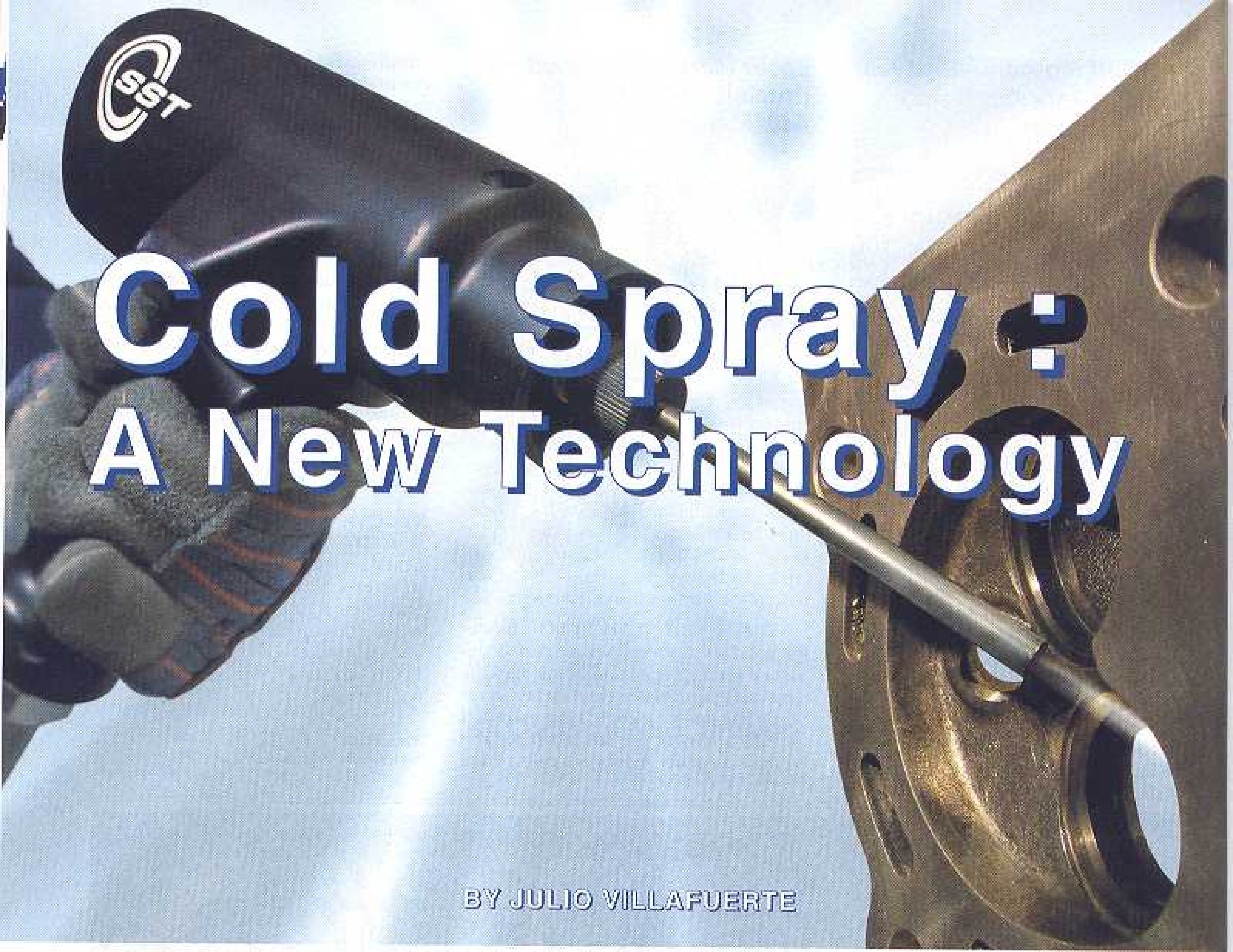

Cold Spray: A New Technology

BY JULIO VILLAFUERTE

Fig. 1 — Restoration of cast aluminum engine heads by cold spray. (Photo courtesy of Supersonic Spray Technologies, a division of Center-Line Windsor Ltd.)

