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Functionally Graded Thermal Spray Coatings: Methods, Parameters, and Post-Spray Treatments

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Abstract

Surface coating on metal substrates has remained a difficult challenge for researchers due to the conflicting requirements for different properties. In recent years, due to their mechanical, thermal, electrical, and tribological properties in many advanced engineering applications, functionally graded coatings (FGCs) have become fascinating materials for researchers worldwide to obtain coatings with specific requirements. FGCs are a novel type of traditional composites in which phases are not equally distributed to form a smooth gradient structure; thus, gradient coatings have shown a new research path.

The present paper tries to describe briefly major thermal spray techniques used to spray functionally graded coatings such as atmospheric plasma spraying, high velocity oxy-fuel spraying, suspension and solution precursor plasma spraying, and finally low and high-pressure cold gas spray methods. The examples of combined spray processes as well as some examples of post-spray treatment including laser and high temperature treatments or mechanical ones, are described.

Keywords: FGCs, Thermal Spray Coatings, Process Parameters, Post-Spray Treatment.

1. Introduction

In engineering applications, components require graded properties from region to region, particularly surfaces undergoing frictional, thermal, mechanical, and chemical, along with electrochemical interaction that harm components in the application [1,2]. This harm cannot be recovered unless the tribological and corrosion phenomena are controlled monitored [3]. In recent years, functionally graded materials (FGMs) have played a vital role in various engineering trends and applications due to their distinctive features through graded characteristics [4-6]. This graded behavior reduced the failure and increased the reliability of parts in many industrial applications [7,8].FGM involves mixing two different materials, which has various properties and volume ratio, in the form of layer by layer, as shown in Fig. 1a. FGM’s can be categorized into three forms, namely: surface coatings, bulk materials, and interfacial layers, as given in Fig. 1b [9-12].The surface coating typically involves one or double-layered, uniform piece-wise coating over the substrates [13,14]. These coatings undergo cracking due to their poor fracture durability [15,16]. Functionally Graded Coating (FGC) is introduced to overcome these traditional coating drawbacks by reinforcing bond cohesion, decreasing residual thermal stress, and significantly increasing resilience and fracture strength [17,18]. Metallic elements must be coated to achieve certain high-temperature conditions. Ceramic coatings provide a distinctive way to separate metallic materials and preserve them [19,20].

There are some benefits to using an FG-TBC as a substitute to link two separate substances, such as ceramic materials and metals, directly together. These benefits include softening of thermal stress distributions layer upon layer, reducing or removing stress levels, and adhesion strength of bonds. The detonation gun (D-gun) spraying method is an effective thermo-spray technique employed to produce excellent FGC structures. Multiple reviewers have addressed various fabrication processes; including thermal spray process (TS), sputtering process (SP), and electro-deposition process (ED) employed for duplex and graded coatings. Some of the main manufacture methods on fundamental principles are shown in Fig. 2.

2. Spray techniques used to deposit Functionally Graded Coatings

The thermal spray methods used frequently to obtain functionally graded coatings i.e., plasma spraying with solid and liquid feedstock, high velocity oxy fuel spraying and cold spraying. Thermally sprayed coatings can be obtained using a number of methods enabling different type of materials such as metals and their alloys and ceramics (mainly oxides and carbides) to be deposited. Also the composites of metal and alloys with ceramics are also very frequently sprayed [21]. Another group of materials, namely the polymer is also possible to spray and the deposits of thermoplastic polymers as poly-methyl methacrylate and fluoro-polymers [22].

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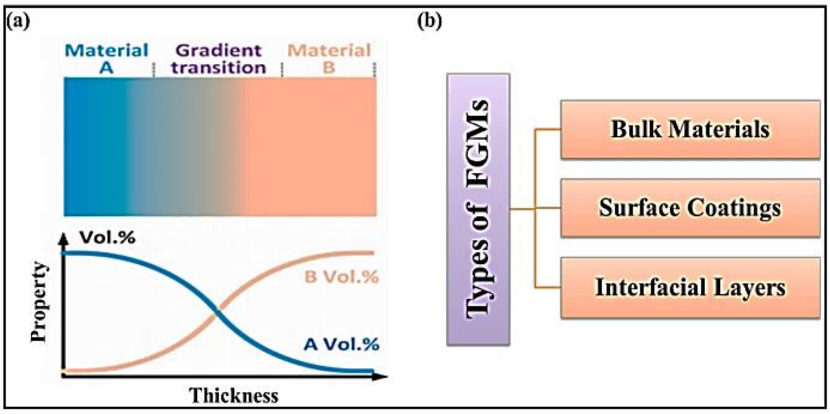

Fig. 1. (a) Basic concept, (b) Types of FGMs [10].

