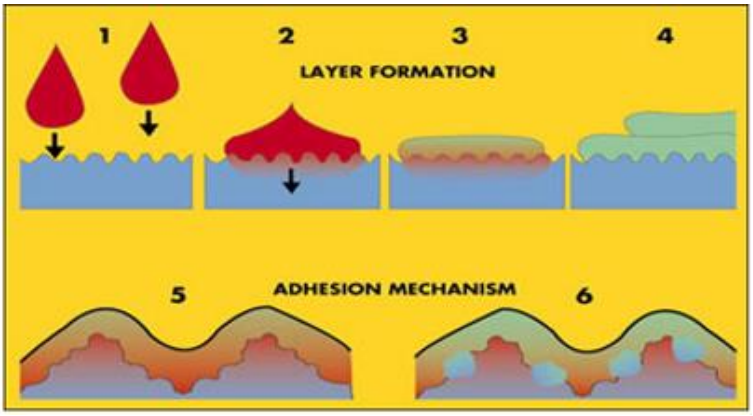

Figure 2 Schematics of Coating formation during plasma spray coating: 1. Transport of spraying particles; 2. Impact on the surface of substrate; 3. Thermal transfer from particles to substrate; 4. Solidification and contraction of particles; 5. Mechanical bond; 6. Local fusion [22]

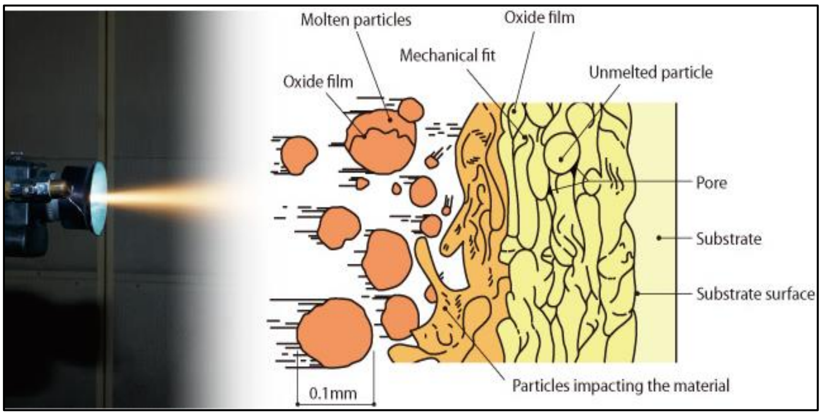

Figure 3 Coating formation by plasma spray [22]

3.2. Effects of porosity on the microstructure of a plasma sprayed coating

Porosity has direct impact on the plasma sprayed coatings. This can be advantageous if incorporated in the design [20] or deleterious if not [23]. 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 is also be affected by the nature of elements and the bonding mechanisms [24]. Mozhegov et al. [25], Ghasemi and Hamideh [19], and Jamali et al.[26] noted that splats structure and morphology, cracks morphology and size of porosity have a direct effect on adhesion and cohesion strength of plasma sprayed coatings. These factors have a base relation to the coating process parameters which need to be optimized to obtain a coating with desirable qualities. Gas entrapments in plasma sprayed coating influence thermal behaviour 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 [19]. It has been reported in other literatures [27-31] that the pores in nano-zone retards 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 [32-34].

Porosity level in plasma sprayed coatings significantly affects the density of the segmentation cracks [35, 36], it also affects the thermal diffusivity and thermal conductivity [37]. Increasing porosity in TBCs can decrease residual stress from thermal expansion mismatch between the substrate and ceramic[38]. Cernuschi F. et al.[39] argued that thickening of TGO led to crack propagation, which compromised the adhesion bonds between bond coat and the top ceramic coat.

3.3. Influences of spray parameters on plasma sprayed coating structure

Set spraying parameters for instance power, powder feeding rate, gas flow rate and distance between sputtering and base materials have great influences on the microstructure of the plasma sprayed coatings [23]. With increase in spraying power, the coating becomes more compact and the bonding strength also increases up to an optimal power. Nonetheless, too much power caused overheating of the previously deposited coating thereby compromising the quality by the introducing cracks and pores [40]. Critical plasma spray parameters (CPSP) [41, 42] as the quotient of input power (W) to the primary gas flow rate (nLPM) as well as the standoff distance (SOD) has effect on the final microstructure hence the porosity and wear resistance. CPSP and SODs are commonly used to quantify the spray powder temperature within the plasma flame region.

