Thermal Spray: Past, Present and Future
A Look at Canons and Nanosplats

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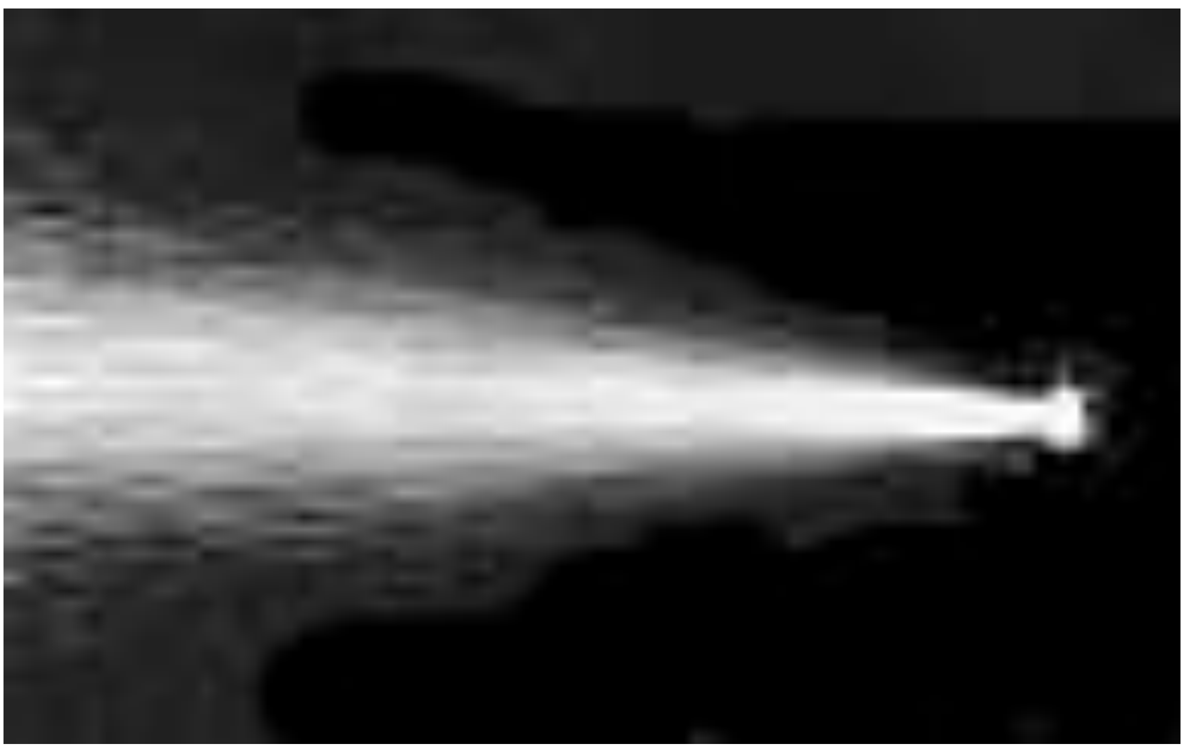
Thermal Spray Term Paper – MATE-580



1. Introduction – What is Thermal Spray

Thermal spray is a technique used for surface coating of many materials in a continuous process, thus forming a system with the substrate where one could not exist without its counterpart. It is a method in which any material can be coated by practically any material. Thermal Spray is a process in which thermal energy is combined with kinetic energy, heat is combined with particle acceleration, to form a dispersion of droplets that impact on the surface of a substrate where they splat, spread, solidify and build up incrementally as the new surface in produced over the original surface. As seen in Figure 1, gas (for some processes air) mixes with energy, in the form of heat, to provide the kinetic and thermal energies needed to coat the substrate by producing a jet of disperse particles to be spray on the original part. This process is usually done for metallic parts that need improvement such as thermal barrier coatings (TBCs), enhanced insulation or conduction, wear resistance, corrosion resistance, decorative additions and abradable parts. With a wide array of processes ranging from Flame Spray to Wire Arc to High Velocity Oxy Fuel (HVOF) to Plasma Spray to Cold Spray, thermal spray can be applied to metallic parts, and many other materials as well can be coated such as wood, ceramics, polymers and even fruit.