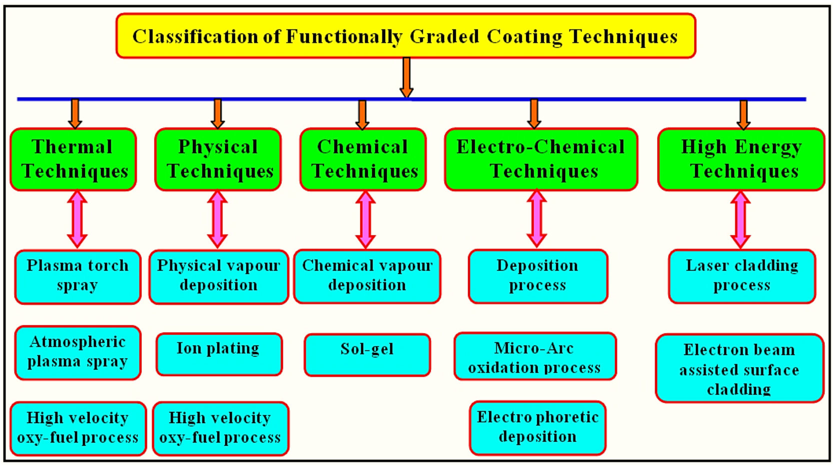

Fig. 2. Classifications of FGCs manufacturing techniques based on fundamental principles [11].

2.1. Atmospheric Plasma Spraying (APS)

There are many methods of coatings manufacturing on the field of TS. Among them, plasma spraying is one of the most frequently used, because of very wide range of applications and of reasonable cost of equipment [21]. The basic technique is atmospheric plasma spraying (APS). The sketch of the APS method is shown in Fig. 3. ([23]). The electrical arc is ignited between copper anode and thoriated tungsten cathode. Plasma gases are ionized, heated, and expanded forming the plasma jet. Then, the powder particles, being transported by a carrier gas, are injected to the hot stream of plasma jet, which are submitted to heating and to acceleration by drag force. Then, these particles hit into the substrate with relatively high kinetic energy and form splats. Finally, the splats solidify and build up the coating [21,24].

The fundamental process parameter is the composition of working gas composition. Two main groups of gases are used: (i) primary; and (ii) secondary ones. The primary gas is frequently argon (Ar) and sometimes nitrogen (N_2). The primary gas should stabilize arc inside the torch’s nozzle. The secondary gases are added to increase heat conductivity of plasma [21,25]. Other important APS parameters are as follows [26]:

- Electrical power;
- Flow rate of the plasma gases;
- Feed-rate of used powder and its size distribution (most frequently, the particles sizes are in the range from 20 up to 90 microns);
- Relative speed velocity of plasma torch with regards to the substrate [26].

Nevertheless, there are many other parameters, which influence also the coatings structure and properties. Therefore, their optimization is very important [27,28].

The appropriate choice of spray parameters should lead to melting of injected particles before their impact on the substrate. However, the powders include frequently small and large particles. The small powder’s particles may get molten in plasma and start to evaporate.

On the other hand, the large ones may remain solid. Generally, the powder is injected radially, with injection angle ranging from 75° to 120° with regard to the torch axis. The powders sprayed by APS method are most frequently oxide ceramics, such as Al_2O_3, TiO_2, Cr_2O_3, ZrO_2, Y_2O_3 as well as their alloys and their mixtures [29,30]. On the other hand,

