

1 Introduction

1.1 General Description

Cold gas dynamic spray (GDS) is a rapidly emerging coating technology, in which spray particles in a solid state are deposited on a substrate via high-velocity impact, at temperatures lower than the melting point of the powder material (Papyrin et al. 2006). As shown by McCune et al. (2000), the methodology for generating surface coatings from metallic particles in solid form was first patented by Rocheville (1963). This process employs a supersonic nozzle into which solid particles of feedstock material are introduced and accelerated toward a substrate, either forming a thin surface coating, or being directly embedded as isolated particles in small depressions on the surface. An alternative technique for producing thick deposits of various metals from “cold” jets was reported by Alkimov et al. (1990). In this method, solid particles ranging in size from 10 to 50 μm are introduced by means of a pressurized powder feeder into the high-pressure, high-temperature chamber of a converging–diverging (de Laval) nozzle and are subsequently accelerated into a supersonic stream by the gas (Fig. 1.1(a)). Here, as the gas has been electrically preheated prior to its introduction into the nozzle, the term “cold spraying” appears to contradict with the nature of this deposition process. For this reason this process is more appropriately referred to as “Gas Dynamic Spray.”

In deposition, spray materials experience only minor changes in microstructure and little oxidation or decomposition. Most metals such as Cu, Al, Ni, Ti, and Ni-based alloys can be deposited by cold spray (Papyrin 2001); even cermets (Karthikeyan et al. 2001) and ceramics (Karthikeyan et al. 2002) can be embedded into a substrate to form a thin layer coating in cold spray.

The most important parameter in the cold spray process is the particle velocity prior to impact on the substrate (Alkimov et al. 1990). For a given material, there exists a critical particle velocity that must be achieved. Only particles whose velocities exceed this value can be effectively deposited, in turn producing the desired coating. Conversely, particles that have not reached this threshold velocity contribute to the erosion of the substrate (Alkimov et al. 1990). Naturally, critical particle velocities vary according to the particular

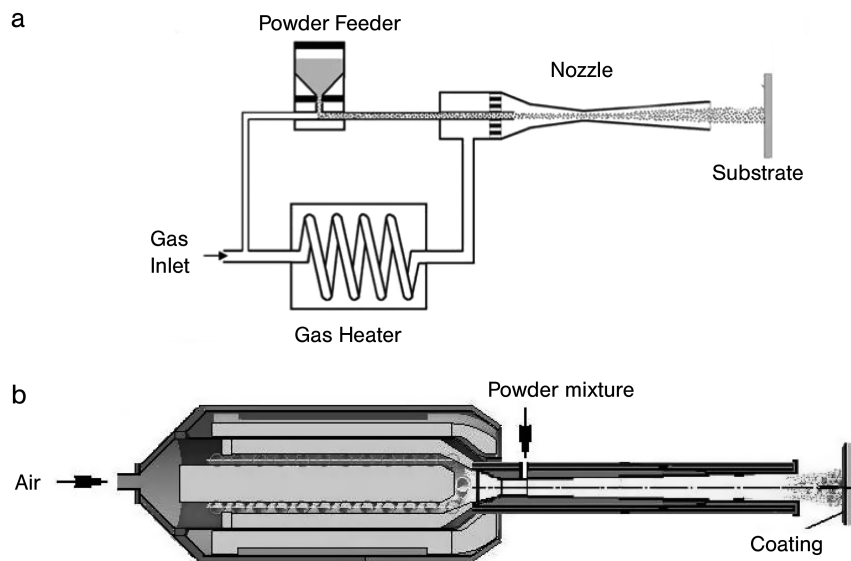


Fig. 1.1 Gas Dynamic Spray operating systems
 Micron-sized particles are accelerated to high velocities by entraining the particles in the flow of a supersonic nozzle: (a) axial injection (Assadi et al. (2003)), (b) radial injection.

spray material that is chosen. In fact, critical velocities are dependent on both the size of the particles and their size distribution of particles (Alkimov et al. 1990, Van Steenkiste et al. 1999) and the particular substrate material (Gilmore et al. 1999). For example, it has been reported that the critical particle velocities of Cu, Fe, Ni, and Al are approximately 560–580, 620–640, 620–640, and 680–700 m/s, respectively (Alkimov et al. 1990).

