FULL CRITICAL REVIEW

The unique abilities of cold spray deposition

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Cold spray material deposition differs significantly from other thermal spray systems in that the cold spray process does not melt particles, particle velocities are very high, and the gas/particle jet plume has a relatively low temperature. Cold spray can thus be applied to applications with heat-sensitive substrates or those applications that do not allow heat-modified deposits. The impact consolidation of high velocity, solid state, particles yield cold spray depositions with high strength, low porosity and minimal or compressive residual stress. This review will be useful to individuals new to cold spray, as well as to the cold spraying community and to product developers needing cold spray capability. The applications presented here can demonstrate capabilities that are of use to new and related uses. The descriptions of the equipment and techniques used to create the cold-sprayed deposits will be helpful to those individuals and firms seeking to produce products requiring similar characteristics.

Keywords: 'Cold spray', Coatings, Particle, Consolidation, Nozzle

Introduction

Originally developed in Russia, cold spray systems have been commercially available for less than 20 years. A group of scientists from the Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Sciences in Novosibirsk, Russia, discovered a means of depositing metal coatings by means of high-speed particle impacts. This effort leads to two USSR patents – the invention of a method[1] and a device[2] for accelerating powder particles by a high-pressure gas at temperatures significantly below the metal melting points in order to apply a dense, highly bonded coating. One of the inventors, Professor Anatolli Papyrin, subsequently moved to the USA, where he pioneered the development of cold spray technology in industry and academia. This process was issued the US patent in 1994.[3] This coating process, which they called the cold gas dynamic spray method, has since successfully permitted the deposition of a large variety of materials such as metals, alloys, polymers or mixtures. While many other patents followed, these three were the fundamental proprietary framework of the cold spray principle.

Cold spray differs significantly from thermal spray systems, such as high-velocity oxygen fuel (HVOF), as the process does not melt particles, particle velocities are very high, and the jet plume and particles have relatively low temperatures.[4] The unique characteristics of cold spray operation allow it to be applied to temperature-sensitive substrates. The high velocity, solid state, particles yield depositions with low porosity and minimal or compressive residual stress. Cold spray can thus be applied to applications that do not allow substrate heating or heat-modified coatings and to those applications that require non-porous, well-consolidated deposits.

Cold spray systems are currently operated at research institutions, universities and corporations worldwide, with more than 10 active countries and hundreds of installations in Europe, Asia and the Americas represented. The new cold spray systems are distinguished by large, stationary systems[5–7] and by smaller, portable systems.[8–10] All cold spray systems operate through the aerodynamic acceleration of small particles, which subsequently form a deposit through impact with a surface or with previously deposited particles. The generic term cold spray is meant to designate this processes, and several other names such as cold gas dynamic spray, kinetic spray, kinetic metallisation (KM) and dynamic metallisation, are also used in practice. Irissou *et al.*[11] summarised all cold spray related equipment and application patents issued between 1900 and 2007. A total of 164 patents and patent applications were reviewed.

Cold spray technology is applicable to many purposes.[12–17] It is often used for protective coatings, where its low temperature deposition and non-porous structure can yield coatings for environmental and wear protection on most substrates, including those that are heat sensitive. Pure metals and alloys of all types can be cold sprayed. Extremely hard metals, such as tungsten, must be cold sprayed with a ductile metal binder. In addition to coatings, cold spray can produce thick deposits which can be used for dimensional restoration of damaged or out-of-specification parts. The high velocity, solid state, particle impact and deposition of cold spray yields a unique structure that is strong and impervious, providing unique repair opportunities.

Emerging applications include coatings, repairs and free-standing structures. The applications vary from trials to commercially available products. The applications are

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similar with respect to their need for the attributes of cold spray operation and deposits. Coatings vary from corrosion protective films to catalytic surfaces. Component repairs include aircraft and castings. Heat exchangers, tubes and gears are some structural applications that have been cold sprayed. Electrical applications include conformal antennas, circuitry and electromagnetic shielding. Biological applications such as self sanitising surfaces and bone repairs can be accomplished with cold spray. This review describes applications that have been identified and how cold spray has been utilised for these applications. Potential applications that have been identified through experimental cold spray work and modifications of the cold spray process that can lead to newer applications will also be examined.

The cold spray process

Physics

Figure 1 is the diagram often used to illustrate this process.[18] The cold spray process as shown imparts supersonic velocities to metal particles by placing them in a high pressure, heated air, nitrogen or helium gas stream that is expanded through a converging–diverging nozzle. High pressures and temperatures yield high gas velocities and high particle acceleration within the gas stream. The particles, entrained within the gas, are directed towards a surface, where they embed on impact, forming a strong bond with the surface. Although initially the gas is heated to 400–1100°C, the term 'cold spray' has been used to describe this process due to the relatively low temperatures (100–500°C) of the expanded gas stream that exits the nozzle. The relatively high gas pressures used for this geometry (10–60 bar) result in the name High-Pressure Cold Spray.

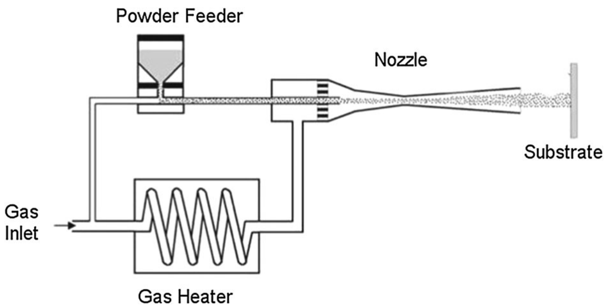
Subsequent spray passes increase the structure thickness. The adhesion of the metal powder to the substrate, as well as the cohesion of the deposited material, is accomplished in the solid state. Figure 2 is a photograph of a cold spray system at the Army Research Laboratory, where a robot arm controls the movement of the nozzle. This arrangement is typical of cold spray systems worldwide.

A variation of this process injects the powder downstream of the nozzle throat where the gas pressure has been reduced through expansion. Generally, but not always, lower pressure gas is used for this geometry. This variation is called low pressure cold spray (LPCS) and is often used in portable systems because high-pressure powder feeders are not required. The low pressure system can be robot controlled or hand-held.