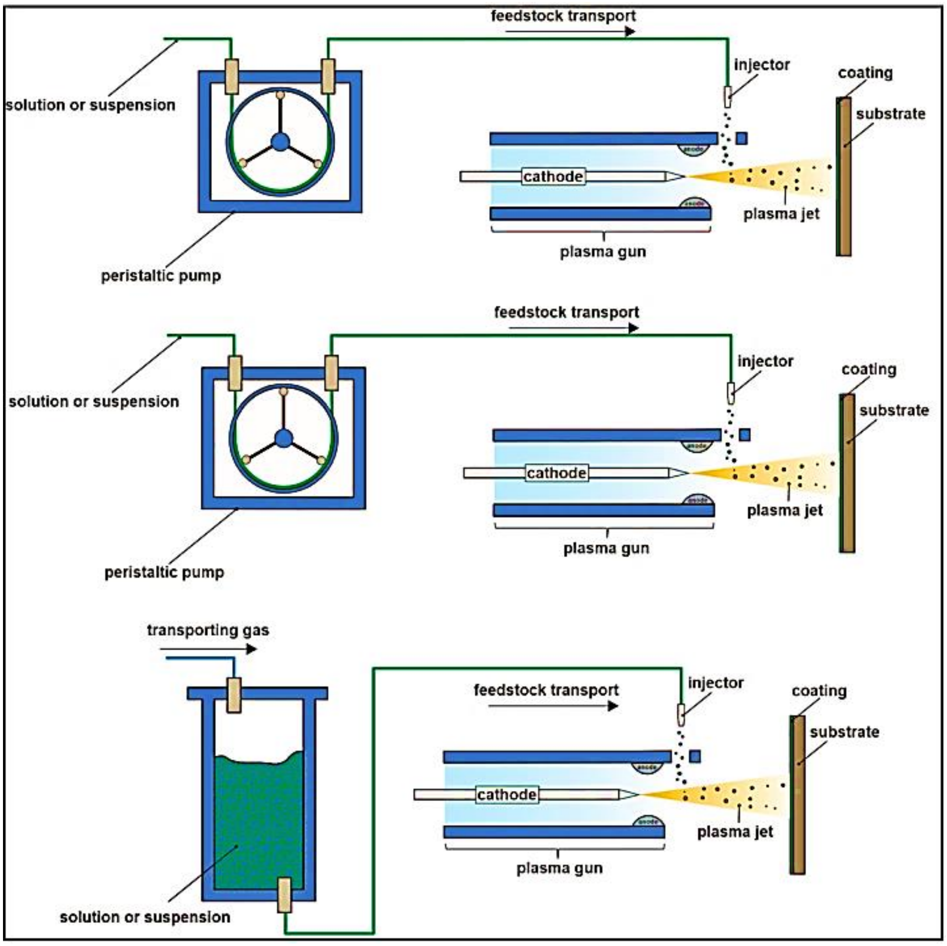

Fig. 3. Schematic representation of the plasma spray deposition processes: atmospheric plasma spraying (APS) (up) and suspension plasma spraying (SPS) and solution precursor plasma spraying (SPPS)-(down) [23].

some of non-oxides ceramics can also be sprayed by APS, namely carbides, nitrides, and borides [31]. Similarly, the cermet coatings can be APS deposited [32,33]. The typical adhesion strength of air plasma-sprayed coatings is in the range from 15 up to 30 MPa. When, the bond coat is used (such as Ni-Al or Ni-Cr or Mo), the adhesion is higher and may reach 70 MPa. APS coatings may be of low (a few %) or high porosity (more than 20%), depending on the processing parameters. Typical coatings' thickness is a few hundreds of micrometers [21].

2.2. Suspension Plasma Spraying (SPS)

One of the serious limitations of conventional, powder-based, thermal spray technologies is the processing of fine powders. Small particles of low density materials are difficult to inject into high-energy jet or flame [34]. This means that obtaining submicron/nano-grained coatings is also limited.

In order to overcome such problem, the innovative idea of using suspensions instead of dry powders [35]. The patent describes that fine solids may be mixed with appropriate solvent (usually water or/and ethanol) and shows the chemical agents necessary to formulate a stable liquid feedstock.

The main advantages of the suspension plasma spraying (SPS) technique, shown in Fig. 3., are as follows [23]:

- Feedstock transport from feeder to torch or gun is easy and may be realized under action of compressed gas pushing the liquid;
- Injection may be realized by atomized or continuous liquid stream (Fig. 4.), creating the possibility to influence the coating's microstructure;
- Fine powders may be more easily introduced to flame or jet in form of droplets;
- Solvent may provide some protection for fine particles against a direct contact with high temperature of flame or jet.