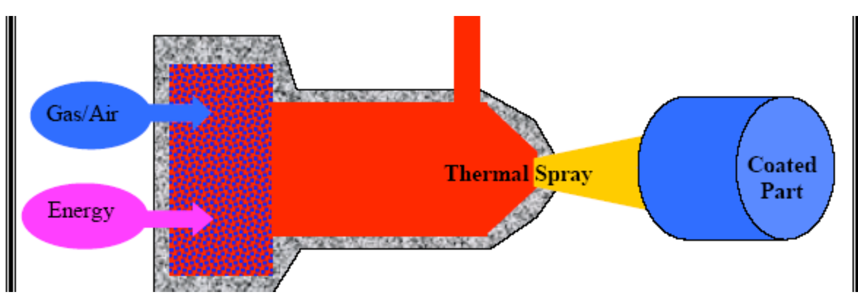


Figure 1 – Schematic of the Thermal Spray process[1]

The size of samples coated does not really matter as very small parts such as nuts and bolts to large "parts" like bridges can be coated. For specific products, very few, small parts may be sprayed or the whole object could be coated. The versatility in spray dimensions is one characteristic of thermal spray coatings.

2. Past – The History of Thermal Spray, From Cannons to Coatings

Thermal spray was first developed in 1910 by Dr. M. U. Schoop in Zurich, Switzerland. His process was the first process to spray metal onto a substrate, eventually leading to the spraying of metal in wire form. This metallization process was done by Schoop, shown in Figure 2 with molten Pb injected into a heat, oxygen and acetylene[1], compressed air jet and atomized[2] as seen in Figure 1[3]. This process was devised from a toy cannon that Schoop's son was playing with. As an on looking Schoop realized that the lead expelled from the toy deformed as it hit a surface he recognized the potential of metallic splats[1].

Schoop commercialized, after selling the process himself in Germany and France, his processes by selling the rights to his "Schoop Process" to Metallizator, a German company. Metallizator made this process available throughout Europe and the United State of America by the early 1920's. Figure 3 shows, an early design of the Schoop gun that became commercially available. Shortly after Metallizator started selling products in the United States, companies began springing up all over the place, most notably Philadelphia's Metal Coatings Company and Metal-weld and the Los Angeles based company, Metallizing Company[4]. These companies were fundamental in undertaking the spraying of railroads, NAVY ship tanks, coal barges and even the Panama Canal's emergency gates[2]. This was also the time that Wire Arc Spray emerged onto the market place.

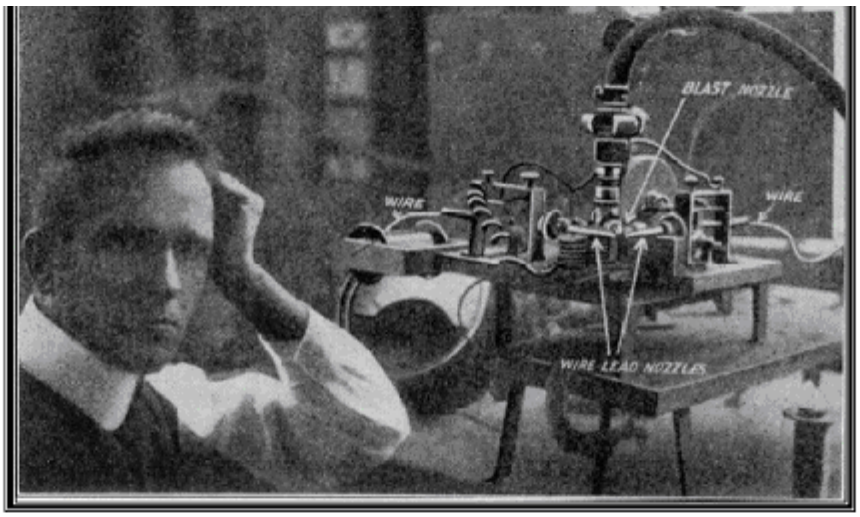


Figure 2 - Picture of The Father of Thermal Spray, Max Schoop[1]