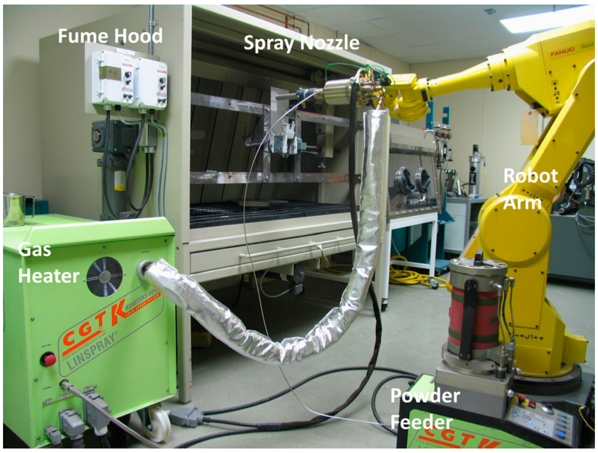
Sprayed particles must reach a 'critical velocity' before impact, which results in consolidation with the surface. This required minimum velocity is different for different metals and typically varies between 500 and 800 m s^{-1}. The gas used for particle acceleration can be nitrogen, helium, a mixture of the two, or compressed air. While considerably more expensive, helium gas produces much higher particle velocities. Equipment is commercially available for helium recycle which can greatly reduce its consumption in those cold spray applications where helium is required. An example of the acceleration of a 20 μm diameter copper particle in a nitrogen gas stream is shown in Fig. 3, which has been created by 1-D isentropic and 2-D, computational fluid dynamics modelling.[19] In this case, the initial temperature and pressure of the gas are 500°C and 30 bar, respectively. The gas expands and accelerates through the 174 mm nozzle as its temperature decreases. Very rapid changes take place at the nozzle throat, where gas sonic velocity is reached. Particle velocity and temperature approach gas values as drag and heat transfer occurs. Particle shape affects the velocity to which the gas flow can accelerate it.[20] A shape subject to higher drag force, such as a granular shape as compared to a sphere, will experience higher acceleration and subsequently higher velocity. Similar model results are presented by many cold spray analysts.[21–26]

Since feedstock powder has a distribution of particle sizes, not all particles will accelerate to critical velocity. Larger and slower particles often do not attain critical velocity and bounce off the surface. The deposition efficiency (powder that deposits divided by total mass of powder sprayed) can vary greatly, from 10% to greater than 95%. Particles that do not deposit can be captured and recycled in the production of new powder.

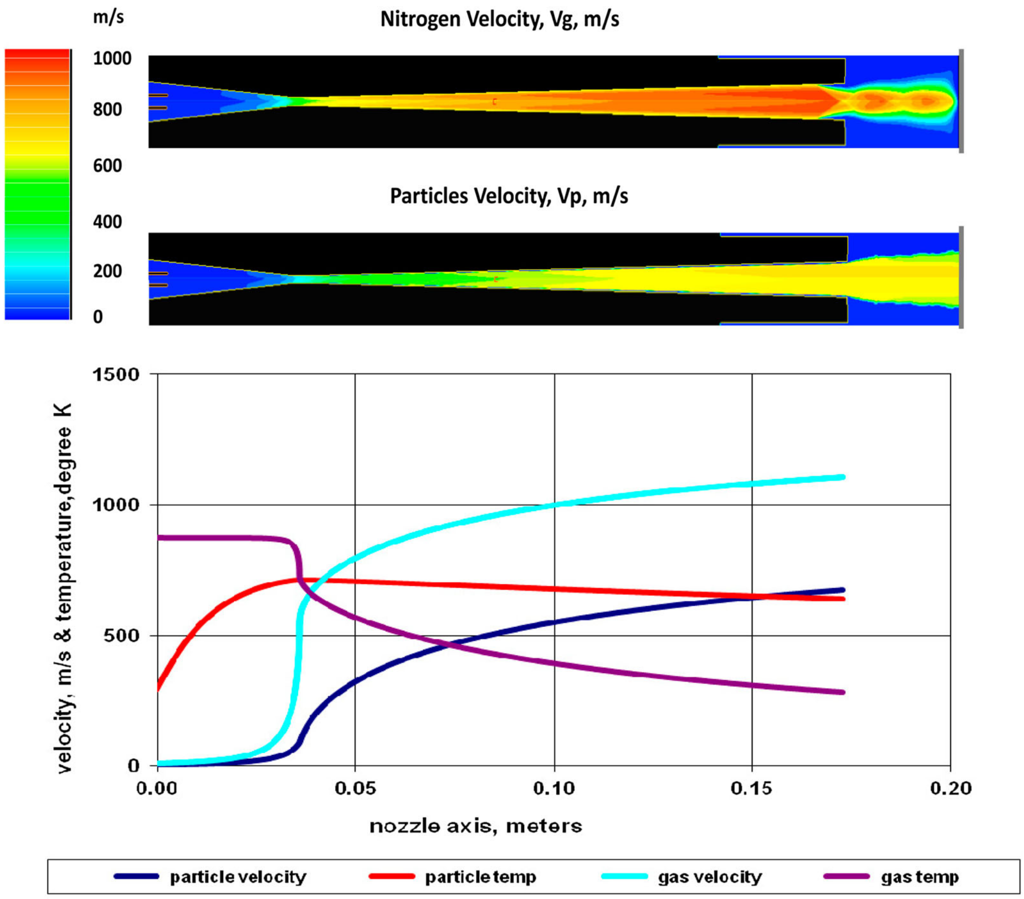
Upon impact with an aluminium surface, the sequence of deformation of a 20 μm copper particle, travelling at 650 m s^{-1}, is shown in Fig. 4.[27] The simulation of the impact process is carried out using the CTH computer code which was developed at the Sandia National Laboratory. The figure shows that as the particle/substrate contact time increases, the particle flattens while the substrate crater depth and width increase. At the same time, a jet composed of both the particle material and the substrate material is formed at the particle/substrate contact surface. Simultaneously, there is a temperature rise, concentrated at the particle/surface interface. This



1 Typical cold spray assembly



2 Cold spray equipment arrangement



3 Particle and gas velocities and temperatures within a cold spray nozzle

temperature rise is an indication of shear instability, which causes extensive flow of material at the corresponding surfaces, and the estimated impact velocity to induce shear instability compares fairly well with the experimentally determined critical velocity of copper. This means that, as in the case of explosive welding of materials, bonding in cold spray is a result of the shear instability at the interacting surfaces. Similar plastic deformation impact models have been developed by many researchers.[22,28–32] Ghelichi *et al.*[33] and Moridi *et al.*[34] utilise impact deformation models to predict particle critical velocities.

