# A Cold-Gas Spray Coating Process for Enhancing Titanium

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## INTRODUCTION

As we approach the 21st century, the importance of and need for improved energy efficiency, along with reduced emissions and other forms of pollution, will steadily increase. Titanium will play a crucial role in this area because of its tremendous potential for weight savings in automobiles and aircraft. However, many of the properties of titanium, such as strength, wear resistance, specific corrosion/oxidation resistance, and its ability to be securely bonded with alternate (metallic and nonmetallic) materials, must be improved to allow all of the potential benefits of titanium to be realized. Moreover, there may also be many applications where it is desirable to modify the behavior of other materials (again, metallic or nonmetallic) with the properties of titanium to enhance their capabilities. In either case, one viable method for overcoming these challenges is through the use of protective and/or enhancing coatings.

Many thermal-spray-coating technologies are currently available to improve the characteristics and performance of the surface. The most widely used methods include high-velocity oxy-fuel (HVOF), detonation guns, plasma spray, flame spray, arc spray, and electron beam-physical vapor deposition. While these methods have been used successfully to improve wear performance, provide thermal barriers for high-temperature applications, and decrease corrosion damage, they are not without potential problems and difficulties. Many of the problems associated with traditional coating methods arise because of the high temperatures required to heat the coating material (usually in particulate form) to a melting temperature and deposit it onto the surface. The high deposition temperatures often preclude the application of titanium or other coatings to the surfaces of low-melting-point materials, such as plastics. Moreover, any materials where phase transformations, excessive oxidation, evaporation, and/or crystallization are possible may not be successfully coated. Additional problems often arise from the residual stresses and deformations induced by the thermal-coefficient-of-expansion mismatch that develops as the coating and substrate cool down after deposition. Even if the coating remains bonded to the substrate, the residual stresses may cause unacceptable distortions, significantly weaken the bond strength, or accelerate fatigue failures. Ultimately, the usefulness of the coating is lowered, and the cost is increased, especially for many demanding automotive and aerospace applications where robust coatings and tight tolerances are required.

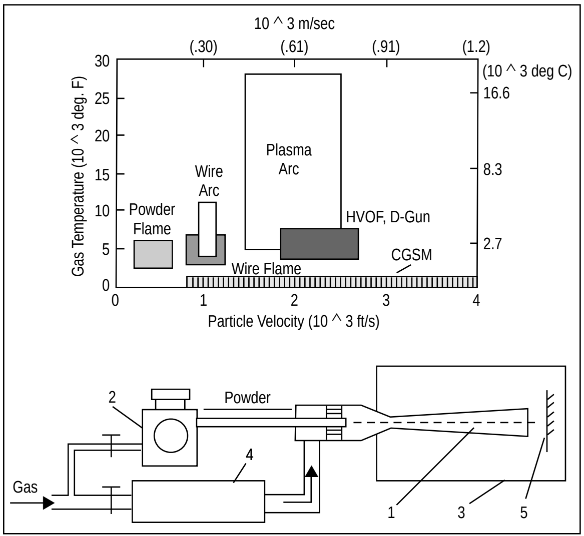


Figure 1. A schematic of the cold-gas spray method (CGSM). 1—supersonic nozzle, 2—powder feeder, 3—dust-insulating chamber, 4—gas heater, 5—a product being deposited.