The use of SPS is advantageous for deposition of functionally graded coatings. The process offers the possibility to design the microstructure (Fig. 5.) for example:

Coatings may be extremely porous (even more than 50 vol.%) or very dense (1–2 vol.%) [36,37], depending on the phenomena occurring in the plasma jet (Fig. 6.) Pores may be of nanometer, sub micrometer, or even micrometer size, having various shapes and forms connected or non-connected networks;

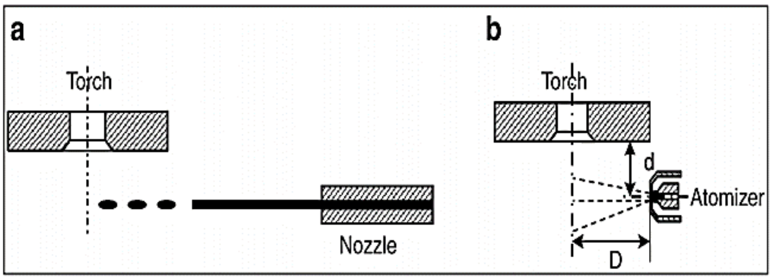

Fig. 4. (a) Injection of liquid using continuous stream, (b) Atomized stream [23].

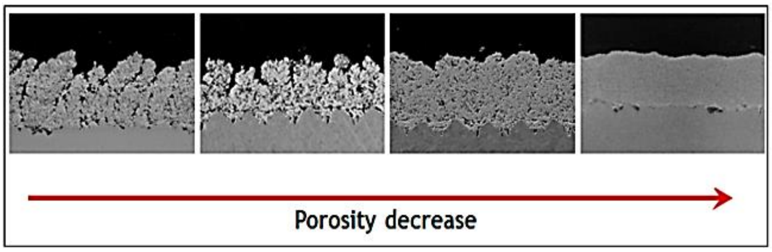

Fig. 5. Various microstructures of YSZ coatings produced by SPS [46].

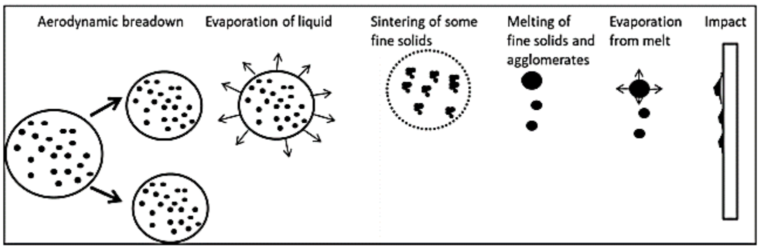

Fig. 6. Phenomena occurring after injection of suspension droplet into plasma jet [47].

- Morphology may vary from dense and homogeneous one, through vertically cracked up to fully columnar [36,37];
- Deposits may be formed by fully molten splats, sintered particles only, or by both as so-called "two-zones structures" [38];
- Roughness of coating's surface may vary in a very broad range [39];
- Thickness may be as low as a few micrometers and reach hundreds of micrometers [40].

Over the past years, many promising examples of using SPS technology in manufacturing functionally graded coatings were presented. One of the most studied topic in that field concerns bioactive coatings [41]. Cattini et al. [42] studied bioactive glass/hydroxyapatite (HA) functional coatings with various designs, namely: composite, duplex, and graded coatings. Tomaszek et al. [43] studied SPS titania-hydroxyapatite functionally graded coatings. In this design, the TiO_2 layer was used as a bond one on Ti-alloy substrate. Thermal barrier coating (TBC) is another example of functionally graded coating system that can be sprayed by SPS. Björklund et al. [44] described the possibility of using hybrid plasma spraying concept to avoid sharp interface between oxidation/corrosion-resistant NiCoCrAlY bond coating and thermally insulating 8YSZ top coating. The hybrid spraying consisted of the manufacturing of bond coating by APS and the top one by SPS. Wang et al. [45] proposed the concept of graded double ceramic insulation layer in which 8YSZ and $La_2Zr_2O_7$ coatings were deposited by SPS.

2.3. Solution Precursor Plasma Spraying (SPS)

The solution precursor plasma spraying (SPPS) allows manufacturing coatings with sub-micrometer and nanometer structures. Many coatings for different applications were sprayed by SPPS. The examples are: thermal barrier coatings (TBC) [48], coatings solid oxy-fuel cells [49], biomaterial coatings [50], photocatalytic coatings [51], coatings for gas sensors [52], environmental barrier coatings [53]. Both techniques, SPS and SPPS use liquid feedstock. Nevertheless, in SPS method, there are some solid particles suspended in liquid solvent. As the solids have small dimensions, the probability of their agglomeration at spraying is very high (Fig. 6). Also, the sedimentation of feedstock during storage can be a serious problem. These problems are negligible for SPPS method, which uses purely liquid feedstock. Such feedstock is suitable to obtain coatings with very fine microstructure [54]. The solution precursors are easier to obtain with high purity, without contamination occurring frequently at suspension preparation [55].