Deposit characteristics

The attributes of cold spray include low temperature deposition, dense structures and minimal or compressive residual stress. In addition to these characteristics, the deposited material possesses strength close to or above that of wrought material. An example of the consolidated deposit produced by the cold spray deposition of 6061 aluminium alloy is shown in Fig. 5.[35] Helium gas was used to accelerate the 6061 aluminium particles. Individual particle splats can be identified and the dense, nonporous nature of the consolidated particles is clear, with measured porosity less than 1%. Similar cold spray microstructures are observed for Cu,[36,37] Ti,[38] Ta[39] and WC–Co.[40] Powders can be created in which individual particles consist of an inner core material, encapsulated within an outer shell of another material. After deposition by impact, the individual deformed particles generally retain a core–shell morphology.[41]

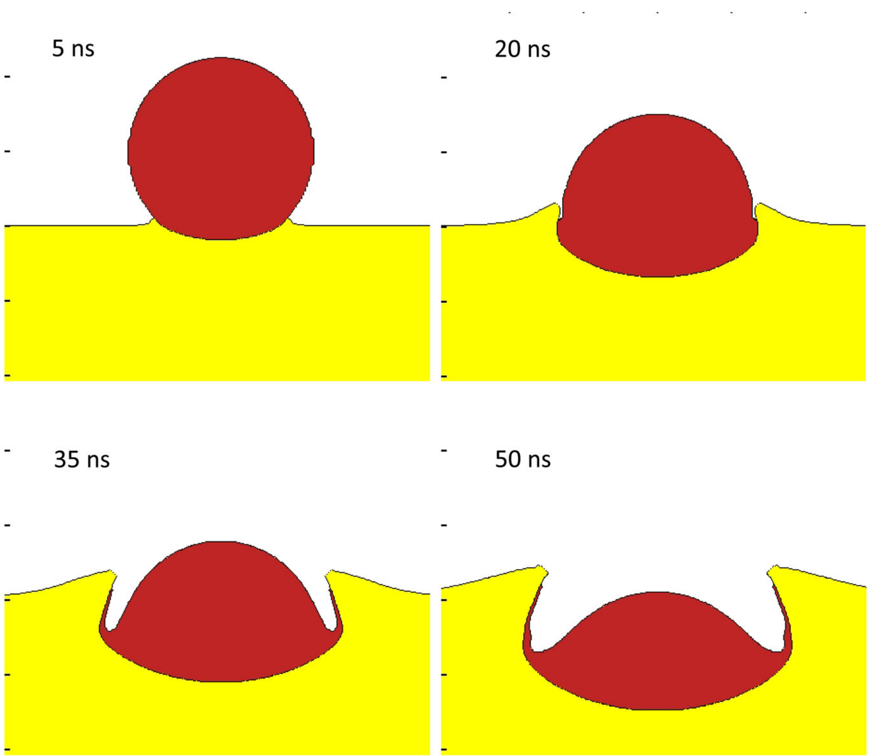
In the as-deposited state, cold spray deposits can exhibit higher strengths than wrought alloys. Figure 6 compares the strength characteristics of cold-sprayed 6061 aluminium alloy with those of wrought 6061 alloys of various heat treatments.[35] When annealed, cold spray deposit strength decreases, but elongation and ductility increase.

These examples show that cold-sprayed materials can have physical characteristics similar to wrought materials. Such characteristics allow cold spray repairs to closely mimic or surpass in strength the material that is repaired. In addition to good strength characteristics, the repairs can be easily accomplished and cosmetically acceptable. Similar results have been reported by Barnes *et al.*[42] for CP Al.

High-velocity particle impact results in work hardening of the completed deposit. Initially soft particles are strain hardened during impact, resulting in a structure that can have a hardness value greater than that which can be achieved by conventional cold working. Champagne *et al.*[43] show that the Vickers hardness of cold-sprayed aluminium can be 25–50% harder than conventionally hardened aluminium, depending on particle deposition velocity.

Uniqueness

Figure 7 presents the operating window for common metal spray technologies. Compared to conventional thermal sprays, cold spray is characterised by the lowest temperature and highest velocity. The operating temperatures of conventional plasma, detonation and HVOF produce



4 Deformation of a 20 μm copper sphere striking an aluminium surface

melted particles, which shrink upon cooling, leaving high tensile residual stresses. Since particles are not melted for cold spray, the resulting deposits exhibit moderate compressive residual stress. In addition, the grain structure of cold-sprayed particles remains largely unchanged during deposition, unlike that of the melted and resolidified particles in conventional thermal sprays.

A military standard, MIL-STD-3021, entitled 'Materials Deposition, Cold Spray', was issued in 2008 and revised in 2011. This standard is approved for use by all departments and agencies of the Department of Defense, and applies to the military equipment repairs described below. The standard describes cold spray operating procedures and test methods.

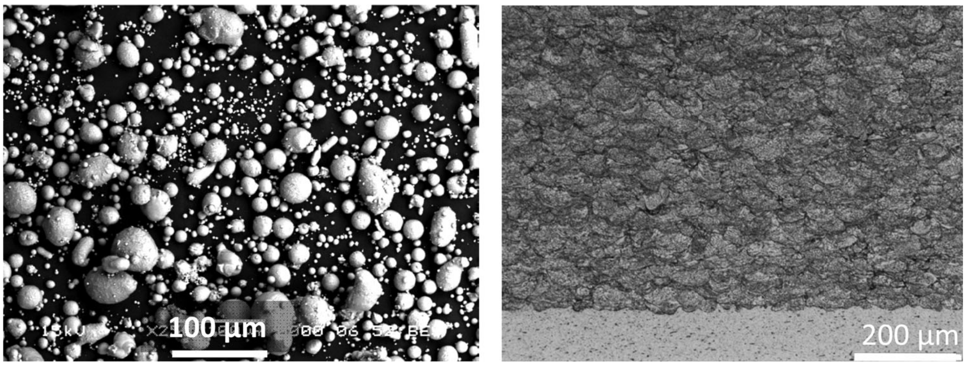
Coatings

Coatings are applied to surfaces for many reasons, often related to protection or surface functionality. Coatings are generally no more than 1 mm in thickness and sometimes less than 0.1 mm. Cold spray is often the method of choice to apply a coating to temperature-sensitive substrates and/or coating powder.