Increasing output power increases the plasma jet temperature which ultimately increases particle temperature[43], besides reducing primary gas flow rate increases particle in flight dwell time thereby increasing particle temperature. High particle temperatures ensures that the particles are sufficiently molted for uniform coating[44]. J.L. Sui et al. suggested [45] that the standoff distance directly affects melting of the feedstock particles. Long standoff distance, guarantees complete melting of feedstock hence uniformity in microstructure of the plasma sprayed coatings. Conversely, the already molten particles can re-solidify inflight if the standoff distance is too long. This could lead to non-melted particles being lodged into coating [46]. Shorter SOD occasioned fully molten and semi-molted particles which developed coating which were bimodal in nature[47]. Moreover, Y. Chen et al. [48] found out that porosity decreased with the spray angle but increased with the velocity of the gun scanning velocity. From the above, spraying parameters are crucial for the quality of coating in terms of microstructure, physical and mechanical properties of the end result component. Varying any of the plasma spray parameters has an effect on the coating quality and hence the percentage of porosity a coating has [42, 47, 49-54].

4. 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 (Pm), (b) pore density per unit area (PDm), (c) maximum pore diameter (Dm), (d) Equivalent pore radius (Rm), (e) Pore size and pore classification, (f) Pore analysis. The above constitute a pore system.

The models of evaluation and analysis can be broadly classified as the direct and the indirect methods. In 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 Fig. 4 can be applied in varying ranges from macro level to nano levels with others overlapping to complement.

