

THERMAL SPRAYING

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Summary

In this chapter, the thermal spraying processes are reviewed. History of thermal spraying, advantages, disadvantages and application are described. The basic principle of thermal spraying process and the way of coating formation are then presented emphasizing the lamellar structure with porosity and oxide inclusions. The following thermal spraying processes are then described: powder flame spraying, wire flame spraying, high velocity oxy/air fuel spraying, detonation spraying, flame spraying and fusing, plasma spraying, arc spraying, laser spraying, molten bath spraying, cold gas spraying and electromagnetic powder deposition. For thermally sprayed coatings, beside good wear and corrosion resistance there is also a need for a good coating/substrate adhesion and reduced level of residual stresses. Therefore, the previously mentioned

properties are also described. Finally, it was concluded that the thermal spraying processes are of great interest in almost all industrial fields. In the recent years, a lot of effort is put into the investigation of thermal spraying and its application in biomedicine.

1. Introduction

Thermal spraying is a deposition technique where a spray of molten particles is directed to the part to form the coating. It is used for the protection of new parts against wear, corrosion and high temperatures thus improving the properties of engineered surfaces. Thermal spraying processes are also applied for repairing damaged and worn parts. Sometimes the thermal spraying can be applied for the decoration thus improving the esthetic properties of parts. Coating material can be either in wire, powder, rod, cord or molten-bath form. By the thermal spraying process relatively thick metallic, polymer, ceramic and composite coatings can be deposited. Operations of the process can be manual, mechanized and fully automated. History of thermal spraying, advantages, disadvantages and application are further described. Thermal spraying was mentioned for the first time in the patents of the Swiss engineer Max Ulrich Schoop (1870-1956) at the beginning of the 20th century. He came to realize that a stream of molten particles colliding with each other can form a coating. In 1909 Max Ulrich Schoop applied for a patent called "Powder metal and wire-flame spraying". At first the lead and tin wires molten in the flame produced by burning acetylene in oxygen were used as coating materials. Only some time after that the powders started to be used. Max Ulrich Schoop also patented the wire arc spraying process in 1911 by which the deposition of a greater number of metal coatings was made possible. In 1917 he was awarded a prestigious John Scott Award for "Schoop's Metal Spraying Process". The award was established in 1822. Max Ulrich Schoop has been inducted to the Thermal Spray Hall of Fame in 1994 "for his landmark contributions as the inventor of the thermal spray process and the subsequent refinement and expansion of thermal spray technology to provide the foundation for the modern thermal spray industry". The biggest advantage of some thermal spraying processes over other deposition techniques lies in the fact that coatings can be deposited at the place of exploitation of a certain part - portability (on site repairs) (for example bridge repairs, off-shore objects) and that their application is not limited by the size and shape of the component the coating is being deposited on. Relatively thick coatings (up to 10 mm) can be obtained at low deposition costs. There is no considerable influence of thermal spraying process on substrate microstructure and substrate distortion, since the temperatures at the substrate/coating interface are between 100 and 300 °C. The molten or partly molten coating material particles do not melt the substrate material on impact but the surface becomes only slightly heated. The exception is the thermal spraying process with simultaneous or subsequent fusion where the high fusing temperatures significant affects the substrate properties. Among disadvantages the main one is a relatively low coefficient of efficiency of the coating material (deposit or spray efficiency) and a rather loud noise, dust and fume during the process. This affects human health. Today there is a wide range of spraying processes and coating materials that can be deposited so that the thermal spraying technique has found its application in almost all industrial fields (power generation, paper, textile, graphic, wood, glass, steel, chemical, automotive industries, agriculture, airplane engines,...). It is of particular importance to mention the increased use of the thermal

spraying process in biomedicine and an experimental application of thermal spraying not only for the formation of coatings but also for the manufacture of complex three-dimensional parts. There are so called biomedical coatings sprayed on the implants in human body. The most often titanium, titanium base alloys, cobalt base alloys and hydroxyapatite coatings are applied. On the eve of its hundredth anniversary, the thermal spraying process is widely used and enabled many technological advances to the industries all over the world. In the recent years many variants of thermal spraying processes have been developing.