As the great Depression impacted the country, there was a push for thermal spray in the form of "flame spraying" headed by Larry Kunkler, Rea Axline, Charles Boyden and Charles Stripp of the Metallizing Company of America. Their push, eventually, led to the formation of the American Metallizing Contractors; a predecessor to today's International Thermal Spray Association (ITSA), which was formed in 1948. The American Axline in conjunction with fellow Americans George Lufkin and Herb Ingham were major players in the advancement of Thermal Spraying in the United States and subsequently, the world. They founded METCO Incorporated in 1933, which has been involved in the Thermal Spray industry from then on, even if they have merged with others[1]. METCO formed a subsidiary, METCO LTD (UK), in 1939 that operated in the United Kingdom and Ireland. METCO eventually became METCO Perkin Elmer Group in 1971 and then Sulzer METCO for its United States operations when the companies merged. By 1940 the first Plasma Spray Gun was invented and in use leading to many more applications of coatings to new substrates.

During the World War II era, the Thermal Spray market exploded as war products were needed that would last in battle, harsh conditions and quick production. A great need of industrial equipment to be coated arose during this era, not only for war production but also for domestic products that still needed to be fabricated to sustain life at home. As Thermal Spray took its hold on commercial use in America more firmly, many more products started being coated by this "old" process, such as large elevated water tanks for municipal and industrial use, tuna fishing boats, chemical industry tanks and tank cars, capacitor castings and pipes[5]. From the push being made into corrosion resistant coatings the International Thermal Spray Association started outlining specifications for the coatings and inspection procedures all designed by engineers, designers and universities throughout the world.

As the 1950's rolled along some new and inventive uses were found for the expanding field of Thermal Spray. As seen in Figure 3, Bridges had started to be sprayed. Although not a common occurrence, this was on of the largest structures sprayed up to this point in time. Davy Metal Industries Flame Sprayed the bridge, and to date, it is still in perfect condition. This bridge in Auckland Harbor, New Zealand, consumed 100 tons of zinc wire to complete the job, which is no small feat.

Figure 3 - A Thermal Spayed Auckland Harbour Bridge, New Zealand[3]

The 1950's were also a time of vast improvement halfway around the world in the United States. This was a time when many improvements were made in the materials used for Flame Spray. Many new coatings were developed as hard facing solutions, fusable alloys and as ceramic coating materials[6].

The 1960's led to physical analysis of thermal spray. The Detonation Gun (D-GUN®), which is a proprietary process of Praxair Surface Technology, process by which combustion and jet expansion are created by using acetylene and oxygen was also starting to be used in 1960. Between the years of 1960 and 1970, Induction Plasma Spraying came to be known and used as a commercial process. In 1973 Vacuum Plasma Spray (VPS) which broke the coating industry wide open and made Thermal Spray a major component of the coatings world[2]. In 1976 the first International Thermal Spray Conference, held in the United States was organized and hosted as a joint project between ITSA and the American Welding Society (AWS). This was a great opportunity for many thermal sprayers, designers and developers to come together and discuss what had happened in the industry, the needs of the industry and how to obtain their goals for this field.

As the 1980's began, HVOF was starting to be more widely used and made on-site Thermal spraying much more available. This supersonic spraying, achieved by pressurizing internal combustion and supersonic jet expansion as the particles leave the gun, increased spraying velocities quite dramatically (to ranging from 200 m/s to 1000m/s). Along with the advent of Controlled Atmosphere Plasma Spraying (CAPS), which is primarily Low Pressure Plasma Spray (LPPS®), being introduced, Thermal Spray led to many more applications for coatings. Most recently Cold Spray, a technique that uses temperatures of about 800 degrees Celsius and has particles speeds of up to 1200 m/s but is limited to ductile metals as feedstock, was introduced in the United States in 1994 after being invented in Siberia, ironically one of Earth's most thought of cold spots.