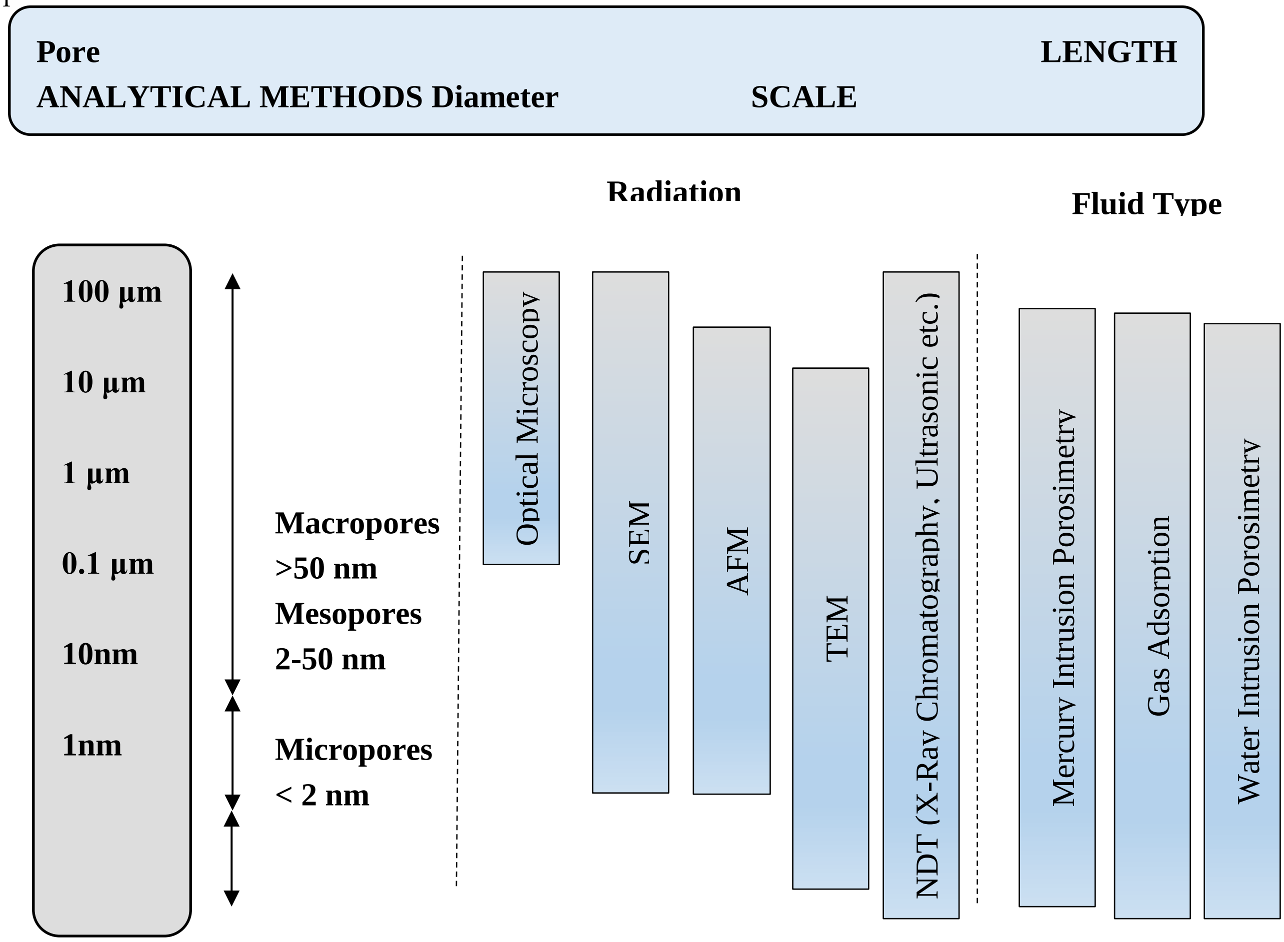

Figure 4 Methods used to determine porosity and pore size distribution (PSD), (Modified) [55]

Fig. 4 gives a summary of the most common methods for used in characterizing porosity on materials. They include: image analysis (of micrographs from SEM, AFM and 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.

4.1. Liquid intrusion

4.1.1. Mercury Intrusion Porosimetry

Mercury porosimetry can be used both in mesopores and macropores diameter analysis. It has been used for assessing surface area and particle distribution. Additionally, the information such as pore shape, network effects, skeletal and bulk densities can be obtained by mercury porosimetry. Fig. 5 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.

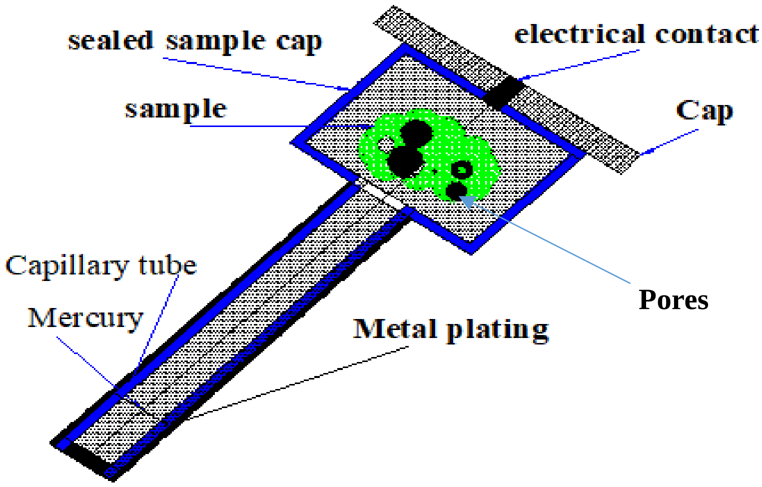

Figure 5 Cross-sectional view of a mercury penetrometer

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 0.0070μm [55]. 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[56].

$$Porosity\ (\%) = \frac{Vt}{Vb} \times 100 \qquad (1)$$

Where Vt is the total volume of mercury in the voids and Vb is the bulk volume of the sample. For volumetric distribution of pores 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 [57, 58]:

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

Where $\sigma\ is\ taken\ as\ the\ surface\ tension\ of\ mecrurcy, usually\ for\ pure\ mecrurcy,$
$484mN/m\ \ and\ \varphi$ 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)[59].

4.1.2 Water intrusion porosimetry

Water intrusion in hydrophobic materials have been suggested. Its use is based on the same principle as that of mercury intrusion [59, 60]. 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 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 [61].

4.2. Nondestructive testing (NDT)

Nowadays, NDT methods also have gained ascendency in evaluating and assessing the extent of porosity in plasma sprayed coatings. Methods such as magnetic particle testing, dye penetrant and

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eddy current methods have been used to assess cracks and integrity of materials, especially in the inspections of materials quality and integrity of structures. The specialized and developed techniques for example ultrasonic and X-ray testing methods are also in use. Parthasarathi et al. [62] 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. Table 1 shows the reliability concepts of each NDT method in application phase. Liquid penetrant is applicable to almost all kinds of engineering materials. It can be used to detect any surface defects like cracks and pores on the surfaces with limited penetration. It is an easy less time consuming method, thou limited when it comes to pore depth analysis and evaluation of pore orientation. Magnetic particle testing is applicable for both surface and subsurface defects with limited penetration. It is only applicable to ferrous materials. The method cannot be used where depth sizing and pore orientation is investigated. Eddy current can also be used to check defects on plasma sprayed coatings. It has an advantage over liquid penetrant and magnetic particle testing since both pore depth sizing and orientation evaluation can be achieved. It is applicable for electrically conducting materials. Radiography and Ultrasonic testing methods which have also developed with advancement in technology, are versatile and are applicable to every kind of material. The detection capability of defects including pores is volumetric. They are both applicable for depth sizing and orientation evaluation.