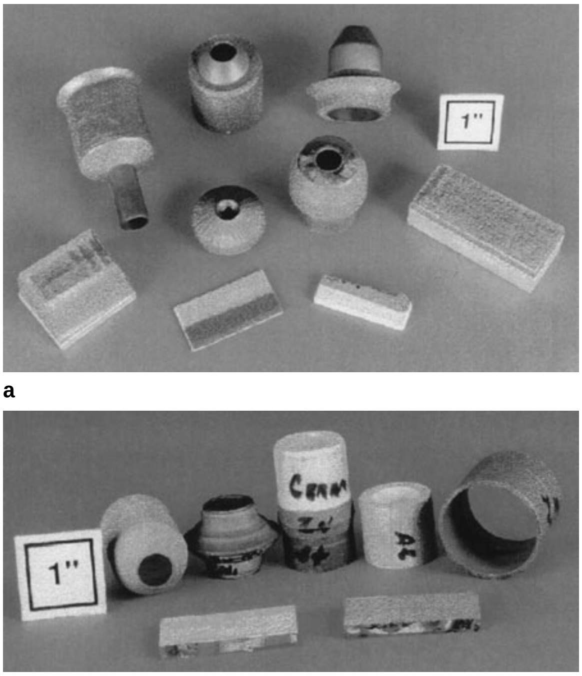
## COLD-GAS SPRAY

To overcome the difficulties of coating technologies, a new method of coating deposition, known as the cold-gas spray method (CGSM), has been developed. Originally conceived in Russia and later patented in the United States in 1994 by inventor Anatoli Papyrin, the CGSM is a promising lower-temperature thermal spray method.[1–7] In contrast to conventional thermal spray methods,[8–18] the cold-gas spray process rapidly and efficiently creates a coating (or new material by solid-state spray forming) through a process related to friction welding by exposing a metallic or dielectric substrate to a high-velocity jet of solid-phase particles. The practical feature of the CGSM is that the solid-phase particles are accelerated by a supersonic jet of gas at temperatures much lower than the melting or softening temperature of the coating and substrate materials.

Figure 1 shows a schematic of the CGSM system. The propulsion gas at an elevated pressure is introduced to a manifold system containing a gas heater and powder metering vessel. Heating of the pressurized gas is accomplished electrically, in contrast to the thermal spray methods. The high-pressure gas is introduced into a de Laval-type nozzle with compression through a throat region and then expanded to nominally atmospheric pressure to achieve supersonic flow. The powder feedstock is introduced on the high-pressure side of the nozzle and delivered by a precision-metering device. Using an enclosure and conventional dust collection devices, it is possible to continuously recycle particles not incorporated into the coating.

To form new materials and/or coatings, three conditions must be met. First, the jet temperature must always be lower than the melting or heat softening temperature of the particulate and substrate material. Second, the particle sizes must be in the range of 1–50 μm. Third, particle velocities must be in the range of 300–1,200 m/s, depending on powder material and particle size.[1,2,4]

In practice, the CGSM can be used with the aid of a supersonic gas jet at a stagnation pressure of 1–3 MPa with a nozzle mach number 2–4. Various gases, such as air, nitrogen, and helium, can be used to provide the necessary particle velocity. Although gas preheating can also be used to increase the gas discharge and particle velocity, the distinguishing feature of the cold-gas method is the ability to produce coatings under relatively low jet temperatures in the range of 0–500°C. As a consequence, the deleterious effects of high-temperature



a

b

Figure 2. The cold-gas spray method can be used to (a) coat and/or create titanium billets as well as (b) coat alternate materials in a wide variety of shapes and sizes.

oxidation, evaporation, melting, crystallization, residual stresses, debonding, and gas release can be avoided.

Additional advantages of the CGSM include the ability to produce coatings with properties that are close to the original powder and/or substrate, the production of composite coatings using powder mixtures, the absence of severe thermal exposure and oxidation of the powder and substrate, safer manufacturing because of the absence of high-temperature jets and excessive noise levels (70–80 dB), higher productivity and reduced use of resources during operation, the ability to continuously recycle powder particles during deposition, narrow coatings with widths of 1–2 mm without masking, and the unique ability to apply coatings to the inside surface of tubes and other complex shapes. Because of these advantages, the CGSM has a strong potential to become an enabling technology for the titanium industry that will allow greater weight savings and energy efficiency by building and using titanium (or other alloys) as a coating or enhanced substrate. Moreover, the coating process itself is more economical, energy efficient, and safer because it does not rely on excessively high temperatures to work.

## ECONOMICS AND MARKET POTENTIAL

The versatility of the CGSM provides a very broad range of potential applications in the energy, automotive, aerospace, shipbuilding, farming machinery, electronic, and instrument industries where the CGSM process and titanium can be used. Many of the research needs are outlined in the report that resulted from the Titanium Technology Roadmap Workshop.[19] One possibility is the development of wear-resistant alloys or the application of wear-resistant coatings on titanium pistons and/or other high-wear components. Wear-resistant coatings could be used on the internal surface of a titanium cylinder block for internal combustion engines, pumps, and hydraulic cylinders for automotive, heavy machinery, medical, and aerospace applications. Electroconductive titanium or other alloy coatings could be used on glass, ceramics, and plastics for automobile rear-window heaters and electronic contacts, as well as for solar-cell power generation. Moreover, titanium coatings on the internal and external surfaces of tubes can improve corrosion resistance and/or thermal performance. The CGSM could also aid in joining different materials (ceramics-metal, glass-metal, etc.) or in the inexpensive repair of titanium or other alloy components.