2. The Present – The Who, What How and Why of Thermal Spray

As thermal spray progressed from its infancy, an idea brought upon by a toy cannon, many new inventions have been developed as well as new materials and processes. Currently there are countless ways to thermally spray an object, ranging from Plasma done at near pure vacuum to low temperature spraying, Cold Spraying, that have come to the forefront in modern Thermal Spray society. Although, the drive for new and improved materials to further enhance the coating placed on parts, has at times, pushed the envelope beyond what could be believed, engineers and designers have modified old techniques and invented new ones to facilitate the spraying of much needed materials such as ceramics fro TBCs and anti corrosion materials. The field has only grown more complex since 1911 when Schoop coated metal with lead. Today, a large number high tech parts must be sprayed, ranging from turbine engines to petrochemical delivery and storage facilities aid in decreasing costs due to wear and corrosion and high thermal cycling that were never envisioned by the father of Thermal Spray.

The driving force behind the advancement of the coatings field has been new materials that must be sprayed on innovative parts that must perform under ever more demanding conditions. As people try to maximize the current techniques for producing industrial equipment that is being placed under the stress of a more demanding world Thermal Spray has aided in the manufacturability of today's products by allowing products to last longer and function in environments that they had never before used.

As seen in Figure 4, there are many different types of Thermal Spray currently used, even though this diagram neglects the recent development of Cold Spray. All of these branches can be expanded, not shown, to include such aspects as controlled atmosphere (vacuum and shrouds of different gases and in the case of Plasma Spray even underwater, UPS) and in air process. Many of these techniques have similarities to other branches, not only in the different types such as inert gas spray in multiple techniques, but also they evolved from each other so processes such as Plasma Spray take advantage of using an arc which was also seen in the 1920's in Wire Arc Spray. Although, similar the processes still vary in their applications.

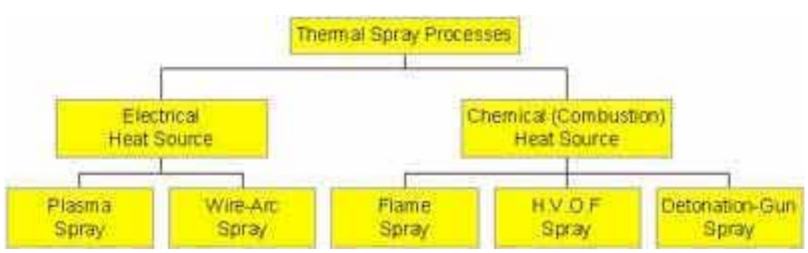


Figure 4 - Diagram showing different Thermal Spray techniques[15]

Flame Spray, or the modified version of Schoop's original atomization process, still uses a thermal source to heat the coating material and accelerate it toward the substrate, it has just been modified to produce a wider range of temperatures, greater than 2500 degrees Celsius, and speeds, up to 80m/s, as well as more efficient deposition. As shown in Figure 5, there are many aspects to the system that play crucial roles in the spraying of a coating; it is not just a blowtorch with powder thrown into the flame, at least not as crudely as mentioned. Powder is injected into the flame and shot toward the substrate to splat and coat the part. Three different forms of material are usually Flame Sprayed, either as powder, wire/rod or pellet like yielding Powder Flame Spray, Wire Flame Spray or D-GUN®, which is a proprietary process of Praxair Surface Technologies, Inc. Currently Flame Spray is used for many applications, ranging from large parts as in bridges to small ones such as L.P.G. bottles. The coatings typically applied are Aluminum or Zinc with many more coatings also available such as zinc chromate and chromium carbide/nickel chromium for corrosion protection. When lubricating coats are needed the sprayed material is more porous, flame spray provides 85-95% density so on the lower end of that range is the more porous coatings, so as to absorb the lubricants. To improve the wear resistance of a product, coats of NiCrBSi alloys can be applied[2].