A thermal spray-like process (without the heat) offers exciting possibilities in industry

A new solid-state spray process (Fig. 1) is quickly being adopted by many industries. Cold spray is capable of providing restoration, sealing, surface modification, wear resistance, thermal barriers, corrosion protection, heat dissipation, rapid prototyping, near net shapes, aesthetic coatings, and many other applications without the undesirable effects of process temperatures or metallurgical incompatibilities among materials.

Cold spray is capable of producing coatings or components made of metals, cermets, polymers, or composites. Its ability to prevent thermal effects such as oxidation, vaporization, melting, recrystallization, grain growth, and residual thermal stresses makes this new process unique for preserving the original characteristics of the feedstock materials. It is especially attractive for the processing of advanced industrial materials, such as those based on nanotechnology.

The process is known as cold gas dynamic spray, gas dynamic spray, kinetic energy metallization, kinetic spraying, high-velocity powder deposition, or simply cold spray. It is a new tool in the large family of thermal spray processes.

Similar to conventional thermal spray processes, cold spray produces coatings or freestanding deposits for a large number of applications in a wide range of industries. However, unlike conventional thermal spray processes, cold spray technology can deposit metallic and nonmetallic materials onto a diversity of surfaces at

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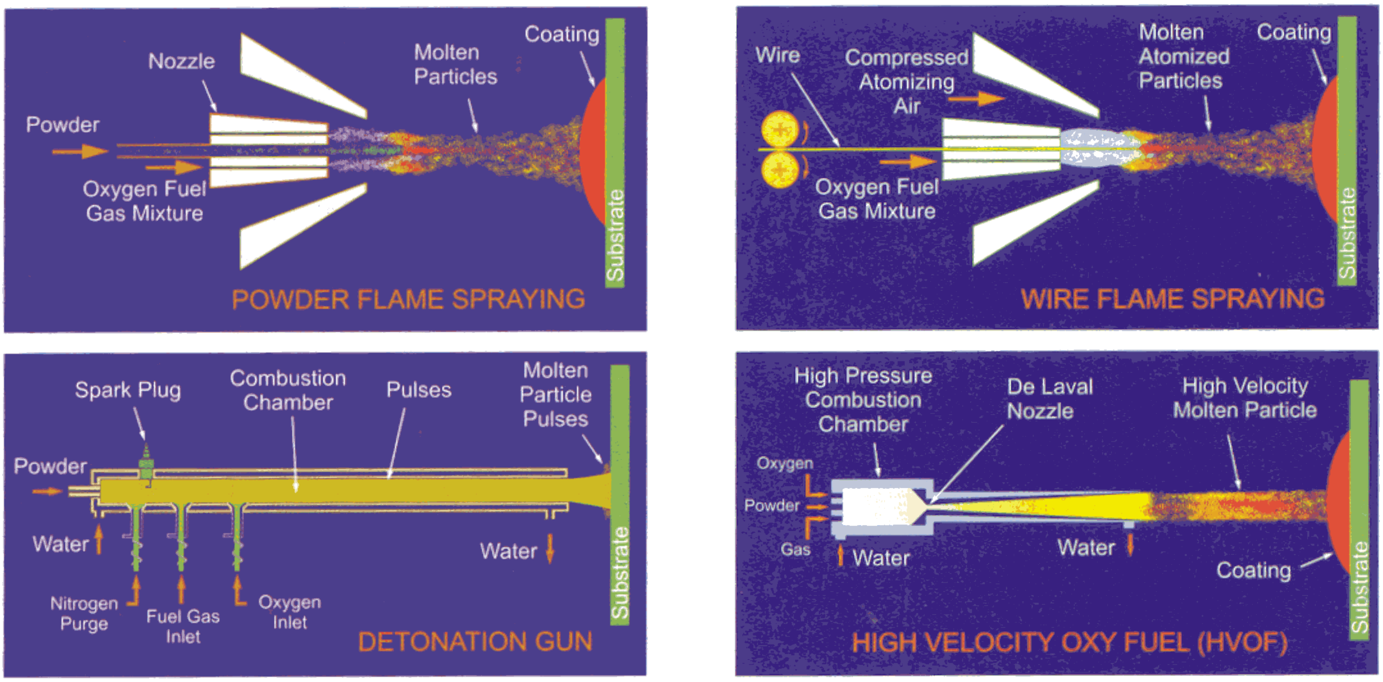