The particle velocity, on the other hand, is determined by the nature, operating pressure, and temperature of accelerating gas, as well as by nozzle design (Gilmore et al. 1999, Dykhuizen et al. 1998). Material parameters such as density, particle size, and morphology influence the acceleration and subsequent deposition behavior of the particles (Van Steenkiste et al. 1999, Gilmore et al. 1999). It has been demonstrated that a dense coating can indeed be deposited through cold spraying if these spray conditions contribute to particle velocities that exceed the critical particle velocity (McCune et al. 1996). However, even in the case of deposition efficiencies greater than 80%, Karthikeyan et al. (2000) reported that porous titanium coatings may be formed.

A unique feature of cold gas-dynamic spraying is its ability to generate a wide range of deposition layer thicknesses ranging from tens of microns up to a centimeter (Li et al. 2004). In this regard, this process extends beyond the concept of “coating” a substrate, providing a means for developing three-dimensional structures (McCune et al. 1996). In fact, in a recent paper by

Gabel and Tapphorn (1997) a material forming process is discussed which utilizes a low-temperature gas stream to accelerate solid particles into a jet. Further, Bhagat et al. (1997) reported the use of cold spray processes for the production of nickel-bronze layers that may be employed in wear resistance applications.

The acceleration of powder particles in gas dynamic spraying is realized within the GDS nozzle. Here compressed gases (having inlet pressures up to 30 bar) flow through a converging/diverging nozzle, thereby developing supersonic velocities. The powder particles are metered into the gas flow immediately upstream of the converging section of the nozzle where they are accelerated by the rapidly expanding gas. It is perhaps obvious that compressed gases that are preheated are able to achieve higher gas flow velocities in the nozzle. However, even with preheat temperatures as high as 900 K, as used by Dykhuizen et al. (1998), the gas rapidly cools as it expands in the diverging section of the nozzle. Hence, the duration of particle interaction with the hot gas is relatively brief, and the temperatures of the solid particles remain substantially below that of the gas (Dykhuizen et al. 1998). Thus, the primary function of the carrier gas is to only to accelerate the particles to above the critical velocity.

The actual mechanism by which the solid-state particles deform and bond has yet been fully characterized. It seems possible that plastic deformation may disrupt thin surface films, such as oxides, and provide intimate conformal contact under high local pressure, thus permitting bonding to occur (Dykhuizen et al. 1999). Though unproven, this hypothesis is consistent with the fact that a wide range of ductile materials, such as metals and polymers, have been cold-spray deposited. Experiments with materials, such as ceramics, on the other hand, have proven unsuccessful unless sprayed along with a ductile powder material. If indeed this is the case, the minimum critical velocity corresponds to the kinetic energy that is necessary to bring about powder material plastic flow during deposition. Calculations by Schmidt et al. (2003) indicate that typical kinetic energies found at impact are less than that which is required to melt the particles. Micrographs of cold-sprayed materials (Dykhuizen et al. 1998) also reveal that the deposition mechanism is primarily, if not entirely, a solid-state process.

Because sufficient particle velocity is essential for successful cold-spray deposition, it is critical to fully understand the relative influence of process variables (such as gas inlet pressure, temperature, and nozzle geometry) on particle velocity. For this reason, discussions of the basic governing equations, computational results, and comparisons with experimental datum, will be take place primarily with respect to the relationship between these variables. It is hoped that this form of analysis will bring about a deeper understand-

ing of the GDS process, and that this book may ultimately serve to widen the study and application of gas dynamic spraying.

1.2 Overview of Competitive Technologies

1.2.1 Coating Characterization

Today numerous surface treatment procedures are used to modify the surface properties of various materials without altering their bulk characteristics. These techniques are used within industrial environments to improve resistance to corrosion, wear, fatigue, and heat. In order to properly analyze and, in turn, distinguish between these methods, it is first beneficial to differentiate between thin and thick layers.

Thin coatings have more been developed on a considerably wider scale. These include techniques such as CVD or PVD (chemical or physical vapor deposition), plasma spraying, ion-assisted deposition, magnetron-sputtered deposition, and chemical deposition under a laser beam. Their thicknesses, being generally less than a few micrometers, have no direct effect on the mechanical characteristics of the treated material; they do not alter such aspects as yield strength or ultimate tensile strength.

On the other hand, thick coatings, including cladding and welding, have thicknesses varying from a few hundred micrometers to several centimeters. They generally serve not only as protective layers, but also add mechanical strength. Most of the problems encountered when welding or cladding materials concern the heat-affected zone (HAZ) and result from the heat generated by a laser (Kalla 1996) or electron beam (Yilbas et al. 1998), or alternatively as a result of capacitive discharge (Simmons and Wilson 1996). In processes characterized by high energy densities such as plasma arc, electron beam welding, and laser beam welding (Sun and Karppi 1996, Tjong et al. 1995), the HAZ is considerably smaller than that in more conventional processes such as gas metal arc and submerged arc welding (Cullison 2001, Kannatey-Asibu 1997). This is primarily due to very short interaction times. Even with a small HAZ, incompatibilities may still exist due to differences in the physical properties of the materials such as fusion points and thermal expansion coefficients (Grodzinski et al. 1996, Conzone et al. 1997). This may ultimately induce cracking (Conzone et al. 1997, Wang et al. 2000), high residual stresses (Wang et al. 2000, Conzone 1997), or brittle intermetallic compounds (Wang et al. 2000).