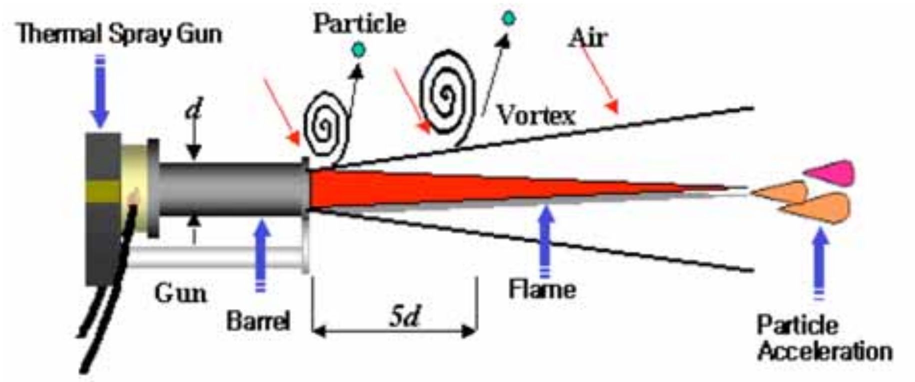


Figure 5 - Flame Spray Process[2]

Arc Spraying is a process in which an arc is produced between two wire electrodes of either the same material or to form a composite coating or alloy, two different materials. This process is the only one that is a direct heating and melting process in Thermal Spray since the conductive feedstock allows arcing by acting as an electrode as shown in Figure 6

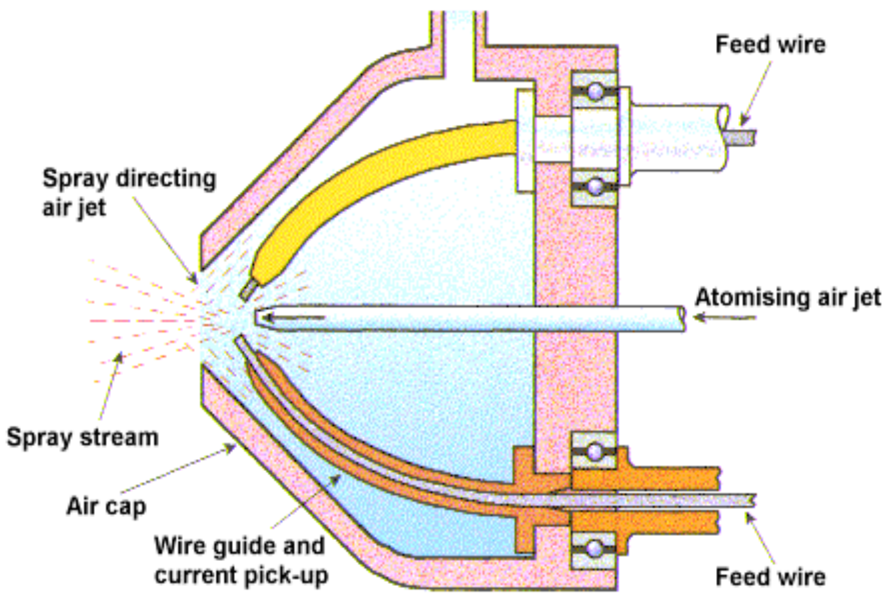


Figure 6 - Wire Arc Spray Techniques[7]

After the D.C. arc is struck, across the two feed wires which have opposite charges, a spray stream is created that proceeds to the substrate for coating. A wide range of materials can be sprayed ranging from metals to alloys to metal matrix composites (MMCs). Newly developed CERamic METals, cermets, have also been applied. Cored ceramic wires such as tungsten carbide in which the ceramic powder is inside the metal wire, can also be used for arc spraying.

Having a higher deposition rate than HVOF and Plasma Spray, Arc Spray is used to cover large structures or high volume of products in a relatively short time. Arc Spray is used to coat structures for corrosion resistance such as bridges and offshore structures with Zinc and Aluminum. Restoration of parts can be accomplished by using steel or bronze wire for a coating material. Conductive coats can obviously be applied by using metal wires of Copper, Zinc and Aluminum. Even molds to produce plastic products can be fabricated from alloy wires of Tin and Zinc mixtures[7].