Table 1 Reliability of Non-Destructive Testing Methods

Properties	Liquid penetrant	Magnetic Particle	Eddy current	Radiography	Ultrasonic
Material applicable	ALL			ALL	ALL
Detection capability	Surface	Surface and Sub-surface	Surface and Sub-surface	Volumetric	Volumetric
Depth sizing	NO	NO	YES	YES	YES
Orientation Evaluation	NO	NO	YES	YES	YES

4.3. 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 200nm. 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[63] . 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[57].

Image analysis via microscopy provides direct measurement which does not require models or making additional assumption. 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 [24, 64].

5. 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 [65, 66]. Nevertheless, plasma sprayed chromium oxide coatings also suffer from porosity defects, which are considered to have negative impact on properties of coatings like hardness, strength, 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.[67, 68]. From earlier researches over the years, several ways of reducing porosity have been studied and other researches are still on going. Johanna Ekberg et al. [34] 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 heat treatment for the cases of coarser pores. They also suggested the use of finely-grained feed stock to reduce porosity. Ganvir A et al. [69] agreed with Johanna Ekberg that heat treatment caused microstructural changes such as densification, coarsening and grain growth . Other researchers [34, 37, 70], 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 a 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 % [38, 71-73] depending on the spraying technique, the material used or the skills of operation.

Currently many researchers have used following: (i) Multilayer coating [74, 75] (ii) Doping using other elements-Co-doping [74, 76-78] (iii) Nanostructured coating in (Multicomponent coating, Gradient coating, Nanocomposite coating, Super-lattice coating, Duplex coating, Adaptive coating) [8, 16, 30, 79].

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

5.1. 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 fig. 6. It has been used to reduce residual stresses to a large extent and inhibit the proliferation of cracks across a coating [74, 75]. Multilayer coating have a reduced grain size. Zhou et al. [80] 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 [81].

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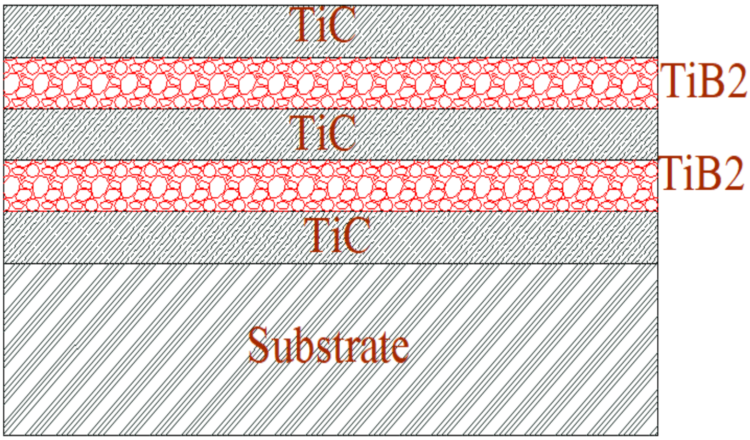

Figure 5 A representation of multilayer coating where two different coating materials are alternated.

The main merits of multilayered coating comes from the kind of layers exhibited by the coating. Multilayer coating can have various approaches. Interface layers; gives a transition from substrate to the following coat, usually providing for a 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 be consisted 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 the individual disadvantages. Thereby complementing each layer by improving on the stress concentration and reduction of chances of crack propagation through layers.

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 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 substrate [82-84]. Examples of elements that can be used in these cases are carbon, silicon and vanadium, which are mostly used for alloying.

5.2. 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. Fig. 7 shows a schematic representation of 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. [85] improved wear resistance of chromium oxide by doping modification and changing the microstructural scale of the coating. They used $\mathrm{CeO_2}$ and $\mathrm{Nb_2O_5}$ which also had improved effects on the porosity of coating [86]. From the above criteria, doping can also be used in densification of the top coat by the way of reducing the level of porosity. Yang et al. [8] noted that modification through doping, for instance $\mathrm{Cr_2O_3} - 3\%TiO_2$ and $\mathrm{Cr_2O_3} - \mathrm{Al_2O_3}$ not only improved wear resistance but also reduced porosity significantly. Sadri E et al. [87] and Leclerc C [88] in their investigation on self-lubrication by adding solid lubricants such as CaF2 and nano-Ag respectively, found out that there is a direct relations 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 [89-91].