2. The Basic Principle of Thermal Spraying

Thermal energy produced by combustion or electrically is applied for heating and melting of coating material (also called consumable, feedstock material, feed material, spray material, surfacing material, raw material). From the spray torch (spray gun, pistol), the molten or semi molten (plastic) particles (droplets) are then accelerated, propelled and deposited on the prepared substrate, forming the coating. Molten particles get kinetic energy usually due to the pressure of atomizing or combustion gases. Besides the term coating, different terms are used. For example: coat, layer, deposit, overlay or sprayed material. The term multilayer coating is also used as well as overlay coating. Besides the term substrate, the term base material is also used, but more rarely. Scheme and photography of thermal spraying process is presented in Figure 1.

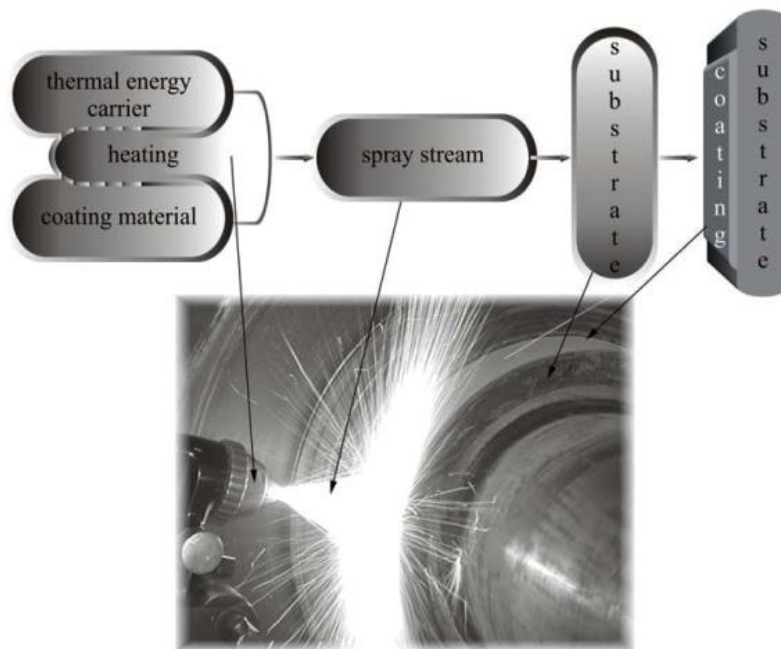


Figure 1. Scheme and photography of thermal spraying process

3. The Structure of Thermally Sprayed Coatings

The immediate result of the impact of molten or semi molten particles onto a substrate surface is the flattening, cooling and solidification of the particles to form a coating, most often of *lamellar structure*. Lamellar structure is layered, sandwich like structure.

This kind of structure is resulted by the deposition of successive layers. The flattened particles (splats) are disc shaped. Lamellar structure is not isotropic, with properties being different parallel to substrate from transverse across the coating thickness. The structure of sprayed coatings is not homogenous but heterogeneous due to the variations in cooling conditions of individual particles on impact. Because of short cooling time as well as different temperature, size, shape and velocity of particles, it is not possible to ensure the same conditions for all particles. The substrate temperature and material also affect the cooling conditions. According to that fact, it is very difficult to predict the properties and the structure of thermally sprayed coatings which are quite different than (from) the structure of wrought or cast materials of the same chemical composition. Some particles can be unmelted and they influence on creating of voids without particles. It causes *porosity*. All thermally sprayed coatings contain some porosity. Porosity is very common for thermally sprayed coatings and depends on impact energy (influenced by particle velocity), spraying angle, particle temperature and size. Ceramic coatings are characterized by the open porosity, so the sealing or impregnating treatment is often applied to improve the corrosion properties. By the increasing of particle velocity, the porosity is decreasing. Figure 2 shows the process of coating formation.