A third form of Thermal Spray is Plasma Spray. In this process an arc is produced to melt feed material at tremendously high temperatures of over 20000K. Although this extremely high temperature which creates a plasma will provide the thermal energy to the feedstock material thus allowing it to be sprayed, it is only a localized process in which the temperature decreases drastically as distance from the arc increases. This means that the substrate will stay relatively cool, unless it is made to be part of the electrode setup, so little or no changes in microstructure will occur to it while spraying. This process maybe the most inefficient as far as power consumption is concerned as it uses roughly 1% of the input power to actually melt the feed material. As shown in Figure 7, the process of Plasma Spraying can been seen in where

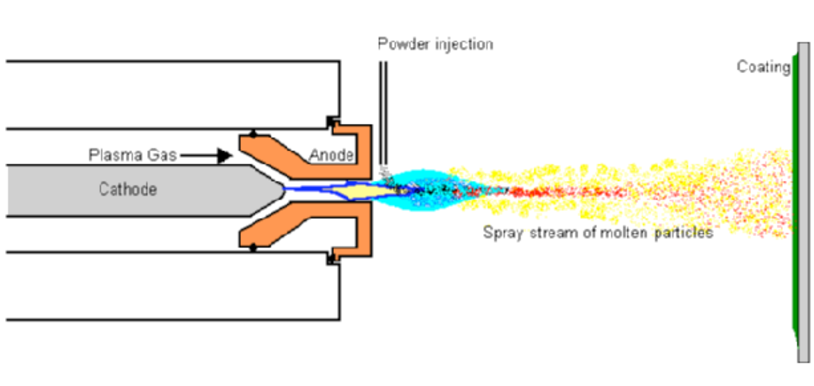


Figure 7 – Diagram of Plasma Spray[16]

the cathode and anode produces an arc to atomize the particles. Plasma Spray can spray almost any known material because of its high temperature capabilities it will atomize almost any feed material; Ceramics, metals, polymers and others can be sprayed. One of the major applications that has fueled the progress of Plasma Spray is the aircraft turbine engine industry. This industry requires a very high tech coating of fretting resistance in the form of Tungsten Carbide-Cobalt and TBC coatings of Zirconia, YSZ, and its many composites such as Yittria Stabilized Zirconia, YSZ. Again the staples of the spraying industry, Aluminum and Zinc, can be sprayed for use on printing rolls. Besides Aluminum and Zinc, Molybdenum is sprayed heavily for engine coatings[7].

Although Plasma Spray has many uses there have been various modifications made to the process. Low Pressure Plasma Spray (LPPS®), Vacuum Plasma Spray (VPS), Underwater Plasma Spray (UPS) and other methods involving atmospheric condition controls have been used to reduce the amount of oxygen that reaches the atomized particles since at very high temperatures particle oxidize very easily thus degrading the coat by introducing oxide stringers.

One of the more recent inclusions in the Thermal Spray family is HVOF, late 1970's. HVOF was a highly sought after process to combat the strangle hold that both D-GUN® and Air Plasma Spray had on the market of Tungsten Carbide-Cobalt. HVOF is a rapid spray process that takes advantage of higher combustion rates than Flame Spray and has a high enough pressure to accelerate particles faster than the speed of sound, reaching supersonic speeds, which can surpass APS by a little; a diamond pattern is created by the shockwaves of the spray. Another benefit of this process is low porosity coating and high bond strength. This process requires fuel gas, propylene, propane, hydrogen, or on rare occasions acetylene, and oxygen.

Many materials can be deposited by HVOF such as low temperature oxides and carbides not usually deposited by Flame Spray can occasionally be deposited. The main coating applied by this method for industrial use in Tungsten Carbide-Cobalt for turbines, as well as many other applications, for aerospace use as fretting and wear, slide, resistance. Wear resistant coatings are made from Cobalt alloys, alumina, chromia, tungsten carbide/cobalt and many others. Printing rolls can be coated from materials such as Copper, Aluminum and Chromia. Dielectrics can even be sprayed in the form of

Alumina and alumina-Titania coatings. For the ever emerging field of bioengineering, biocompatible materials such as hydroxyapatite (HA) can be sprayed[7].