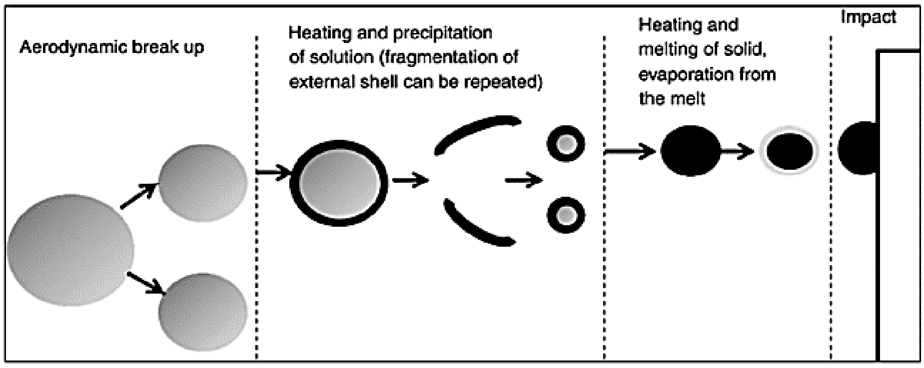

Fig. 7. Phenomena occurring in plasma jet during SPPS process [62].

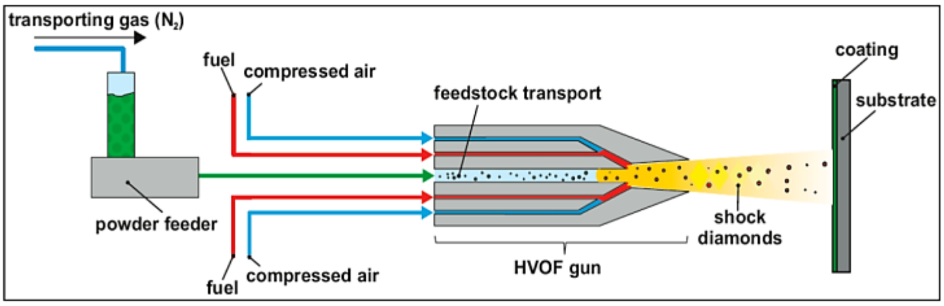

Fig. 8. Schematic of high velocity oxy-fuel spraying [21].

The composition of deposited coatings changes the initial feedstock [56]. This change is easy to carry out in SPPS technology. Consequently, it is possible to enlarge the area of thermal spray applications [57]. Another important technological advantage is the possibility of using conventional plasma spray equipment. Also, the solution feeder in SPPS can be the same as suspension feeder in SPS [58]. The precursors used to spray are generally the mixtures of compounds, such as salts, acetates, or nitrates. The mixtures are dissolved in a solvent to form final solution.

The solvent is frequently an organic liquid or/and water. It should be stressed up, that the mixing of the precursors occurs on the molecular level [59]. The schematic presentation of SPPS set-up is shown in Fig. 3. There are many process parameters that influence the coatings microstructure and properties. The phenomena occurring at SPPS process are shown in Fig. 7. Recently, the hybrid processes of thermal spraying were studied. There are two possible hybrid processes which include solution precursor plasma spraying, namely: (i) APS and SPPS shown by [60]; and, (ii) SPS and SPPS [61]. These processes take a profit from the advantages of both methods for new applications.

The SPPS method is a novel process that allows manufacturing a nanometer-scale coating, which results in many interesting functional properties impossible to reach in APS-deposited coatings. The advantages of this method are: pure feedstock with controlled chemical composition and different coating’s microstructure adapted to application [62].

2.4. High Velocity Oxy-Fuel and High Velocity Air-Fuel Spraying (HVOF and HVAF)

HVOF (high velocity oxy-fuel) and similar processes such as HVAF (high velocity air fuel) (Fig. 8.) or HVSFS (high velocity suspension flame spraying) use gas combustion as energy sources for melting and accelerating powder particles.

The HVOF process enables reaching higher particles velocity and lower particle temperature than APS. Consequently, the process is characterized by high deposition efficiency, good adhesion of coatings, which have low content of oxides and low porosity [63].