Thermally sprayed coatings are used extensively within a wide range of industrial applications. These techniques generally involve spraying molten powder or wire feedstock that has been melted using oxy-fuel combustion or an electric arc (plasma). The molten particles are subsequently accelerated toward a properly prepared (often metallic) substrate. Solidification occurs at rates akin to those obtained in rapid solidification technology, resulting in deposits that have ultrafine grain structure, with similar microstructure characteristics.

Thermal spray is a highly flexible process which is able to generate dense, tenaciously bonded coatings with low porosity. It is commonly used to shield surfaces from wear, high temperatures, and chemical attack, along with environmental corrosion protection in infrastructure maintenance engineering. Typical materials that are sprayed in this method include most metal alloys and ceramics. In fact, virtually any material can be thermal sprayed if it does not decompose prior to melting.

Various thermal spraying methods, such as flame spraying (including high-velocity air-fuel (HVOF) and high-velocity oxy-fuel (HVOF) thermal spray devices), plasma spraying, and electric arc spraying, have been used to coat both metallic and nonmetallic surfaces. A general overview of existing spraying techniques is given below.

1.2.2

Flame Spraying

Although *flame spraying* was one of the earliest thermal spray processes to be developed, its usefulness endures even today. In this method, metals, ceramics, or cement-like materials are deposited onto a substrate by means of the combustion reaction. The flame spray device includes a combustion chamber that receives a mixture of fuel (e.g., propylene or propane) and oxidant (e.g., oxygen or air) in the form of a high-temperature, high-pressure gas stream. This combustion stream is initially directed into a flow nozzle where the spray material (e.g., a powder, a solid rod, or a wire) is introduced and at least partially melted and “atomized” (Neiser et al. 1995). It is then propelled in this form to the target substrate. Depending on the design, particle streams may be accelerated up to supersonic or hypersonic velocities. This supersonic particle stream may be generated by a single- or two-stage combustion devices, or alternatively by those that produce steady-state, continuous detonations.

In HVOF techniques, propylene, propane, or hydrogen (depending on user requirements) is combined with oxygen in a proprietary siphon system in the front portion of the diamond jet gun. The thoroughly mixed gases are then ejected from a nozzle and ignited externally from the gun. Meanwhile, the coating material (in powdered form) is fed axially through the gun using ni-

trogen as a carrier gas. Thus, the ignited gases form a circular flame configuration which surrounds and uniformly heats the powdered spray material as it exits the gun and is propelled to the specimen surface.

It should be noted that due to the high kinetic energy transferred to the particles by the HVOF process, the coating material generally does not need to be fully melted. Instead, the powder particles are heated to a molten state and flatten plastically as they impact the surface. For this reason coatings are formed having more predictable chemistries that are very homogeneous and have a fine granular structure (Li et al. 1996).

Through this use of an efficient and controlled thermal output with a high kinetic energy, HVOF processes produce dense, very low porosity coatings that exhibit very high bond strengths (exceeding 12,000 PSI or 83 MPa), have low oxidization and yield extremely fine finishes, even without further processing. The resultant coatings exhibit low residual internal stresses and can be sprayed to thicknesses that are not normally associated with dense, thermal sprayed coatings.

1.2.3

Arc Wire Spraying

Arc wire spraying uses two metallic wires as the coating feedstock. These wires are electrically charged with opposing polarity and fed into the arc gun at matched, controlled speeds. When the wires are brought together at the nozzle, their opposing charges create enough heat to continuously melt their tips. Compressed air is used to atomize the subsequently molten material and, in turn, accelerates it toward the surface, forming the coating. In arc wire spraying, the weight of the coating that can be deposited per unit of time is a function of the electrical power (amperage) of the system, as well as of both the density and melting point of the wire. New arc wire spray coating systems have unique, advanced mechanisms such as synchronized “push-pull” wire feed motors which ensure consistent wire delivery.