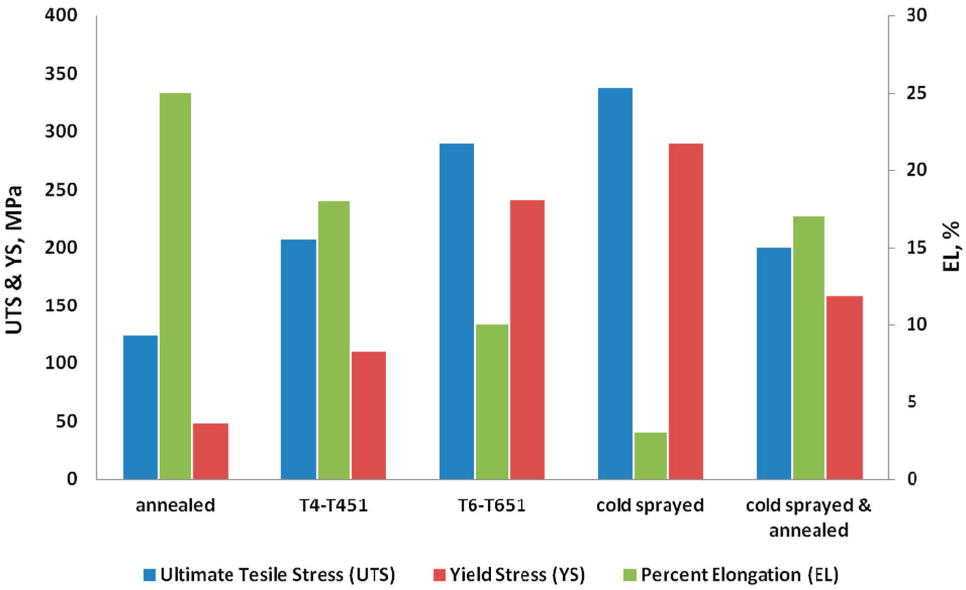
Corrosion protection

Magnesium is approximately 35% lighter than aluminium and has exceptional stiffness and damping capacity. Accordingly, Mg alloys, because of their high strength-to-weight characteristic, are used for the fabrication of many components on military aircraft, especially for complex components such as transmission and gearbox housings on helicopters and fixed-wing aircraft.

Magnesium is a very active metal electrochemically and is anodic to all other structural metals. Therefore, it must be protected against galvanic corrosion in mixed-metal systems because it will corrode preferentially when coupled with virtually any other metal in the presence of an electrolyte or corrosive medium. Many of the corrosion problems associated with Mg helicopter components occur at the contact points between ferrous



5 6061 aluminium powder (left) and its' consolidation by cold spray (right)

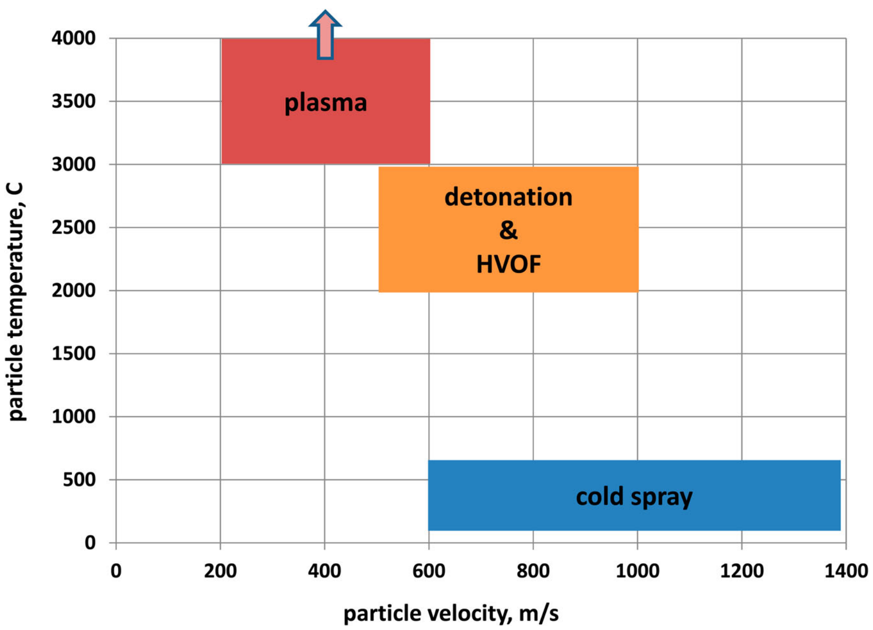


6 Comparison of cold-sprayed 6061 aluminium characteristics with those of wrought materials

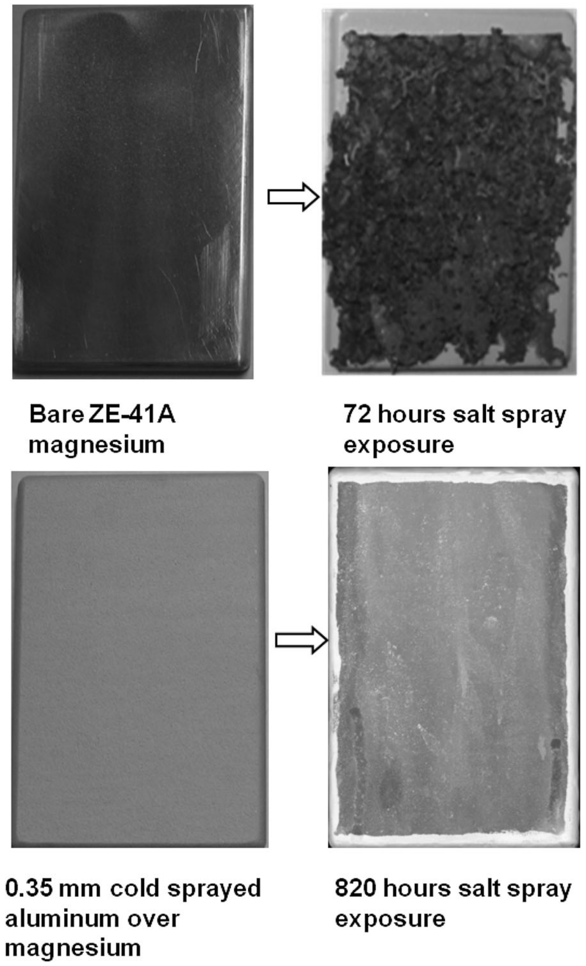
metal inserts or mating parts, creating galvanic couples. Corrosion occurs at attachment points where a dissimilar metal is in contact with the Mg component. These include flanges, mounting pads, tie rods, lugs and mounting bolts.