In spite of relatively low deposition temperature, the thermal stresses are still present in the deposited coatings. This is the main reason for applying functionally graded coatings, FGC [64].The FGC enables gradual change in coefficient of thermal expansion (CTE) and in Young’s modulus which decreases stress level and increases bond strength. The FGC are particularly useful in reducing thermal stresses in thick deposits [64]. Hardness and ductility are the HVOF coatings properties which are often tailored to avoid the brittle breakup of coating’s spallation [65]. The FGC may be obtained by:

(i) Using premixed powders or (ii) co-injection of different powders [66].

The co-injection of different powders seems to be more beneficial because the spraying process is continuous and the effort of powder preparations is reduced.

Different ways of simultaneous powder co-injection are feasible such as e.g., the use of: (i) commercial twin powder feeder; (ii) two differences between the injected powders, it is possible to vary the location of powder injector with regard to the torch [67]. Among the parameters influencing the deposition of FG, the most important are spray distance and working gases (fuel and oxygen) flow-rate [68]. The coatings quality can be controlled by the control of the particles in-flight temperature [69].

Moreover, in case of FGC it is suggested to control the powder with the lowest melting point in order to avoid excessive evaporation [70].

Hydroxyapatite coatings are usually deposited using APS. However, HA decomposes at high temperature deteriorating the coatings properties.

As the temperature of the HVOF flame is lower than that of plasma jet, it may be considered as a promising alternative for APS. The technical solution would be an application of FGC to avoid stresses and the failures at the interface HA coating – Ti substrate [71].

The HA/TiO_2 graded coatings on Ti implants seem to be a possible system to reduce the: (i) Mismatch of CTE values and resulting thereof temperature gradients between the HA coating and Ti substrate; and, (ii) risk of ions diffusion from the substrate to humane body [71].

2.5. Low Pressure Cold Spraying and High Pressure Cold Spraying (LPCS and HPCS)

A main advantage of cold spraying is the low processing temperature compared to other thermal spray processes [72]. Instead of high thermal energy, the kinetic energy of gas is used to deposit powder particles, which deform the substrate [73]. The low gas temperature in cold spraying has some advantages, such as reduction of oxidation at spraying [74], avoiding of phases transformations, and reducing coating porosity [75]. The compressive stresses resulting from peening effect at impinging of solid particles enable deposition of many different metals and alloys [76].The high kinetic energy at impact with substrate results from very high particles velocity. The particles are accelerated by working gas, as nitrogen, helium, or air, to reach the supersonic velocities. The working gases are pushed through de Laval type nozzle of the gun. The initial pressure of working gas enables categorization of cold spraying method as: (i) high pressure cold spraying, HPCS (gas pressure > 1 MPa); and, (ii) low pressure cold spraying, LPCS (gas pressure < 1 MPa). HPCS (Fig. 9.) uses usually nitrogen or helium as the working gas.

A stream of carrier gas passes through a powder feeder and transports powder to the gun. The powder is injected axially into the gun’s nozzle. The working gas is heated before reaching the nozzle. The heating leads to an increase of the powder particles temperature which favors plastic deformation of particles upon impact. LPCS (Fig. 9.) operates with nitrogen or air supplied by a compressor. The gas is also heated prior to arriving to the gun. The powder is injected radially to the gun’s nozzle. The LPCS installation is much cheaper in equipment price and processing costs than the HPCS one [77]. On the other hand the sprayed particle reaches much lower velocity than that in HPCS installation. Therefore, the application of LPCS is significantly limited to deposit the easy-plastic-deformable materials such as tin, zinc, copper, aluminum, and nickel. The deposition of composites as the cermet’s is also possible and becomes increasingly frequent [78].

One of the current trends in cold spraying is the manufacturing of multi-coatings as FGCs in additive manufacturing [79]. The FGC obtained by cold spraying use a mixture of: (i) different metal powders; or, (ii) metal with ceramic powders. The mixtures can be prepared by (Fig. 10.): (i) mixing of powders, (ii) mechanical milling followed by agglomeration and by sintering; and, (iii) powders cladding. The mixing of powders having particle size of -50 + 5 µm is the most popular feedstock preparation method in cold spraying [80].