Fig. 2 Thermal spray processes based on combustion.

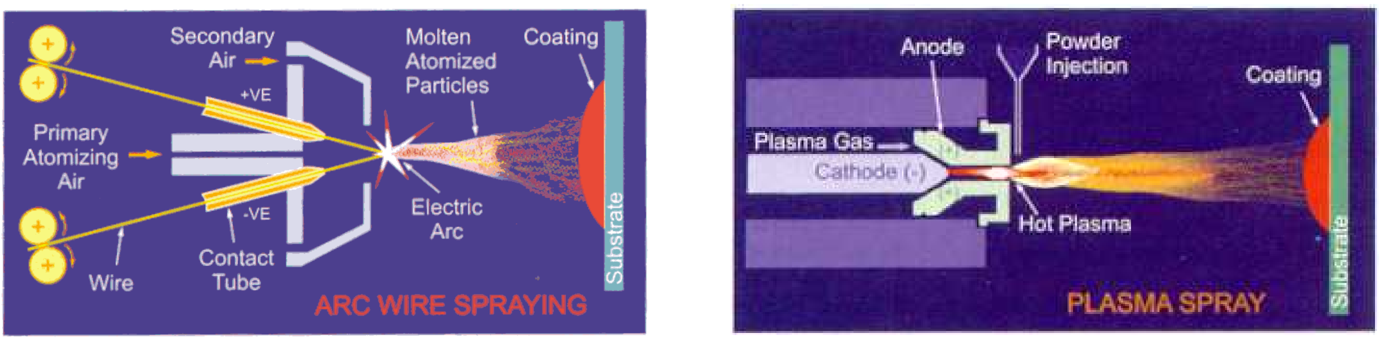

Fig. 3 Electric arc thermal spray processes.

much lower temperatures, virtually avoiding thermal effects. This article reviews the evolution of cold spray and describes its technology, applications, and benefits.

History of Thermal Spray

Thermal spray encompasses a family of coating processes used to apply metallic and nonmetallic coatings to a variety of metal substrates. In traditional processes, a feedstock material (typically in powder, wire, or rod form) is heated by combustion or electric arcing to form molten particulates, which are then confined and accelerated toward the substrate by a jet of hot gas. Upon collision with the surface, the particles become splats that conform and adhere to the substrate, solidifying and building up into a laminar structure.

Thermal spray, invented in the late 1800s, was originally known as flame spraying or metallizing. It was primarily used to restore worn metal parts and apply protective coatings. It became more important during and after World War II to repair tank and aircraft components.

Today, the number of applications for thermal spray is countless. Thermal spraying is used to improve resistance to corrosion, elevated temperatures, oxidation, and wear, as well as to enhance lubricity, restore lost material and provide aesthetic surfaces. The applications for thermal spray are found in aerospace, automotive, power generation, biomedical, heavy equipment, nuclear, mining, chemical, and electronics. The aircraft industry is perhaps one of the largest beneficiaries of thermal spray technology in applications such as the deposition of yttria-stabilized zirconia on engine components for thermal protection.