The military and the aerospace industry have expended much effort over the last two decades to develop specific surface treatments to prevent corrosion, to increase surface hardness, and to combat impact damage for Mg alloys in order to prolong equipment service life. However, the means to provide dimensional restoration to large areas on components where deep corrosion has occurred remains a challenge. The use of the cold spray process to deposit commercially pure aluminium for providing dimensional restoration and protection to magnesium has been developed by the U.S. Army Research Laboratory Center for Cold Spray Technology.[44] The cold spray process was viewed as the best possible method for depositing aluminium coatings onto Mg and is viewed as part of an overall strategy of replacement of the environmentally unacceptable chromate processes currently in use today, eliminating environmental and worker safety issues, while significantly improving performance and reducing lifecycle costs.

The evaluation programme for magnesium protection by cold-sprayed aluminium included tests for corrosion resistance, bond strength, hardness, microstructure and fatigue. For corrosion testing, the edges of the panels were sealed with epoxy so only the front and back surfaces were exposed to the salt spray. The panels were exposed to salt spray according to the requirements of ASTM B117. The results are shown in Fig. 8, where, except for some discolouration of the aluminium, no corrosion is evident on the panel that was cold sprayed with aluminium.



7 Windows of operation for plasma, detonation, HVOF and cold sprays



8 Salt spray corrosion of uncoated and aluminium coated magnesium

Other corrosion susceptible metals have been demonstrated to be protected by cold-sprayed deposits. Some of these coating/substrate combinations are listed in Table 1. The processes resulted in good protection when properly carried out in every case.

ZE41A-T5 magnesium, cold spray coated with CP Al and 6061 Al, was fatigue tested by means of the R.R. Moore rotating beam test. Cycles exceeded 107 and results showed no debit and some credit of the cold-sprayed samples.[35]

Table 1 Efforts in corrosion protective cold-sprayed surfaces

Reference	Coating	Substrate
DeForce *et al.*[45]	Al–5%Mg, CP-Al, HP-Al, AA5356, AA4047	ZE41A-T5 Mg
Chavan *et al.*[46]	Zinc	Steel
Koivuluoto *et al.*[47]	Tantalum	Steel
Koivuluoto *et al.*[48]	Ni, Ni–Cu	Steel
Ma *et al.*[49]	Aluminium	NdFeB
Marrocco *et al.*[50]	Titanium	Steel
Wang *et al.*[51]	Titanium	Steel
Barbosa *et al.*[52]	Titanium	Aluminium alloy 7075

Wear protection

Cold spray deposition of powders requires some deformation of particles as they impact. Because of this, the deposition of hard, wear resistant materials is difficult. Nevertheless, cold spray can address this difficulty as will be described. The most common method used to form a wear resistant coating by cold spray is to spray a mixture of hard particles with softer, ductile particles. The soft material can deposit on contact with the substrate, while the hard, wear resistant particles are embedded within the ductile layer. The resulting deposit is a matrix of hard (often ceramic) particles within a metal binder. Figure 9 shows cold-sprayed deposits of WC–10Co embedded within the more ductile WC–75Co[53] and tungsten embedded within copper 80% W-20% Cu.[54] Wolfe *et al.*[55] deposit a Cr_3C_2 – 25 wt-%Ni blend on 4041 alloy and showed that Vickers hardness beyond 900 HV could be achieved.

Repairs

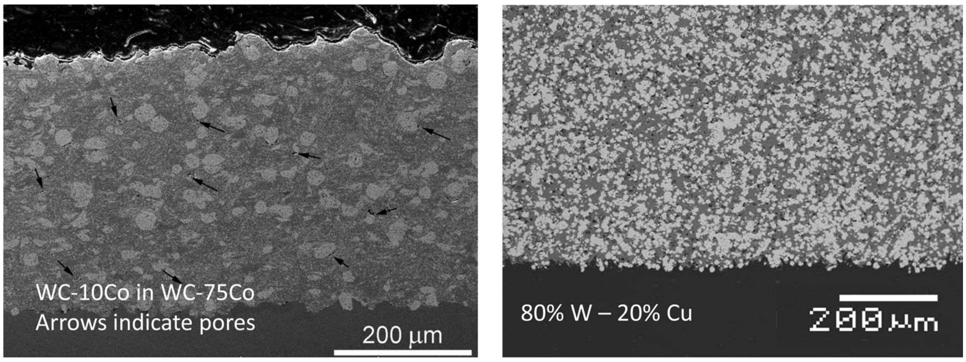
Repair by cold spray is generally aimed at dimensional restoration. The metal powder sprayed for part restoration may or may not be the same metal as the part being restored. In some situations, a different metal may yield improved characteristics over those of the part itself. This can be especially true in the case of corrosion damage, where a more corrosion resistant metal can be used for repair. In any case, the repair itself must meet the service requirements of the part.

The aerospace industry is potentially the largest beneficiary of repair by cold spray.[56–58] Significant wear problems are experienced for certain aerospace materials, especially magnesium alloys that are used to fabricate aircraft components. Prior to cold spray, many of the parts could not be reclaimed because there was not an existing technology that could be used for dimensional restoration.