The HPCS enables better coatings properties to be achieved. On the other hand, the LPCS is the cheapest method enabling cermet coatings to be obtained. Therefore, a lot of recent studies deal with deposition of metal matrix composites (MMC). The MMCs coatings can have various applications. Their frequent function is regeneration of surfaces [81], electrical conductivity [82], corrosion resistance [83], wear resistance [84], biomedical [85], etc. These coatings combine elevated wear-resistance, machinability, and reasonable thermal conductivity. A low cost of technology makes it an attractive alternative to deposition of the complex and expensive alloys. The composite powder mixtures can be used in both HPCS and LPCS.

Many reports show advanced technology of functionalization of the coatings sprayed using mechanically alloyed powders.

This powder production technology enables introducing the crystal refinement strengthening effects in the composite powders. Cold spraying enables preserving these small crystal sizes in coatings. The contributions of the strengthening mechanisms including work hardening, dispersion strengthening, and crystal refinement enabled increasing the hardness of cold-sprayed coatings [86].

2.6. Post-Spray Treatment

The as-sprayed coatings need frequently a treatment after deposition to meet the specifications. The treatment can be useful in: (i) obtaining the final dimension; (ii) improving the properties (especially wear-, corrosion resistance, and adhesion strength);

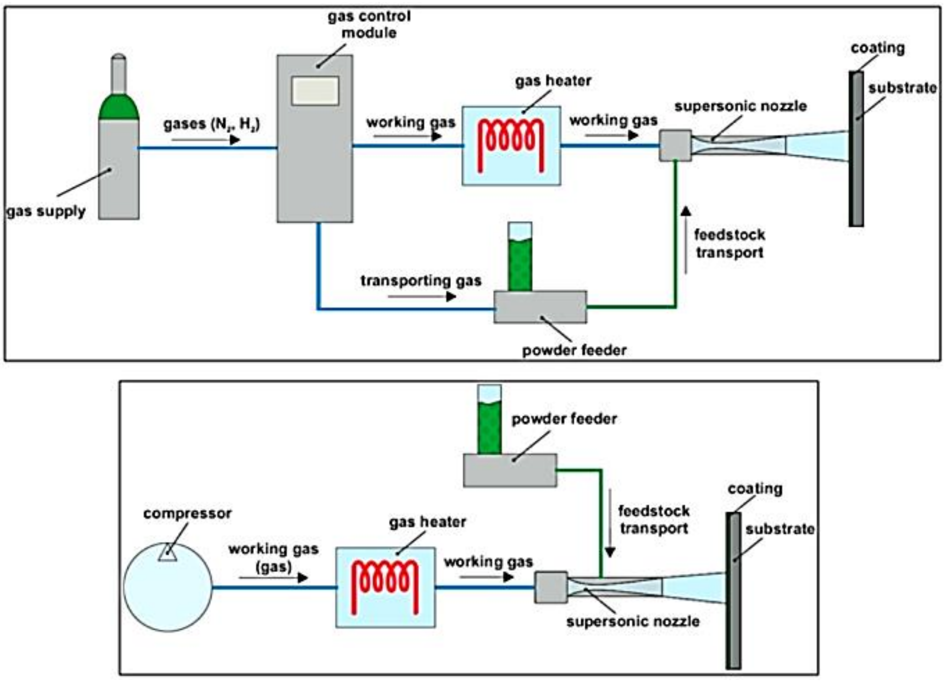

Fig. 9. The schematic and principle of high (up) and low-pressure (down) cold spray systems [77].

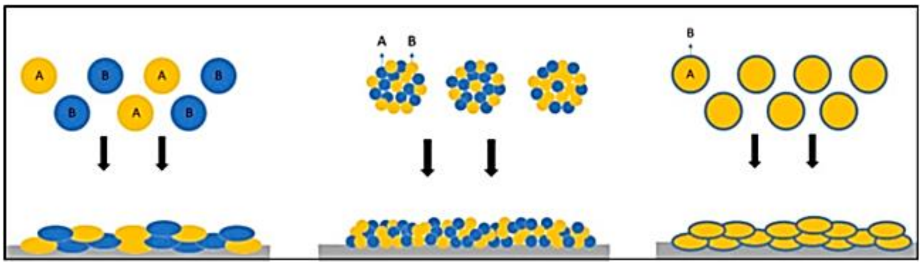

Fig. 10. Methods of powders preparation in composite coatings deposition: mixture of powders (left), mechanically blended powders (middle), and cladded powders (right) [79].