1.2.4

Plasma Spraying

Plasma spraying is perhaps the most flexible of all of the thermal spray processes in that it can create sufficient energy to melt any material. Further, because it uses powder as the coating feedstock, the number of coating materials that can be used in the plasma spray process is almost unlimited. In this method, the plasma gun consists of a cathode (electrode) and an anode (nozzle) with a small gap forming a chamber between the two. As gases are passed through the chamber, DC power is applied to the cathode and, in turn, arcs across to the anode. The powerful arc is sufficient to strip the gases of their

electrons, forming a state of matter known as plasma. As the coating material is introduced into this gas plume it is rapidly melted, forming a particle-plasma stream which is accelerated up to a hypersonic velocity and propelled toward the substrate.

In this process, various mixtures of nitrogen, argon, and helium (usually two of the four) are used in combination with the electrode current to control the amount of energy produced by a plasma system. Since the flow of each of the gases and the applied current can be accurately regulated, repeatable and predictable coatings can be obtained. In addition, the point and angle at which the material is injected into the plume, as well as the distance between the gun and the target, can be precisely controlled. This provides a high degree of flexibility in developing appropriate spray parameters for materials having a very wide range of melting temperatures.

1.2.5

Rapid Prototyping

In materials processing specific parts are manufactured to particular specifications from a variety of materials. For viable product realization in the marketplace, a spectrum of issues regarding performance, cost, and environmental impact must constantly be addressed. Novel processing methodologies, as well as the innovation of new materials, provide opportunities for product development, improvements in product performance, reductions in cost, and minimization of environmental impact through the complete lifecycle (Zhang et al. 2001). One of these innovations, namely additive manufacturing, has allowed for product modification through controlled consolidation, layering, and/or coating, in turn leading to superior product attributes. In fact, the idea of fabricating components through the addition of material led to the establishment of the rapid prototyping industry approximately 15 years ago (Zhang et al. 2003b).

Rapid prototyping was initially considered a tool for the rapid development of 3D models and prototype parts, used almost exclusively to verify the design feasibility rather than for functional application. Currently available commercial rapid prototyping techniques, such as stereolithography, selective laser sintering (SLS), laminated object manufacturing, fused deposition manufacturing, and 3D printing are able only to produce prototypes using wax, plastic, nylon, paper, polycarbonate materials, etc. There are, however, many difficulties that must be addressed when attempting to replicate these processes techniques using materials with high melting temperature such as metal (Li et al. 2000). These include poor material strength, high porosity, oxidation, warping, “step” effects, etc. There is, however, great interest in further developing current materials additive manufacturing (MAM) techniques or

alternatively, to create new methods which are capable of directly producing metal parts.

The MAM techniques that can be used to directly manufacture metal parts can be divided into two groups: 3D cladding (Mazumder et al. 1997, Milewski et al. 1998) and 3D welding (Schmidt et al. 1990). In 3D cladding, a laser beam creates a weld pool into which powder is injected and melted (Choi et al. 2001). The substrate is then scanned by a laser-powder system in order to trace a cross-section which, upon solidification, forms the cross-section of a part. Consecutive layers are then additively deposited, thereby producing a 3D component (Jeng et al. 2000). An example of this technique, known as laser engineering net shaping (LENS), was developed by Sandia National Laboratory. In this method metal components are fabricated directly from CAD solid models, thus further reducing the lead times for metal part fabrication. A similar process by the name of *directed light fabrication* (DLF) is under development at the Los Alamos National Laboratory (Milewski et al. 1998).

1.2.6

Plasma Deposition Manufacturing

Plasma deposition manufacturing (PDM) is a newly developed direct metal fabrication process that belongs in the category of 3D welding. In this technique, a supply head delivers a well-defined flow rate of metal powder, which is deposited in a molten pool formed by controlled plasma heating. In this way, full strength parts with the single or multifarious materials can be built up, layer by layer, by melting and rapid solidifying the feed material into a particular shape.

The PDM process has many advantages over traditional material subtractive technologies: (1) conventional metal melting and casting techniques frequently require considerable time and expenditure with respect to mold production, particularly in low volume manufacturing. PDM, by contrast, allows for the direct production of individual parts in a single step. Also, the manufacturing materials may be varied either between parts or within a single component. (2) Most MAM techniques are limited to the production of parts composed of plastic, wax, or paper; thus, the required engineering properties cannot always be obtained. The PDM process, on the other hand, allows for the direct fabrication of metal or end-use-material components. Further, the deposition rate and particular materials used in PDM can be adjusted through a wide range, making this technology extremely flexible. (3) PDM can be used as an effective remanufacturing tool, helping to increase product lifecycle.