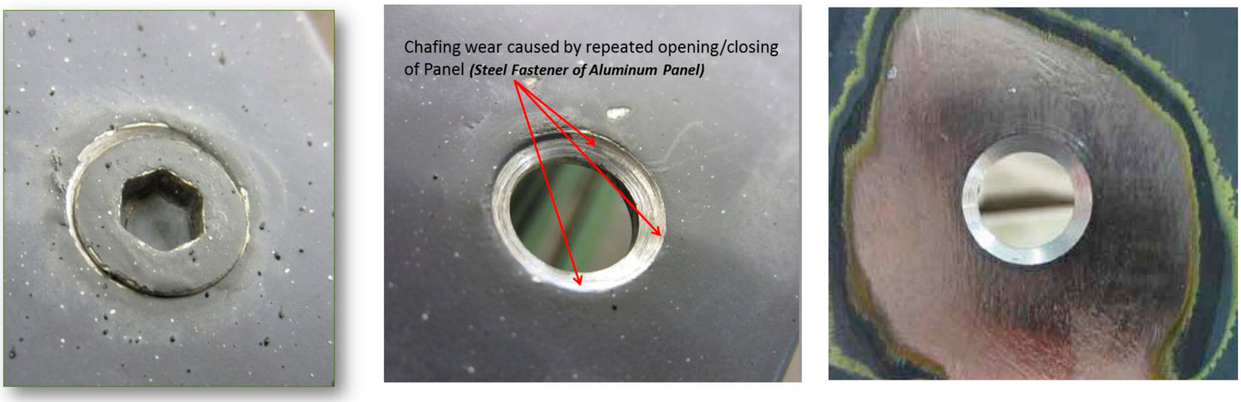
The examples below show the diversity of repairs that can be accomplished with cold spray. In most cases, the ability to apply the repair metal at relatively low temperature is critical to the application. A successful repair meets the service requirements of the part, such as dimensional integrity, bond strength to the part, porosity, corrosion resistance, or strength. Tests for these characteristics are described in MIL-STD-3021.

Access panels

A common problem on military aircraft is wear due to chafing around fastener holes in skin panels. This chafing results in skin panels that exceed fit tolerances at the fastener locations. The fasteners are designed to be installed flush with the panel for laminar airflow over the skin surface. In service, the chamfer wears, causing the fastener holes to become elongated. This renders the panels unserviceable. The damage is accelerated by air turbulence on elongated fastener holes. A panel repair by cold spray is shown in Fig. 10. The panel is made from 2024-T6 aluminium. The cold spray repair utilised 6061 Al powder. The results demonstrated the capability of cold spray to provide a permanent repair for this application, restoring the full capability of the panel.[59] Cold-sprayed coupons met or exceeded the required bearing loads for the parent material and fastener type for this application.



9 Wear resistant coatings by the cold spray of hard materials in softer binders



10 Repair of an aircraft panel fastener hole

Aluminium cladding

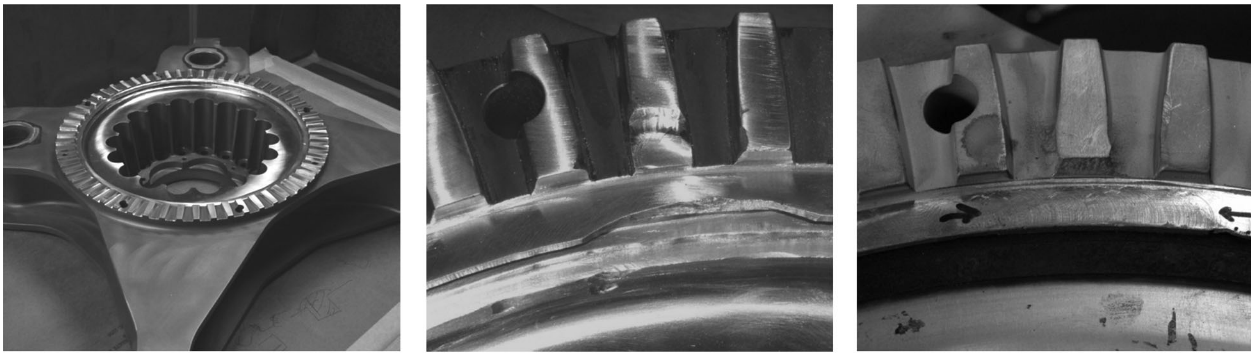
Aluminium cladding has long been used as a non-structural coating for high strength aluminium alloys as a protective measure to reduce or prevent corrosion. It can also be brightly polished as an attractive and conductive cosmetic finish. High impact and wear areas, however, can be damaged by foreign objects, debris or repeated polishing. This can expose the underlying material to corrosive elements, leading to corrosion damage and an unsightly appearance. Cold spray can be used to repair areas where cladding has been lost, restoring its original finish and corrosion protection without altering or affecting the underlying parent material. The cold spray process has been investigated to deposit pure Al coatings onto AA2024 Al substrates.[60,61] The photographs in Fig. 11 demonstrate the repair of ion vapour deposition (IVD) coated aluminium panels. The IVD panel shown is similar to aircraft skin. A shallow groove was machined into the panel to represent damage. The groove was then cold sprayed with aluminium and polished.

Sansoucy *et al.*[62] show that the cold spray application of the alloy Al–13Co–26Ce onto an AA2024 substrate yields superior bending fatigue resistance than bare AA2024 and IVD coated (Alclad) substrates.

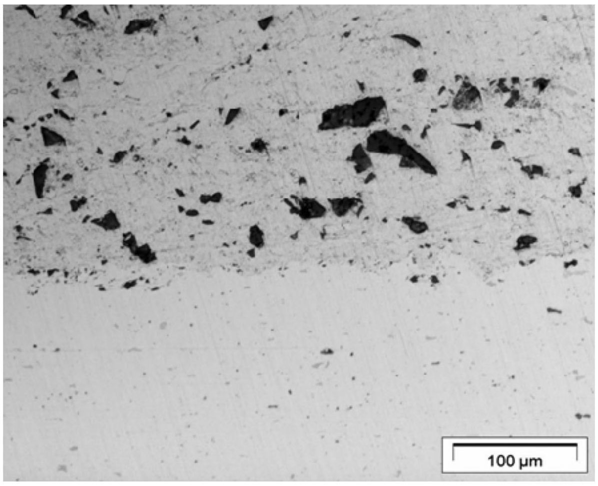
Structural repairs

Corrosion and mechanical damage has rendered a number of Apache Helicopter mast supports non-serviceable for continued use. The U.S. Army Research Laboratory