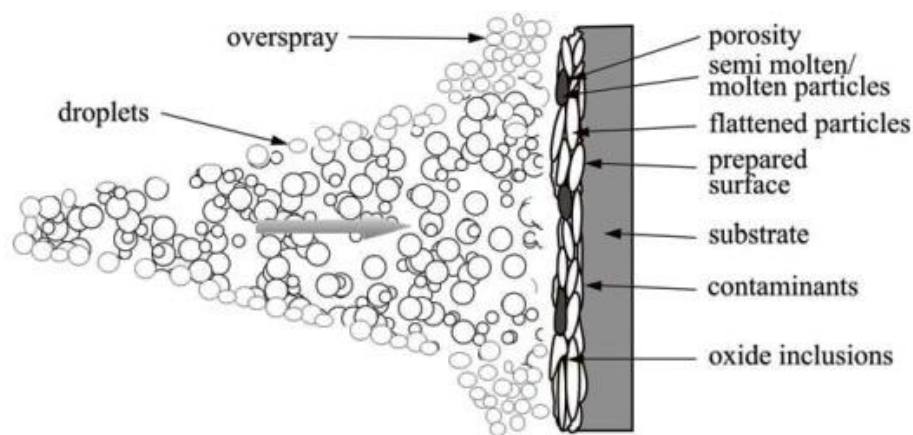


Figure 2. Basic scheme of coating formation

Apart from porosity, *oxide inclusions* are also present in thermally sprayed coatings. Oxide inclusions in a coating generate due to the oxidation of molten particles on their way to the substrate and due to the oxidation of previously solidified flattened particles on the substrate. While the sprayed powder particles move towards the substrate they melt but also react with air. The particles oxidize over their surface forming an oxide shell. The turbulent flow of the molten particles causes oxide shell crack so that the oxide is redistributed along the whole volume of the molten particle. While flattening on the substrate surface the upper parts of the particles are exposed to the atmosphere rich in oxygen so that oxidation occurs even after the particles impact onto the substrate surface. There are some disadvantages of the presence of oxide inclusions. Metal coatings of dissimilar structure with metal and oxide phases can be exposed to degradation at elevated temperatures due to different thermal expansion coefficients of metals and oxides. Carbide coatings can have a reduced amount of carbides due to oxidation, thus reduced wear resistance too. Generally, the coatings with oxide

inclusions are difficult to be machined. The level of oxidation is lower if the thermal spraying operations are performed in protected atmosphere or in vacuum. During the impact and very fast solidification of the sprayed particles, mechanical bond between the substrate and the coating most often is occurred. Mechanical bonding occurs mainly if the temperatures involved at the substrate/coating interface are low. This kind of bonding is characteristic of ceramic coatings. Spraying and fusing process is performed at high temperatures and a stronger metallurgical bond (also called diffusion bond) between the coating and the substrate is forming. Chemical reactions and sometimes partial melting of the substrate/coating interface are possible, too. The quality of sprayed coatings will depend on the coating/substrate *bond strength* (also called adhesion strength). Factors affecting bond strength between the substrate and the coating are as follows: the substrate preparation, surface area, applied thermal energy, velocity of molten particles (kinetic energy) as well as properties of the substrate and coating material. Bond strength is increased if the substrate material is made rough by grit blasting (blasting material is sand, steel, slag, ...) or by rough thread machining, etc. The surface area is thus enlarged which in turn increases the coating bond strength. Therefore, careful substrate preparation is necessary so as to remove contaminants, moisture, corrosion, grease etc. Apart from chemical cleaning and degreasing, the substrate surface has to be roughened to ensure good adhesion. After that the spraying procedure must be conducted as soon as possible to prevent the substrate from getting contaminated again. In some cases the substrate is heated to remove moisture. De-bonding will occur when the stresses acting are higher than the bond strength between the substrate and the coating. Generally, adhesion of coatings is estimated as the stress required to de-bond the coating from the substrate, i.e. the resistance of the substrate/coating system to the failure at the coating/substrate interface during practical application. Bond strength is measured by the ASTM C633 standard– tensile adhesion test. If the failure or de-bonding occurs at the substrate/coating interface it is known as adhesive failure while the failure occurring in the coating is known as cohesive failure. In Figure 3, light optical microphotography of cohesive failure of NiCrBSi coating on carbon steel substrate, is shown.