There is, however, a primary disadvantage to the PDM process in that the effects of local melting due to the high temperatures cannot be avoided. For this reason it seems reasonable (and quite advantageous) to apply the prin-

ciples of PDM to GDS. In this case, the solid-state bonding mechanism will allow the deposited material to retain its original structure.

The most efficient among the thermal spraying methods is plasma deposition, combining a high-temperature gas jet with the high productivity of a coating process. Unfortunately, while plasma spraying can produce high-quality coatings, this method suffers from several minor limitations. Firstly, the necessary apparatus is relatively complex and expensive. Secondly, although plasma spray processing is a well-established method for forming thick coatings, in coatings thinner than 100 μm it is difficult to control material properties. Also, in spite of the plasma jet velocity being about 1000 to 2000 m/s, and the particles being accelerated up to 50 to 200 m/s (and even up to 350 m/s in extreme cases), the acceleration process is not yet efficient enough. The primary imperfection associated with plasma spraying, however, is its high processing temperature, making a number of substrate materials unfit for treatment due to local heating, oxidation, and thermal deformations. Further, the high-temperature jet that is incident on the product surface intensifies chemical and thermal processes, causing phase transformations and the appearance of oversaturated and nonstoichiometric structures which bring about structural changes in the substrate material. Also, the high cooling rates result in the hardening of these heated materials. And finally, the liberation of gases during crystallization brings about both porosity and the appearance of microcracks.

In short, thermal spraying methods have the following disadvantages: (1) A high level of thermal and dynamic effects on the surface being coated; (2) substantial changes in the properties of the material to which the coating is being applied (i.e., electrical and heat conductance, etc.); (3) changes in the material structure result from the chemical and thermal effects of the plasma jet and the hardening of overheated melts; (4) ineffective powder particle accelerations due to the low density of the plasma; (5) intensive evaporation of fine powder fractions having sizes ranging from 1 to 20 μm ; (6) insufficient cost-per-mass ratio of the applied material; (7) reduced equipment portability due to the high-temperature requirements of the method.

1.2.7

Explosive Cladding

The processes which are best able to avoid the problems associated with thermal changes appear to be spot welding (Turgutlu et al. 1995, 1997), impact welding (Date et al. 1999), or explosive cladding (EC). These methods allow for flyer plate velocities that exceed plasma and detonation gun spraying – both of which result in poor bonding and increased surface roughness (Li Ohmori 1996). Explosive bonding is considered to be a solid-state weld-

ing process since melting is not required at the interface of the two materials in order for bonding to occur (Zimmerly et al. 1994). Moreover, as there is little to no diffusion between the two metals or alloys, each retains its intrinsic properties (El-Sobky 1993). This process makes it possible to join materials having greatly differing melting points without the need for intermetallic compounds – even those having the historic reputation of being incompatible (e.g., titanium and stainless steel, nickel and aluminum, etc.) (Gerland et al. 2000). This is contrary to what occurs in other techniques such as laser cladding (Kalla 1996, Yilbas et al. 1998).

Explosive cladding (EC) is a solid-state fusion welding process in which the joining of two metals is accomplished through the application of a shock pressure that results from the detonation of an explosive pack (Raybould et al. 1981). Material interaction at the mating surfaces during EC produces a “surface jetting” effect, ultimately resulting in a strong bond being formed between the metals (Raghukandan 2003). As it turns out, an effect analogous to this “surface jetting” is the main feature of GDS processes, suggesting that the EC and GDS are of the same fundamental nature. One should further note that the impact velocities of EC vary in the range of 1400 to 3900 m/s, while the particle velocities of GDS are known to have lesser values ranging from 500 to 1600 m/s for different carrier gases. Therefore, the intensity of “surface jetting” or jet flow in the GDS process seems to be less than that of EC. Unlike in EC, however, the particle impact velocity in GDS may be precisely controlled; it is through this control that the structure and material properties of the deposited layers may be managed.

1.3

Concluding Remarks

A comparison of competitive spraying technologies clearly shows that cold gas dynamic spraying has been established as a viable coating technology in the thermal spray processes family. The dense and oxide-free coatings that may be produced through GDS have brought about a multitude of new applications which, up to now, have not been feasible using traditional processes. As a result of many years of targeted and process-oriented groundwork by various researchers and manufacturers alike, both high- and low-pressure GDS engineering have reached advanced technological levels, facilitating efficient operation with a high degree of process reliability. As a result, practical solutions may be readily observed within such industries as automotive and electronics manufacturing. Despite this great progress, however, the full potential of high-pressure and low-pressure GDS has not yet been fully realized.