11 Repair of damage to and IVD coated aluminium panel



12 Repair of a helicopter aluminium mast support



13 Magnified cross-section of an alumina–aluminium blend on an aluminium alloy substrate

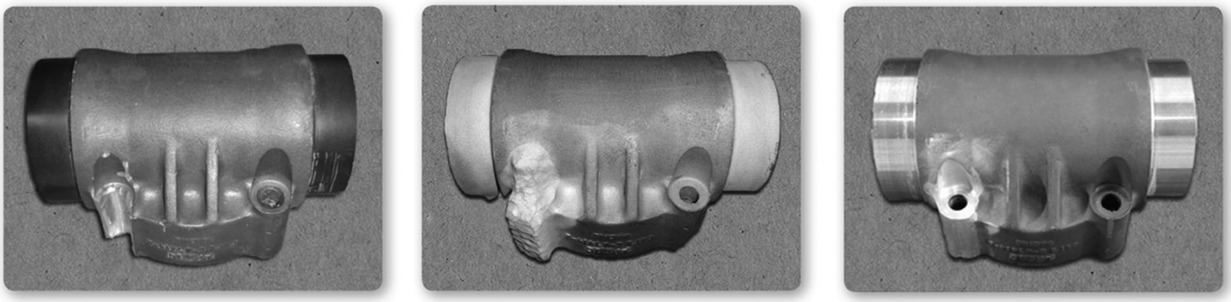
developed a method to repair both the corrosion and mechanical damage by blending and machining damaged areas, re-building lost material using cold spray with aluminium powder and finish blending and machining to the original dimensions.[63] Figure 12 shows the Aluminium Alloy 7149 mast support, its damage and repair by cold spray. A portable LPCS cold spray system was utilised, and an alumina–aluminium powder blend was sprayed. The addition of alumina to aluminium powder is often used with LPCS systems to enhance deposition. Figure 13 shows a magnified cross-section of the repair. The dark areas are alumina, while lighter areas are aluminium. The tight interface and the non-porous nature of the repair are evident.

Ghelichi *et al.*[64] find that cold spray application to AL 5052 alloy can result in a significant improvement to bending fatigue strength. They find that the fatigue strength of the part will be equal to that of the bulk coating material. This means that aluminium repair with a fatigue resistant alloy will transfer some of this quality to the repaired part.

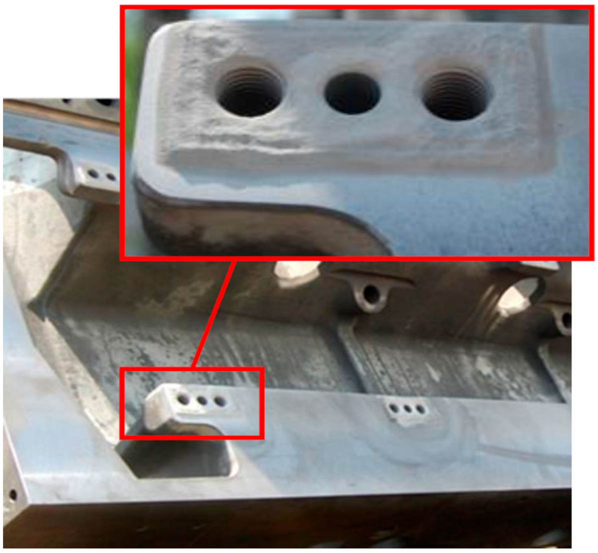
The damaged transmission housing of a KC-135 aircraft was repaired by means of cold-sprayed aluminium alloy.[65] Figure 14 shows how the damaged magnesium casting was back filled with aluminium and machined back to original dimensions. Components on legacy aircraft are becoming geometrically intolerant due to damage, and a dwindling supply chain makes replacement parts difficult to find and expensive to replace.

Cast iron engine block

The cam bearing mounting pads of a large cast iron engine were found to be undersized due to a machining error. Repair by welding or thermal spray would have warped the pads. A nickel alloy was cold sprayed onto the pads in order to restore the needed dimension as shown in Fig. 15.[66] Machining subsequently created a flat mating surface. A portable cold spray system was used for this repair (Centreline SST), which allowed the repairs to be made without unloading the engine block from its transport truck.



14 Repair of a KC-135 magnesium transmission housing

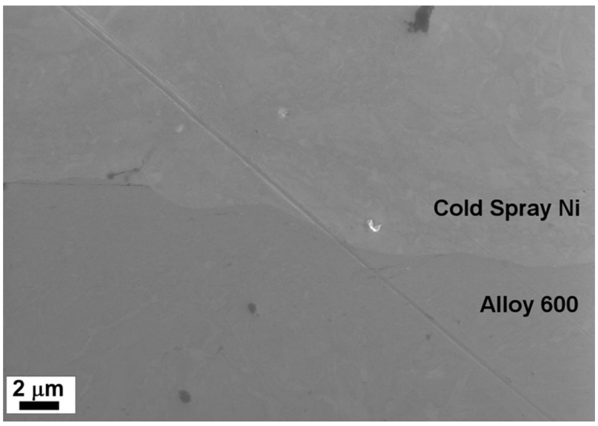


15 Dimensional restoration of an iron engine block mount

Nuclear support materials

Austenitic Ni and Fe alloys comprise the bulk of wetted surfaces in nuclear power plants. These alloys are susceptible to stress corrosion cracking (SCC) especially after extended service life.[67] Cold spray is an acceptable vehicle for repair of these alloys because there is no heat affected zone, minimal surface preparation is required, deposits have high adhesion, the deposits can be easily applied using robotics, and the surface can be inspected with dye penetrant or ultrasonic testing. Nickel is preferred for nuclear system repair because nickel is much more resistant to SCC at primary water conditions than austenitic alloys and nickel comprises about 70% of wetted non-fuel surface area in a plant. It is isotropic, homogeneous, and does not have any secondary phases.

Figure 16 shows the cross-section of cold spray deposited nickel on an Inconel substrate commonly used for nuclear applications. The clean, well-bonded interface and pore-free deposit are clearly evident. Figure 17 shows a 7.6 cm stainless steel pipe coated with nickel, which repairs it and increases its burst strength. The figure also shows a carbon steel plate back filled with nickel after its corrosion was removed.[68]



16 Nickel cold spray deposit on Inconel

Additive manufacturing

Although often used for coatings, there is no theoretical limit to the thickness that a cold-sprayed deposit can achieve. Thick (several centimetre) deposits are frequently cold sprayed from many feedstock powders. Accordingly, the cold spray process is capable of creating 3-D shapes of various geometries. The cold spray nozzle must be directed toward a suitably shaped mandrel upon which metal is deposited. The nozzle is robotically controlled to follow the contours of the desired shape. Multiple layers of material are thus deposited until the desired thickness is achieved. The mandrel is subsequently detached and finish machining can be carried out.