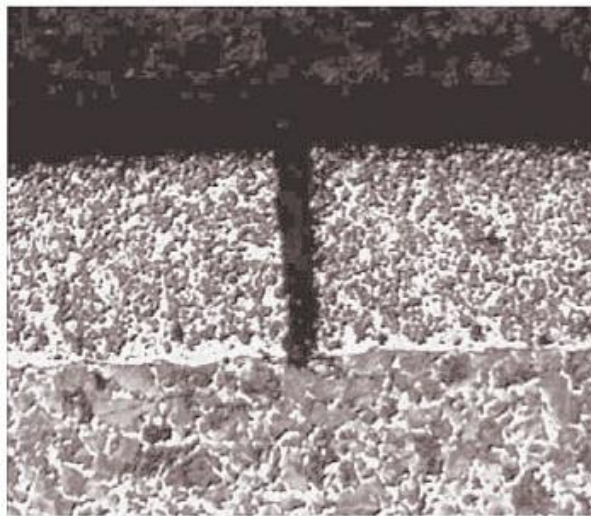


Figure 3. Cohesive failure of NiCrBSi coating on carbon steel substrate (Longitudinal section of the sample, 120x magnification, nital etched)

It can be concluded that the structure of thermally sprayed coatings is very complex. The structure is mainly lamellar with the great amount of porosity and oxide inclusions. Therefore, the significant effort is directed to increasing of particles velocity and decreasing the porosity. Conclusion can also be made that the structure and properties of coatings cannot be the same for the same chemical composition of coating material, but obtained by different thermal spraying processes.

4. Thermal Spraying Processes and Applied Coatings

The thermal spraying technology can be divided into several processes that differ according to the thermal energy carrier (source) and the respective kinetic energy of the sprayed particles. Flame spraying is the oldest thermal spraying process patented by the above mentioned engineer Max Ulrich Schoop. Different variants of flame spraying are developed. Arc spraying is also patented by Max Ulrich Schoop. Plasma spraying is later developed as well as many other thermal spraying techniques. Metallic, ceramic, polymer and composite coatings can be obtained by thermal spraying. Among metallic coatings pure metallic and metal alloy coatings can be deposited mostly for the protection against wear, corrosion and high temperatures and as bond coats. Most important metals are molybdenum, titanium, nickel, copper, chromium, zinc, tungsten, copper, tin, aluminum. Cobalt, iron and nickel based hard alloys (MCrAlY alloys, where M is standing for Co, Fe or Ni) are used very often in thermal spraying processes. These alloys are highly resistant to high temperature corrosion and oxidation. Aluminum bronzes are also used and applied coatings are characterized by good machinability. Self-fluxing (also called self-fusion) alloys represent a complex Ni-Cr-B-Si-Fe-C system. These alloys have high wear, heat and corrosion resistance due to hard phases (carbides, borides, silicides) and presence of chromium. Due to the presence of boron and silicon these alloys have self fluxing properties i.e. good viscosity. These alloys are mostly applied by flame spraying with fusion.