(iii) modifying coatings' microstructure (decrease porosity level and increase homogeneity); (iv) reducing the residual stresses or oxide content; and, (v) polishing the coatings' surface. Generally, post-spray treatment can be mechanical, physical (including heat treatment), and chemical. There are also combined processes [21].

2.6.1. Mechanical Treatment

The mechanical post-spray treatment is applied in order to obtain specified coatings thickness and to reduce the surface roughness. The processes, which can be applied, are turning, grinding, polishing, and lapping. The choice of treatment's technique depends mostly on coating material. The mentioned mechanical post-spray treatments are most frequently used to reduce the roughness of as-sprayed deposits which improves also their tribological properties [87].

Another important method is shot peening. This treatment is used in order to improve the fatigue resistance of coatings. It generates compressive stresses at their surfaces. Also, it allows closing the open porosity and flatten coating's surface. Similar treatment is rolling [88].

2.6.2. Heat Treatment

The post-spray heat treatment is carried out mainly in furnaces under the operating temperature lower than the melting point of the coating material. During such type of treatment, diffusion and stresses relaxation take place. The first one may result in the improvement of the bond strength and in enhancing the inter-particle cohesion in coatings.

The latter improves their wear and corrosion resistance. Moreover, the heat-treated coatings may become more ductile and may have greater fracture toughness and elastic modulus.

On the other hand, the hardness of heat-treated coatings decreases and crystal grains grow-up. It is possible to carry out the heat treatment under controlled atmosphere or in vacuum. Other type of the heat treatment is remelting the sprayed coating [89]. The remelting of coatings can be carried out using: laser beam [90], electron beam [91], and, electric arc [92].

2.6.3. Chemical Treatment

The most frequent goal of chemical treatment is to close open porosity in as-sprayed coatings. The impregnation is a useful method. The impregnation consists of application of liquid sealants, which penetrate inside the coating by capillary actions, fulfilling the pores and solidifying thereafter. The sealing protects coatings and substrates against actions of corrosive media. There are three methods of impregnation, depending on the applied sealant pressure: low-pressure, atmospheric, and high-pressure. It is also possible to combine these methods [21,26,89]. The sealants may be organic [93] or inorganic [94].

2.6.4. Physical Treatment

There are two methods belonging to physical treatment: physical vapor deposition (PVD) and ion implantation [95]. The improvement of the coating's properties was slightly greater at ion implantation.

However, this treatment is more expensive than the PVD one [95].

2.6.5. Combined Treatment

Hot isostatic pressing (HIP) combines two treatments by using simultaneously high temperature and high pressure (up to 300 MPa). The temperature of treatment depends on material type being in the range of 0.7 to 0.8 × Tm. This treatment is carried out in vessels under the inert atmosphere, mostly in argon [21,26]. The HIP allows improving adhesion strength as well as corrosion resistance of the coatings. Moreover, it may enhance fracture toughness and reduce the residual stresses. Nevertheless, this treatment is limited in application to rather small sized pieces and is relatively expensive [96]. The HIP treatment is used mainly for ceramic and cermet coatings [97] and less for alloy ones [98].

Another combined process, in which temperature and pressure act simultaneously, is spark plasma sintering. The temperature is up to 1800 K and pressure up to 50 MPa, being lower than in HIP process. The principle of spark plasma sintering bases on the Joule effect caused by electronic and ionic conduction. The main advantage of such sintering is short treatment time, being shorter than that of HIP. The size of the treated piece is limited [21,96]. The spark plasma sintering treatment is used for ceramic, cermet, and composite coatings [99].

3. Conclusion

The functionally graded coatings are an important part of thermal spray technology evolution. The FGC enables better association of different materials serving as coating and as substrate. This evolution is carried out on more or less conventional way. The conventional way includes spraying of multi-coatings using mixtures of powders or injecting them separately. The emerging methods include e.g., the hybrid technologies which use different feed-stocks such as e.g., powder and suspensions or suspension and solution.

The paper briefly reviews the application of functionally graded coatings obtained by thermal spray technology. Initially, the conventional thermal spray techniques such as atmospheric plasma spraying (APS) and high velocity oxy-fuel (HVOF) were described. Then new processes such as suspension and solution precursor plasma spraying (SPS and SPPS), and finally low and high pressure cold gas (CGSM) spray methods were shown. Some examples of post spray treatment of coatings used to improve the coatings' properties were described.

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