Based on the nature of the heat source, traditional thermal spray processes can be classified into two groups: ***combustion processes*** (powder flame spray, wire/rod flame spray, detonation spray, and high-velocity oxygen fuel) and ***electric arc processes*** (arc wire spray, plasma spray) (Ref. 1).

Combustion Processes

Flame spraying uses the heat generated by the combustion of fuel gases, typically acetylene, hydrogen, propane, or propylene, to melt the feedstock material, which can be fed into a spraying gun as powder, wire, or rod — Fig. 2. In powder flame spraying, powder is fed directly into the flame by a stream of compressed air or inert gas. In wire flame spraying, solid wire or rod feedstock is fed into the flame at a controlled feed rate. The combustion process is external, and the molten particulates are accelerated to relatively low velocities (< 100 m/s) by a compressed annular air jet.

The detonation gun or D-Gun™, a proprietary technology of Praxair Surface Technologies, uses a long water-cooled barrel with inlet valves for gases and powder. Oxygen and acetylene are fed into the

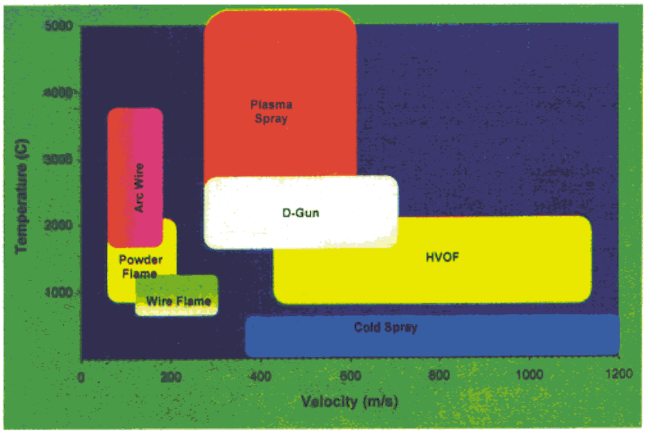

Fig. 4 — Process temperature and particle velocities for thermal spray processes.

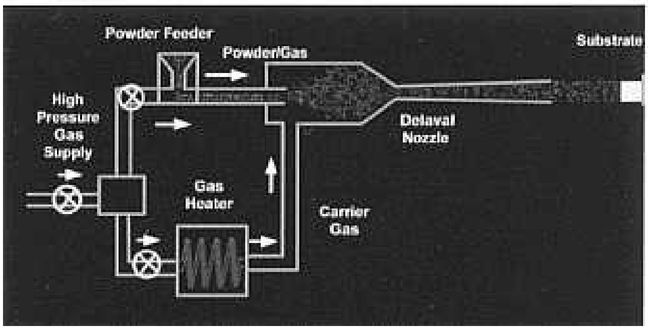

Fig. 5 — Schematic diagram of one cold spray system configuration (Ref. 3).

Table 1 — Existing Applications for Cold Spraying

Applications	Examples
Metal restoration and sealing	Engine blocks, castings, molds, dies, weld joints, auto body, HVAC, refrigeration, cryogenic equipment, heat exchangers (Ref. 8)
Thermal barriers	Aluminum piston heads, manifolds, disc brakes, aircraft engine components
Heat dissipation	Cu or Al coatings on heat sinks for microelectronics
Soldering priming	Microelectronics components and printed circuit boards
Electrically conductive coatings	Cu or Al patches on metal, ceramic, or polymeric components (Ref. 12)
Dielectric coatings	Ceramic coatings for aerospace, automotive, and electronic packaging
Antistick properties	Deposits impregnated with release agents such as PTFE or silicone
Friction coatings	Rolls for papermaking
Localized corrosion protection	Zn or Al deposits on affected helms, weldments, or other joints in which the original protective layer has been affected by the manufacturing process
Rapid prototyping and near-net manufacturing	Well-defined footprints. Fabrication of parts with custom composite or gradient structures
Biomedical	Biocompatible/bioactive materials on orthopedic implants, protheses, dental implants. Porous coatings of these materials on load-bearing implant devices facilitate implant fixation and bone in-growth, replacing cements and screws
Wear-resistant and decorative coatings	Numerous applications

barrel along with a charge of powder — Fig. 2. A spark is used to ignite the gas mixture and the resulting detonation heats and accelerates the powder at high velocities down the barrel. A pulse of nitrogen is used to purge the barrel after each detonation.