The CGSM has additional economic and energy advantages over traditional thermal spray methods. For instance, typical deposition efficiencies for thermal spray methods, as well as for the CGSM, are around 50%. However, for traditional thermal spray methods, any residual powder cannot be reused because of oxidation at the high jet temperatures required for the process. In contrast, the CGSM is free from this disadvantage due to the lower jet temperatures used during the coating process. Because the powder is relatively unscathed during the process, great savings can be achieved by recycling the unused powder in subsequent coat cycles. With continual recycling, coefficient-of-powder-use rates of up to 100% can be reached.

The potential benefits of the CGSM are not just limited to the reduced materials and/or the possibility of recycling unused powder. As mentioned earlier, the CGSM provides high-quality titanium coatings at jet temperatures of 150–200°C compared with the much higher temperatures (2,000°C) required for traditional thermal spray methods. In this case, a relatively simple calculation can show that the power required for the CGSM jet heating is about 5-6 kW at powder feed rates of 3–5 kg/h. In contrast, the typical power requirement for jet heating in a plasmatron is approximately 30 kW for the same or lower powder feed rates. Although data on the number of coatings applied each year are not available, the potential for large industrial savings in terms of the cost and energy required is tremendous.

Because the high temperatures used by traditional thermal spray methods are limiting, the industrial potential and relevance of the CGSM becomes even more important when coatings with special properties and/or repairs to or with titanium are required. One such requirement for many applications is to provide coatings with low levels of oxides. It is difficult to solve this problem with traditional thermal spray units because of the high jet temperatures required by the process and the rapid oxidation that ensues. Special equipment and processors, such as shroud systems on the base of the inert gas and deposition in vacuum, must be used to avoid oxidation. As would be expected, these requirements are expensive, often costing tens of thousands of dollars for the equipment alone. In contrast, the cold-spray apparatus provides low levels of oxides without any additional equipment (and, hence, additional expenses) because of the low-temperature nature of the process.

Another promising quality of the CGSM is its ability to repair components that have been damaged by mechanisms such as wear during usage. While thermal spray methods can be used to repair titanium components in some instances, all of the problems associated with the high-temperature jet and associated costs will remain. In contrast, the CGSM is capable of making repairs without causing any damage to the substrate materials or powder used for the repair. In fact, there is no reason why the CGSM cannot be used repeatedly to manufacture and repair worn or damaged components over a number of operational cycles. The cost savings for a relatively simple repair operation using the CGSM compared with manufacturing new components from new or recycled titanium (as well as other alloys) can be significant.

While traditional economic analyses focus on the costs of materials, energy, and equipment, the CGSM also offers a number of distinct health, safety, and environmental advantages over traditional thermal spray methods. Because of the lower jet temperatures used by the CGSM, the amount of thermal radiation and metal vapor the operators are exposed to is significantly reduced. This, in turn, makes the entire coating/repair process, much safer for the operators. Moreover, the process is quieter than traditional thermal spray methods with relatively low levels of noise (70–80 dB). In contrast to the CGSM, many thermal spray methods, such as plasma, HVOF, or detonation guns, generate unusually high and damaging noise levels of 130–140 dB+.[12,16,18] Because of these hazards, special (and costly) rooms and remote control protections for the operator are required. As a consequence, additional expenses, including energy usage (thousands of dollars), are added.

## KEY EXPERIMENTAL RESULTS

Before the goals and benefits of the CGSM can be realized, the process must be developed and demonstrated as viable for the spray forming of new materials, as well as for the application of coatings to a variety of engineering materials. Because of these needs, a study was conducted to demonstrate the viability of the proposed process.

The program mandate was modified to incorporate spray forming, according to Battelle's request. The first task of the study was to demonstrate the feasibility of using the CGSM to produce billets of new material and the potential for spray forming complex shapes. During this important phase of the study, 45 µm (±15) powdered titanium (supplied by F.J. Brodman and Company of Harvey, Louisiana) was spray formed onto flat and cylindrical mandrels at deposition rates as high as 13.1 $cm^3$/min. using 1.5 MPa jet pressure (nitrogen) at a jet temperature of 260°C. The spray distance was 3.8 cm. The gas-flow rate was 1.68 cmm, and the powder-feed rate was 6.8 kg/h. The deposition efficiency was ≥50%.