The most recent Thermal Spray process to emerge is Cold Spray which by some people is not considered a Thermal Spray process even though it does use thermal energy, in the range from 20 – 700⊠C, to heat particles. Cold spray has subsequently been dubbed “room temperature” spraying.   Similar to HVOF, Cold Spray accelerates particles at supersonic speeds through a de Laval nozzle[8]. The splats have very high bond strength since they can be accelerated up to 1500m/s[9]. As seen in Figure 11, the maximum speed of the Cold Spray process is still being determined at Sandia National Laboratories.

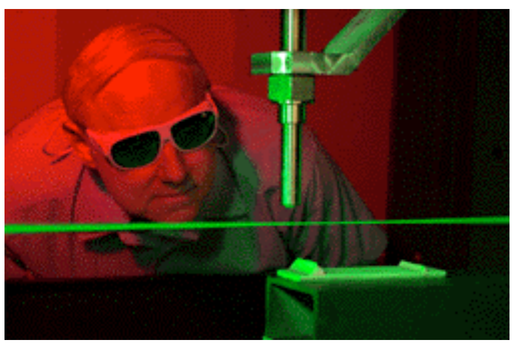


Figure 8 - Speed check of Cold Spray velocity with a police radar gun from Sandia National Laboratories[10]

This process, after more thorough testing, may be used for tougher coatings of ductile metals on turbine engines made from light-weight composites. From this high speed acceleration Cold Spray does not present an oxidizing environment for the coating. High density coatings are also a characteristic of this novel process. Even the deposition rate is comparable to the traditional thermal spray processes. Experiments at Sandia National Laboratories have produced coatings of Aluminum, some steel and Nickel alloys and even a few metal-ceramic composites[10]. The limiting factor of Cold Spray is that only ductile metals can be sprayed.

As many of the previous techniques have been around for some time in one fashion or another, many new and emerging technologies are making breakthroughs in Thermal Spraying. Not all of the advances are in the actually processing some come from new materials, material preparation and even from simulations.

The Future – 2004: A Thermal Spray Odyssey

Through the evolution of thermal spray many new processes, materials and techniques have developed as a result of laboratory science but above all from need by specific industries such as the aerospace industry. Although a few universities, as well as companies, are conducting research to improve thermal spray, the mechanism of progress has been led by industrial push for novel and complex types and specifications of coatings. This in itself is unique in that instead of science paving the way for innovation it was the push from commercialization that drove thermal spray to become the industry it is today.

As a new trend has emerged in science and engineering, even "old" industries are moving toward the future by implementing new techniques. As thermal spray has evolved, it has primarily relied on the needs of industries such as aerospace and the chemical industries. As their needs changed, the technology from thermal spray has molded itself to fulfill this void. Although thermal spray may always be dependent on its customers, it also has new areas into which to delve and form new techniques and materials for coatings.

One new tool being used by engineers, and other scientists, more often is the method of modeling. Modeling has been around for years in many industries and has achieved some success in certain areas, although limited. This limited success has come from the fact that as technology progresses, computers become faster and can manage more information in a timely manner. The down side to this advancement in technology is the other side of this double edged sword; as technology improves and aids scientists in understanding more about the ways materials act; it also complicates the processes by realizing there are many more aspects to materials than just the comprising elements such as dislocations and grain boundaries. Computers have become more advanced but the new processes that they are being used to model are growing more and more complex every day as researches are able to know more about there fields through the use of more powerful tools such as TEM's that have resolution on the nanometer regime. These tools allow for a more comprehensive understanding of the materials used but also show that more processes determine characteristic then just the specific elements