This process is repeated many times per second. The high kinetic energy of the hot powder particles results in the buildup of dense coatings on impact.

A recent addition to the thermal spray family is a process known as high-velocity oxygen fuel (HVOF). It uses the combustion of acetylene, hydrogen, propane, or propylene inside a pressurized chamber to produce a hot high-pressure flame. The flame is forced through a DeLaval nozzle to accelerate the carrier gas to supersonic velocities — Fig. 2. Feedstock powder can be fed axially into the high-pressure combustion chamber or directly through the side of the nozzle. The HVOF process has been established industry-wide as an alternative to the D-Gun™ and other thermal spray processes.

Electric Arc Processes

Arc wire spray uses a DC electric arc between two continuously fed consumable wires to produce molten spray material — Fig. 3. Compressed air or inert gas produces a spray of fine molten particulates that are accelerated toward the substrate at subsonic velocities (< 300 m/s). The process is simple and economically feasible for the deposition of conductive materials and the limited selection of ceramic materials that are available in wire form.

Plasma arc spray uses a DC electric arc between two nonconsumable electrodes (a thoriated-tungsten cathode and a copper anode within the torch) to ionize the inert gas to produce the high-temperature plasma jet — Fig. 3. Powder feedstock is introduced into the plasma jet where it melts and is accelerated to high speeds. The extremely high temperature of the plasma (> 10,000°C) makes this process suitable for spraying elevated-temperature materials, including a wide selection of ceramic materials.

How Different Is Cold Spray?

Traditional thermal spraying processes can produce high-quality coatings on a wide selection of materials, but their inherent high process temperatures expose the deposits and substrates to oxidation, metallurgical transformations, and residual thermal stresses caused by the uncontrolled solidification rates of individual particles as they hit the substrate.

The invention of cold spray is credited to a group of Russian researchers in the 1980s working at the Institute of Theoretical and Applied Mechanics at the Russian Academy of Sciences in Novosibirsk (Ref. 2). They demonstrated that when small particles (1–50 microns) struck a substrate at supersonic velocities, a bond could occur on impact. This differs from traditional thermal spray processes where particle velocities are generally lower, but particle temperatures can be quite high, as illustrated in Fig. 4.

How Does Cold Spray Work?

In one configuration (Fig. 5), helium or nitrogen is injected at high pressure into a pressurized chamber and heated to 300°–700°C — not to heat the particles, but rather to increase the velocity of the gas jet. Powder feedstock is introduced into the gas stream, which is not hot enough to melt the particles. The solid powder/gas mixture is then passed through a DeLaval nozzle where the particles are accelerated to supersonic velocities (Ref. 3). The particles impact the substrate with enough kinetic energy to produce mechanical/metallurgical bonding without melting and/or solidification.