The production of relatively thick billets of different shapes and sizes is clearly possible using the CGSM (Figure 2). Moreover, the direct deposition of titanium also demonstrated the potential of the method to produce near-net-shape billets for both planer and axisymmetric configurations. The addition of computerized multi-axis positioning would allow the process to be used for increasingly complex shapes.

The CGSM was also used to coat and enhance alternative materials with titanium. For this portion of the study, titanium was deposited onto the surface of an alumina ceramic and a plastic, as shown in Figure 2. The results of these studies indicated that titanium could indeed be applied to these materials; however, an intermediate bond coat was required for the alumina ceramic tested. While the direct deposition of titanium onto a plastic was possible, an intermediate layer may also be required to ensure adequate electrical conductivity. Nonetheless, in both cases, the study demonstrated that titanium can be directly deposited onto a variety of materials, with the potential of properties improvement.

Another important aspect of the program was to demonstrate the ability of the CGSM to enhance the surface and wear properties of titanium. Toward this goal, a wear-resistant $Cr_3C_2$-20Ni-5Cr coating was applied directly to a titanium substrate. Jet pressure (nitrogen) was 1.5 MPa at a temperature of 482°C. The spray distance was 2.5 cm. The gas-flow rate was 45 cfm, and the powder-feed rate was 9.5 kg/h. The deposition efficiency was ≤50%.

The 45 µm (±15) powder used for the coating was supplied by Sulzer Metco (Troy, Michigan). Initially, the desired coating was set to be approximately 3.1 mm thick to facilitate bond strength measurements. However, during the coating process, it was found that the maximum coating thickness that could be practically achieved was restricted to 1.5 mm because of the limited ability of $Cr_3C_2$-20Ni-5Cr to bond with itself during deposition. While the apparent inability to generate thicker $Cr_3C_2$-20Ni-5Cr coatings resulted in a reduction of the overall deposition efficiency, the relatively hard coating was still able to bond reasonably well with the underlying titanium in thicknesses deemed sufficient for the reduction of wear.

The next phase of the testing involved an evaluation of the wear characteristics of the $Cr_3C_2$-20Ni-5Cr coating relative to uncoated titanium using a pin-on-rotating-disk configuration. With the rotating speed set to 600 rpm and the contact pressure held constant at 3.4 MPa, the coated and uncoated 6.35 mm diameter pins were first worn against the circumference of a titanium disk until the originally flat pin conformed to the curved surface of the disk. Once the wear-in period was completed, the loading process was repeated for five 10 s intervals to ensure measurable wear. The pins were then allowed to cool and were weighed. The volumetric loss was computed using a $Cr_3C_2$-20Ni-5Cr density of 6.02 $g/cm^3$. This process was then repeated until sufficient data points in the steady-state (linear) wear region were obtained. As expected, the titanium on titanium produced relatively high steady-state wear rates of $1.58 \times 10^{-6}$ $cm^3/m$ as a result of excessive galling on the mating surfaces. However, the addition of a protective $Cr_3C_2$-20Ni-5Cr coating resulted in an order-of-magnitude reduction in the steady-state wear rate to $1.4 \times 10^{-7}$ $cm^3/m$.

Bond-strength measurements were also made using unworn pins and a custom shearing device. During these tests, a shear load was applied to the side of the $Cr_3C_2$-20Ni-5Cr coating until debonding occurred. The required shear stress for failure was then calculated using the cross-sectional area of the 6.3 mm diameter pins. Based on a limited number of tests, a relatively high bond strength of 413 MPa was measured. This reasonably high value, combined with the survival of the pins during the wear testing, indicates the robustness of the coating and process. While further study is warranted, the coatings appear to be quite capable of remaining intact under relatively severe wear conditions.

## FUTURE DEVELOPMENT

Because of the many possible applications and potential for the method, further R&D is warranted. However, because the method and equipment are already past the prototype stage, these efforts should focus on further optimizing the method and parameters required for specific applications. The parameters requiring further application-specific studies include, but are not limited to, deposition rates, gas and gas temperature, properties grading, and in-situ alloying. Furthermore, research into intermediate bond coats to enhance bond strength, electrical properties, and/or corrosion properties is also warranted. Finally, engineering research is required to help develop the equipment and method for industrial production of coatings and new alloyed/graded materials. The inexpensive production of new materials with carefully controlled and/or graded properties holds tremendous potential for many industries and technologies.

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