Modeling may be a good tool to use for simple processes, such as traffic flow patterns around a new suburban mall, but can modeling help with a process that has many small steps and independent activities? Modeling for thermal spray, like many other fields, is dependent not only on the specific process, such as plasma spray or HVOF, but many other factors are also important such as the materials used in the process and operating conditions. Thermal spray is dependent not only on what material is sprayed but also on many facets of that particular powder such as particle size distribution, velocity at which the particle travels to the substrate, the temperature of the spray, the substrate to be deposited on, the temperature of the substrate and degree of solidification of the particle during spraying[11,12]. Process, spray material and substrate are all very important to modeling but every other factor that plays a role in thermal spray is also important such as humidity, atmosphere and even characteristics of the material too be sprayed can vary from batch to batch. According to Mostaghimi[11] there are three processes that must be modeled independently from each other for accurate thermal spray simulations. First is the model of spray particles (particle size, temperature, velocity and impact sites). Second, particle impact and splat formation must be simulated. Finally, the actual coating microstructure must be able to be modeled. All of these factors make modeling difficult yet rewarding if they can be done.

Besides developing techniques to facilitate the path to follow for Thermal Spraying, the nano invasion has penetrated into the spraying world. With increased funding to anything related to nanotechnology the Thermal Spray world has used some of its funding to develop coatings for its own industry. Two of those coatings, TiC-Ni nanocrystalline cermet and FeAl powders will be discussed.

The TiC-Ni cermet powder produced by Eigen et al. is produced by high-energy milling. The properties related to nano sized particles make nanopowders good candidates for wear resistance because of high hardness and fracture toughness in the same powder, as demonstrated for WC-Co, a staple in the coating industry for wear resistance. Since sample preparation is an important step in Thermal Spray, even if the same powder is used in the same process different processing routes may yield completely different coating structures.

High-energy milling provides a potential low cost approach to producing very useful nanopowders[13]. If tube vibration mills can be used, instead of attritor mills, the scale up to tons of powder produce in a cheap fashion would be a benefit for the coating industry. Although problems of creating useful powders in the 5-50μm range have not been solved, it is still an interesting approach since the TiC-Ni may provide not only a wear resistance but also a corrosion resistance aspect as well[13]. Further work must be done to produce usable quantities at low cost if there is to be any impact in the Thermal spray industry where cheap, good materials are a premium.

Another milled powder that has sparked interest is the metallic FeAl powder. By Thermal Spray deposition, FeAl has been used to produce nanocrystalline coatings with better properties than its micron-scale counterparts. This can be done for both ceramic and metallic powders.

To take advantage of these particles, they must first be agglomerated by spray drying because Thermal Spray equipment requires micron sized powder to be fed into the devices. The goal of this type of deposition is to retain some nanocrystalline particles when the splats hit the substrate. The process used by Gang et al. uses the HVOF method to spray not only FeAl but also Nickel alloys and Co-Cr alloys. The deposition of these agglomerated nanostructures have led to Transmission Electron Microscopy, TEM, analysis of the coatings allowing for studies to be done on the structure of the coating once deposited[14].

Although this may be promising work by both Eigen and Gang, it like many of its other nano counterparts must undergo many more tests to yield reproducible results. Until nanotechnology produces any useable results any claims made by people will be looked through skeptic's eyes or those of dreamers seeing much more than is really there.

Conclusion – From Canons to Nano(ns) (nanoscale)

From the invention of Thermal Spray by the model of a toy canon, Schoop led to a discovery that has changed the face of coatings in the world. Not only have many processes been developed in Thermal Spray such as HVOF, Plasma and Cold Spray but many new ideas for coating uses have also risen from Schoop's original ingenuity. Coatings for bridges, coatings that allow people to fly at supersonic speeds and coatings that may some day provide both wear and corrosion resistance at the same time. As Thermal Spray has advanced by necessity and by profit of the aerospace industry, new processes have led to new materials have led to new processes have led to techniques that may some day predict, what powder under hat conditions spray by a specific process, the microstructure for a nanocoated turbine engine to be used in outer Mongolia. Numeric modeling and nanotechnology are just two aspects that may push Thermal Spray into the 21^{st} and 22^{nd} centuries as well as some other innovated ideas by the next Schoop.

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