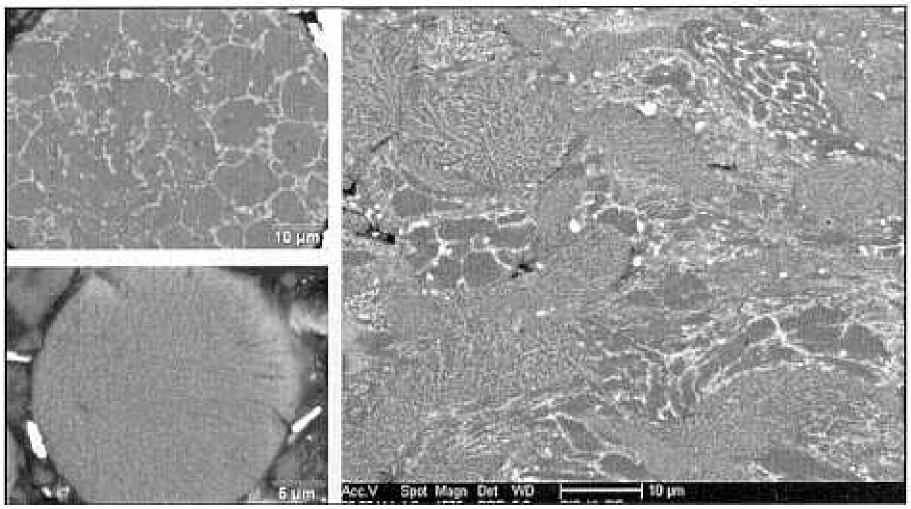

Fig. 6 — Left: Particles of AA2618 aluminum alloy with equiaxed (top left) and columnar (bottom left) grain structures. Right: Cold spray deposit produced with a blend of these two powders showing the preservation of the original grain structure for each of the powder constituents (Ref. 5) (Photo courtesy of the University of Ottawa, Canada.)

Upon deposition, sprayed materials do not exhibit significant microstructural changes, as illustrated in Fig. 6. Cold spray preserves the original microstructure of feedstock materials making it ideal for depositing nanograined materials — Fig. 7.

For a given material, there appears to be a range of supersonic velocities above which bonding most likely occurs, i.e., the deposition efficiency is considerably higher. Below this critical velocity range, particles are likely to be deflected from the surface causing surface erosion similar to shot or abrasive blasting. At velocities above this critical range, the deposition efficiency increases and the quality of the coatings improves (Ref. 4). The critical velocity ranges for pure metals such as Cu, Fe, Ni, and Al have been estimated at greater than 550 m/s (Ref. 2).

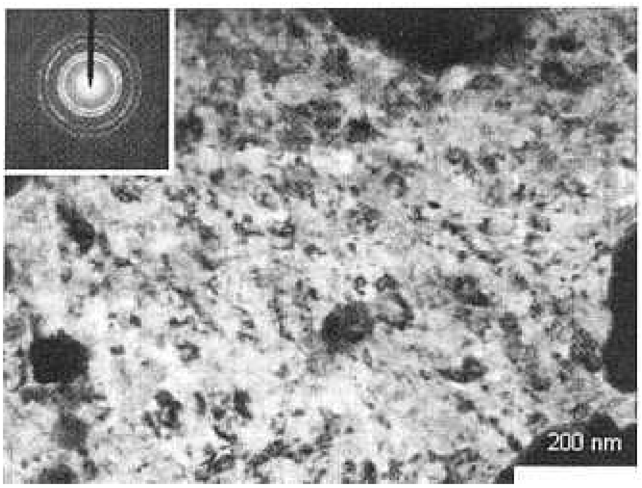

Fig. 7 — Transmission electron microscope photos showing nanograined structure of AA5083 aluminum deposited by cold spray (Ref. 6). (Photograph courtesy of the University of Ottawa, Canada.)

In a variation of this technology (Ref. 7), the powder feedstock is introduced downstream into the diverging section of the nozzle (Fig. 8). This eliminates the requirement for injecting powder into a pressurized compartment and avoids potential nozzle erosion and clogging. Through this approach, the development of portable cold spray equipment has been made possible — Fig. 9. The process only requires clean dry air at 80–90 lb/in.^{2} for its operation.