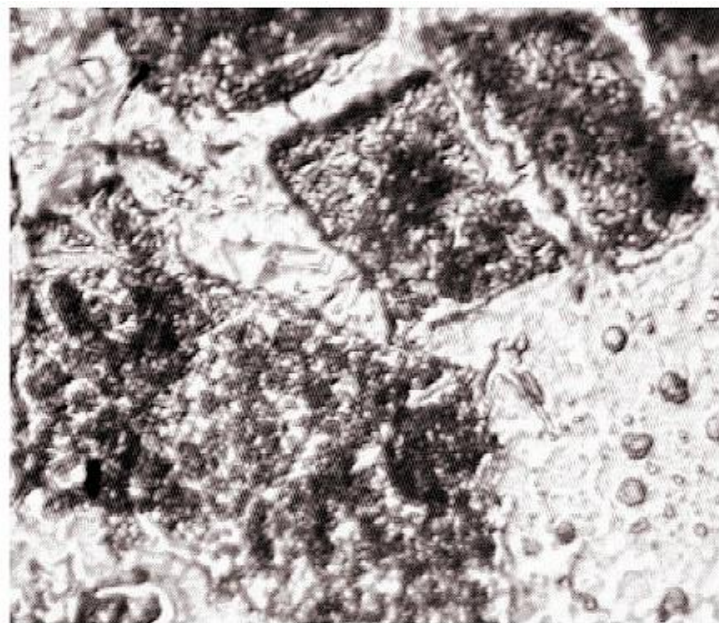


Figure 4. NiCrBSi coating with the coarse hard WC particles, 450 x magnification

Composite coatings (also called blends or mixtures) are also in use. Figure 4 shows light optical microphotography of composite coating produced by the flame spraying and fusing of NiCrBSi matrix powder mixed with tungsten carbide WC particles as hard phases (black rectangular shapes, Figure 4).

Ni matrix is tough and WC particles are extremely hard (micro hardness is approximately 2000 HV_{0,1}), so obtained coatings have excellent resistance to abrasive wear. The open porosity (Figure 5) and very poor machinability (grinding) are the main disadvantages of these coatings. Open porosity is the characteristic of the ceramic coatings, too.