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

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based and spinel coatings, when used for doping [77]. Some of the elements that can be used in doping of chromium oxide are cerium, niobium, silver, calcium, fluorine, titanium etc.

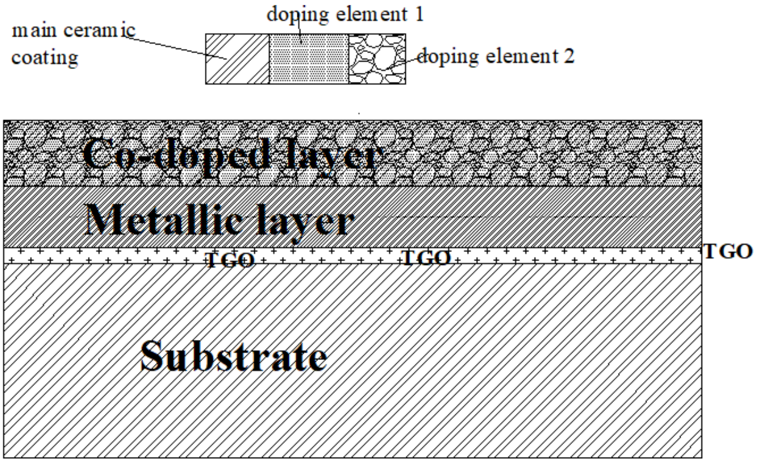

Figure 6 Schematic representation of codoping coating

5.3. Nanostructured coating

The microstructural length scale for nanostructured feedstock fall between 1-200 nm[92]. Nanostructured powder may cause agglomeration before they are used in plasma spray so, not all the particles are molten, which have 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 this special structures of sprayed coatings benefit the properties of nanostructured coating, especially the improvement of denser coating with better hardness surface and better strength [93-95].

From these previous work, it is evident that nanostructured materials produce better coating compared to the conventional ones [8]. 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 top coat using heat. This has been recorded by Jamali et al. [26] as a viable practice. They also agreed that nanoparticles resulted to a bimodal structure which improved bonding strength together with porosity network. Fig. 8 shows a representation of nanostructured coating. In nanostructured coating, there arise two kinds of powder. One that is fully molten and the other which is partially molten.

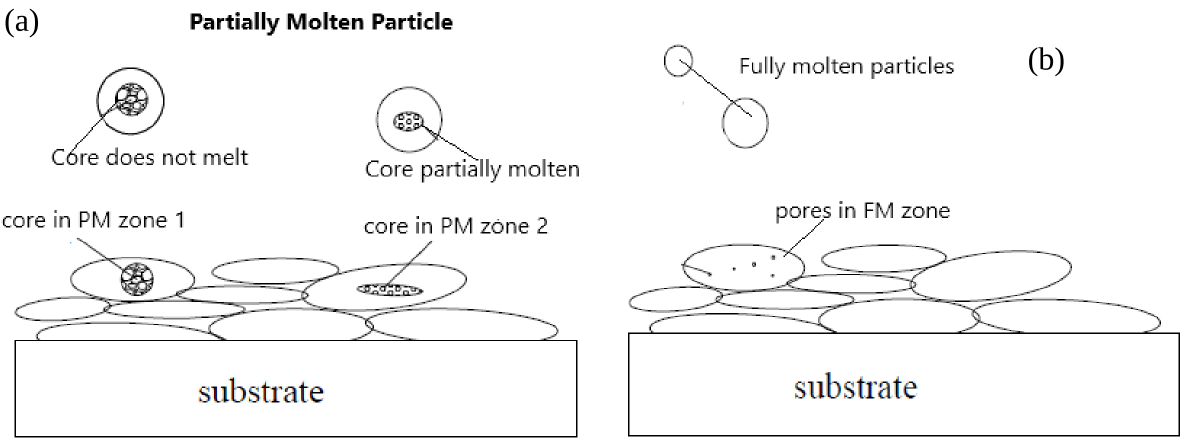

Figure 7 Schematic illustration of the creation mechanism of nanostructured coating with bimodal microstructure during plasma spraying of agglomerated nanostructured zirconia based powders. (a) Partially molten particles (b) Fully molten particles.

6. 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. Because nanoscale feedstock have 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 operation costs from consumable and machine parts configurations. Many research work is still needed to achieve optimal results.

7. Conclusion

In this work, the origin of porosity in plasma sprayed coatings are 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 solidifies and cools 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 determination of pore parameters. Also advanced NDT methods like X-ray micro-tomography and ultrasonic testing methods can be applicable. For most of the laboratory experimental works, SEM can be coupled with 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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