In this process, air is preheated to 200°–400°C inside a DYMET™ gun (Ref. 7) to maximize supersonic velocities at the diverging section of the nozzle. By using this method, a wide selection of materials can be deposited, including metal mixtures, metal alloys, cermets, epoxy resins, polyurethane, and thermoplastic poly-

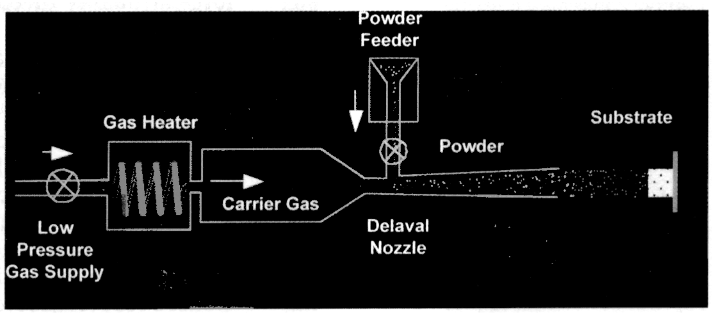

Fig. 8 — Schematic diagram of a variant of the cold spray process, where the powder is injected downstream in the DeLaval nozzle (Ref. 7).

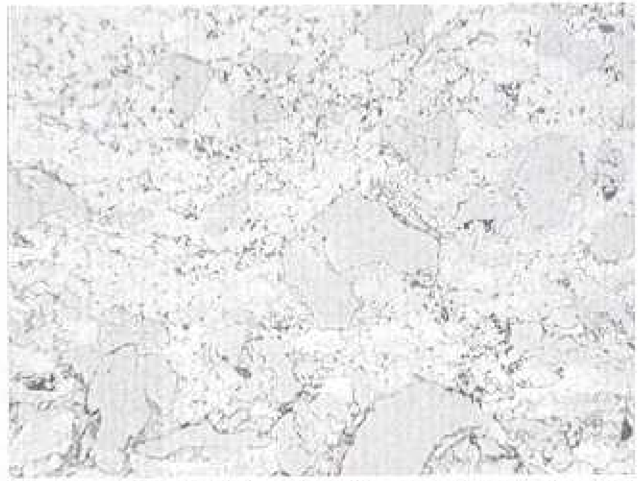

Fig. 10 — 50% Ti, 10% Al, 40% Zn particle blend deposited by cold spray using air as a carrier gas. (Photo courtesy of the University of Windsor, Canada.)

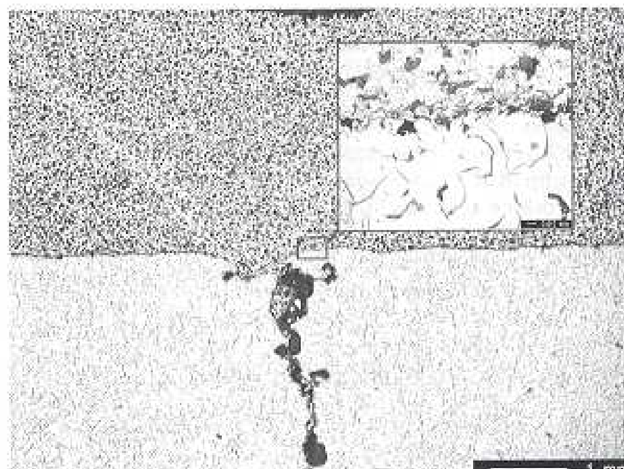

Fig. 9 — Portable cold spray machine using the configuration where the powder is injected directly into the downstream of the DeLaval nozzle. This design uses regular compressed air as a carrier gas. (Photo courtesy of SST, a division of CenterLine Windsor Ltd.)

Fig. 11 — Al-Al_2O_3 powder mixture on cast iron deposited by air cold spray to repair a shrinkage void in an engine block. (Photo courtesy of the University of Windsor, Canada.)

mers, over a wide range of substrates, as illustrated in Figs. 10, 11 (Ref. 8).