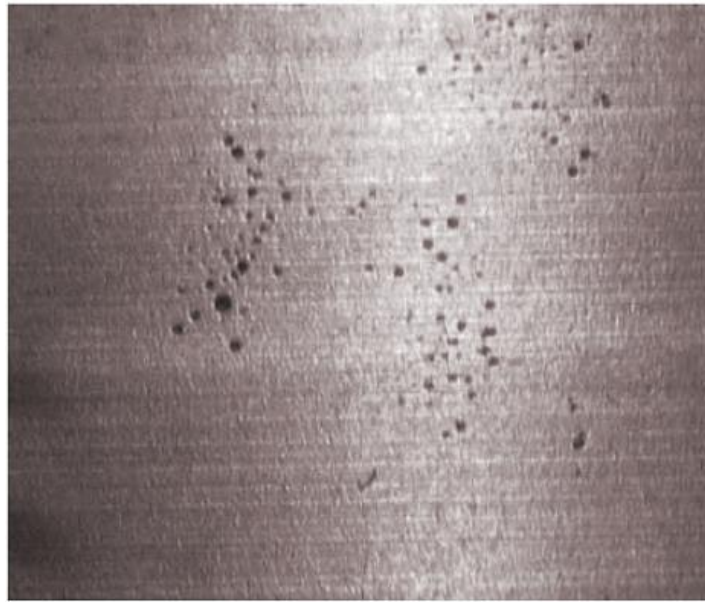


Figure 5. Open porosity of NiCrBSi coating with the coarse WC particles

Due to their high hardness, good chemical and electrical properties as well as thermal stability ceramic (oxide) coatings are widely used as thermal barrier coatings (abbreviation TBC is used) and coatings resistant to wear and corrosion. The most widely used are aluminum oxide Al_2O_3 (alumina), aluminum oxide and titanium oxide $\text{Al}_2\text{O}_3+\text{TiO}_2$, zirconium oxide ZrO_2 , and chromium oxide Cr_2O_3 , due to high hardness and chemical resistance. Ceramics have high melting point. Therefore, the thermal spraying processes with high temperature producing possibility are applying for the deposition of ceramic coatings. Generally, ceramic coatings have a high porosity level (even open porosity) that can be decreased by the subsequent treatment. The porous layers are sealed by polymer or metallic dense coatings to improve their corrosion resistance. Sometimes the porosity problem is solving by the laser re-melting of the coating surface. In order to achieve satisfactory bond strength and to compensate the substrate/coating coefficient of thermal expansion mis-match, the substrate materials are roughened and lined with a bond coat (for example NiCr, NiAl, Mo, Ni, MCrAlY). Polymer coatings are being increasingly used to improve the resistance to corrosion and wear, to reduce friction, for bioactive surfaces, electrical insulation and for decorative purposes. The thermal spraying of polymers has the following advantages over the other polymer deposition processes: no solvent is necessary, large surfaces can be coated in

almost any environment and the application of a high viscosity molten polymer is also possible. This is particularly important for high viscosity polymers and polymer composites with a high amount of hard phases. The thermal spraying of polymers does not require solvents since the coating materials are in the form of powder. Due to the high kinetic energy of spraying processes, the powder particles need not be completely molten to be able to expand on the substrate surface. Polymer coatings can also be used as bond coats when non-polymer coatings (Cr_2O_3 , WC/Co) are deposited on substrates. By the addition of strengthening agents (mineral, organic or metal) *polymer composites* are obtained with improved mechanical properties. The objective is to develop magnetic polymer composites (with the addition of ferrite) to be applied in the aircraft, automobile industries and in electromechanical devices. The composite polymer/high temperature alloy coating is applied in gas turbine engines. In such application the polymer evaporates at high temperatures and a coating of controlled porosity is obtained. In addition to the accelerated development of new spraying processes, new coating materials have also been developed and used. To be mentioned are nanocrystalline (nanostructured) fine grained powders by the microstructural length from 2 to 100 nm, used for *nanocrystalline coatings* of higher hardness, strength and corrosion resistance than conventional coatings of the same composition but coarser grained coating material. Nanocrystalline coatings provide more homogeneous and dense structure. Despite the fact that the research on these coatings has only begun, due to their excellent properties their industrial application is expected before long. Beside the nanocrystalline coatings, since the discovery of quasicrystalline materials in 1982, *quasicrystalline coatings* have been increasingly used due to their excellent tribological, thermal and electrical properties. Quasicrystalline materials differ from traditional crystalline materials in that the crystal lattices are arranged in a rotationally symmetric way and not periodically translatory. The quasicrystalline structure has been observed in Al-Cu-Fe-Cr, Ti-Zr-Ni, Al-Co-Ni, Al-Mn systems, for example, by the neutron diffraction method. It is due to such crystalline structure that the quasicrystalline materials have very low electrical and thermal conductivity so they can be used to provide insulation coatings or as thermal barrier coatings. The quasicrystalline coatings also provide high strength, hardness and good resistance to wear and corrosion.

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Biographical Sketch

Katica Simunovic was born in Osijek, Republic of Croatia. She received her diploma degree in mechanical engineering from the Mechanical Engineering Faculty in Slavonski Brod, Republic of Croatia in 1994. She got masters degree in mechanical engineering at the Faculty of Mechanical Engineering and Naval Architecture in Zagreb, Republic of Croatia in 2000. She received PhD degree in mechanical engineering at the Faculty of Mechanical Engineering and Naval Architecture in Zagreb, Republic of Croatia in 2004. Materials science and the optimization of tribomechanical systems by the application of the flame spraying and fusing process was the major field of her study.

Today she is assistant professor of materials management and optimization of tribomechanical systems at

the Mechanical Engineering Faculty in Slavonski Brod, Republic of Croatia. Since 1994 she had been working at the Mechanical Engineering Faculty in Slavonski Brod, Republic of Croatia as a research novice (research fellow) in scientific-research projects. Her current research interests are the materials management and the optimization of tribomechanical systems by the application of flame spraying. Assistant professor Simunovic is the member of the Croatian Society for Materials and Tribology and Croatian Association of Production Engineering.