Bonding Mechanisms

The exact bonding mechanisms for cold spray are not clearly understood. Some propose that the high-velocity impact disrupts thin oxide films present on particles and substrate surfaces, pressing their atomic structures into intimate contact with one another under momentarily high interfacial pressures, which promotes localized atomic bonding (Ref. 9). On the other hand, the critical supersonic velocity for bonding appears to correlate with the velocities required to trigger a material instability known as "adiabatic shear instability," which often occurs in a plastically deforming material as it undergoes rapid shear straining (Ref. 10). This may be similar to the interfacial deformation mechanism associated with explosive cladding or shock wave powder compaction (Ref. 10). Plastic deformation of the powder material also helps enhance the mechanical properties of the deposit by work hardening.

Applications for Cold Spray

The range of materials and the metallurgical quality of cold spray deposits largely depend on the range of velocities that can be attained as well as the mechanical characteristics of the particles and substrate.

Helium is known to provide the highest supersonic flow velocities and, therefore, is capable of successfully depositing the widest range of materials in an oxygen-free environment. However helium is expensive, which requires the use of specialized recovery/recycling equipment to minimize cost. Nitrogen is cheaper and capable of providing an oxygen-free coating environment. However, the supersonic velocities obtainable with nitrogen are lower than with helium, which limits the range of coatings that can be produced. Air, on the other hand, offers the least-expensive alternative but has the narrowest range of known applications. Air is generally limited to applications not extremely sensitive to the presence of oxygen at low temperatures.

Localized plastic deformation at the particle-substrate interface appears to be necessary for the kinetic energy transformation. For this reason, the successful powders and substrates for cold spray are mostly metals with relatively high ductility. Nevertheless, mixtures of metals and ceramics can be successfully sprayed onto metallic surfaces and, conversely, metal powders can be successfully applied to ceramic substrates. Apparently the presence of a metallic component appears to compensate for the lack of ductility of the ceramic component. In general, the range of materials that could be successfully sprayed include pure metals such as Al, Zn, Cu, Fe, Ni, Ti, Nb, and Ta, composites such as $Al\text{-}Al_2O_3$, $Al\text{-}B_4C$, Cu-W, Cu-Pb-Sn, Co-WC, and ceramics such as TiO_2 (Ref. 11). Table 1 provides a list of known applications for cold spray. Figure 11 shows the microstructure corresponding to an $Al\text{-}Al_2O_3$ cold spray deposit on gray cast iron using air as the carrier gas.

The Benefits of Cold Spray

One of the greatest benefits of cold spray is its ability to deposit material at low temperatures. It virtually suppresses any metallurgical transformations or thermal reactions in either the deposited or substrate materials. Because grain growth, phase changes, recrystallization, thermal stresses, and oxidation are prevented; the process is uniquely suitable to deposit a wide range of sensitive and advanced materials. Other added benefits of this technology include the following:

- Extremely high density and compaction of deposited material
- No thermally induced residual stresses
- Minimal or no surface preparation required
- A wide selection of coating materials, including dissimilar materials
- Ability to custom-build the chemistry of multilayer deposits
- No generation of toxic gases, radiation, or undesirable chemical reactions
- Waste powder can be recycled
- Operates under normal temperature, pressure, and humidity conditions
- Well-defined localized coatings with near-net shape characteristics
- The shape of the deposit can be predetermined by the nozzle geometry.

Future Trends

Cold spray is an emerging technology that addresses many of the shortcomings of conventional thermal spray processes. The prospects of cold spray as an alternative process are wide open for novel applications unachievable with current practices. Already, cold spray has found multiple applications in many industries. However, much more research is needed to better understand and optimize the process so that its applicability can be extended into fields where existing practices have limitations. For example, since cold spray does not thermally affect the microstructure of powders or substrates, the process may be suitable for the deposition of nanocrystalline materials. Also, the ability of cold spray to produce compositional gradients could be further explored to develop ways of producing functional three-dimensional structures that may benefit from gradient structures.

Many new material combinations and applications are yet to be developed and therefore, the technology will go through multiple iterations in the endless pursuit for new and better ways of processing engineering materials.♦

Acknowledgments

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