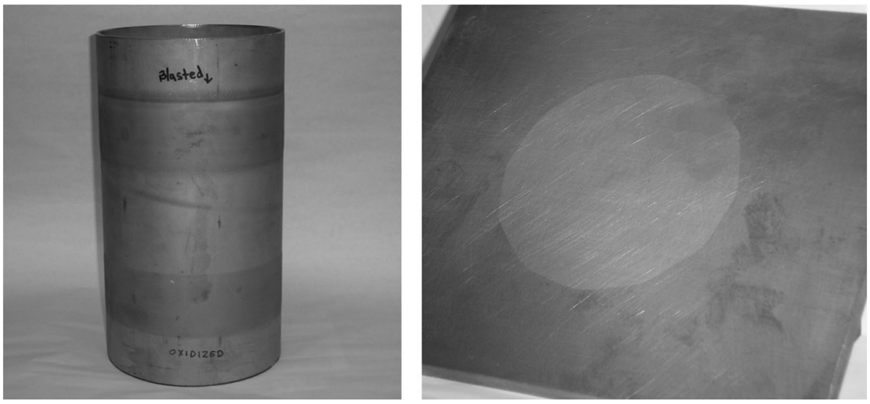
Several shapes have been created by cold spray at the US Army Research Laboratory.[69] One such example, shown in Fig. 18 is the consolidation of an Ni–Al composite in the form of a hollow cylinder. Machine threads were cut into one end of the cylinder and a screw-on lid was similarly created. A more complex shape was created by United Technologies Research Center.[70] The bracket is shown in Fig. 19. The figure shows how the structure is initially sprayed over a shaped mandrel substrate. The substrate is subsequently removed and the bracket is finish machined.

Cold spray-generated finned heat exchangers have been produced by Canadian researchers.[71] These structures were created using masks of wire screen mesh. The spray could only deposit in the mesh openings, and Fig. 20 shows the resulting deposition after the screen is removed. The motivation for these heat exchangers is heat recovery in micro-turbines. By spraying over the mesh, pyramidal structures were formed on the substrate below. These structures serve as fins in conventional heat transfer. The pyramids produced were typically 2 mm in height. Convective heat transfer by the cold spray deposited pyramidal fins was found to be superior to that of conventional square cut fins, especially at higher gas velocities.

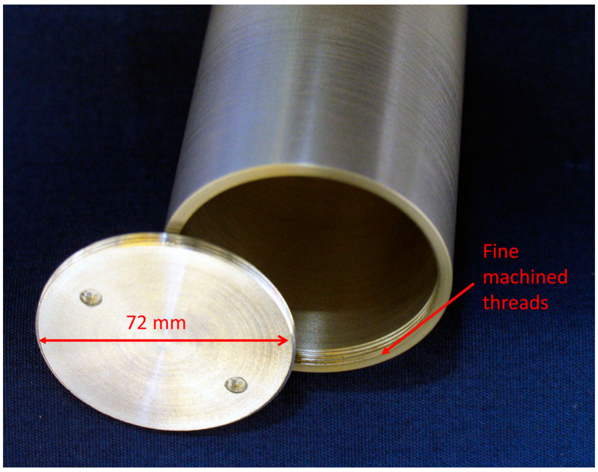
Catalysis

The ability of cold spray to maintain powder particles at low temperatures prevents many crystalline transformations that would occur for higher temperature thermal spray processes. For example, titanium dioxide (TiO_2) is a promising material for photocatalyst coatings; however, it is difficult to fabricate a TiO_2 coating with a photocatalytically active anatase phase by conventional thermal spray processes due to a high temperature thermal transformation to rutile phase. Low temperature cold spray deposition allows initially anatase powder to remain in that phase after deposition.

As a ceramic, TiO_2 is difficult to deposit. Researchers at Toyohashi University of Technology[72,73] have developed a process to cold spray ceramic TiO_2 onto appropriate surfaces using helium as the accelerating gas. An SEM image of the cross-section of the TiO_2 deposit on steel is shown for inlet gas temperature of 400°C is shown in Fig. 21. Catalytic activity was measured as the percentage of oxidised nitric oxide following contact with the UV irradiated TiO_2. In most cases, the deposited material had more activity than that of the feedstock material. This was explained as surface area being exposed through impact fissures.



17 Steel nuclear containment materials repaired with cold-sprayed nickel



18 Cylinder and end cap produced by cold spray

Yang *et al.*[74] compared the photodecomposition of acetaldehyde on the surface of cold-sprayed TiO_2 with that of HVOF-sprayed material. Upon exposure to a UV radiant intensity of 1 mW cm^{-2}, the cold-sprayed surface showed much greater photodegradation effectiveness of acetaldehyde than that of the HVOF-sprayed surface, see Fig. 22. XRD analysis indicated that the cold-sprayed TiO_2 film is in the pure anatase phase, while HVOF-sprayed TiO_2 coating is composed of both anatase phase and rutile phase. It was further shown that annealing subsequent to deposition can result in improved photocatalytic activity.[75]

Catalyst surfaces for fuel reforming applications have also been deposited by cold spray.[76] NiO/AlO_3 catalyst coatings on stainless steel and aluminium substrates, $CuO/ZnO/Al_2O_3$ catalyst coating on Al substrate have been prepared by cold spray technology. Microstructure analysis by SEM and EDX showed that the coatings retain the original composition and porosity of the catalyst feedstock, assuring that the catalysts retain original activities.

Biological, medical

Bone implants

The bioceramic hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, also known as HAP has been widely used in dental and orthopaedic implants, due to its chemical and crystallographic similarity with bone minerals. HAP has been conventionally deposited by plasma spray technique; however, due to the high temperature of the plasma spray, deleterious effects such as evaporation, phase alteration, residual stress, debonding and gas release commonly occur in these coatings.

Researchers at the University of Michigan have developed a method to deposit bioceramic coatings at temperatures well below their melting point by cold spray, using composite powders of titanium and HAP.[77] Although the cold-sprayed surface is not pure HAP, the implant need not be completely covered by HAP for bio-integration with surrounding tissue, and in fact implant surfaces consisting of a fraction of area covered by HAP can effectively integrate to the bone.

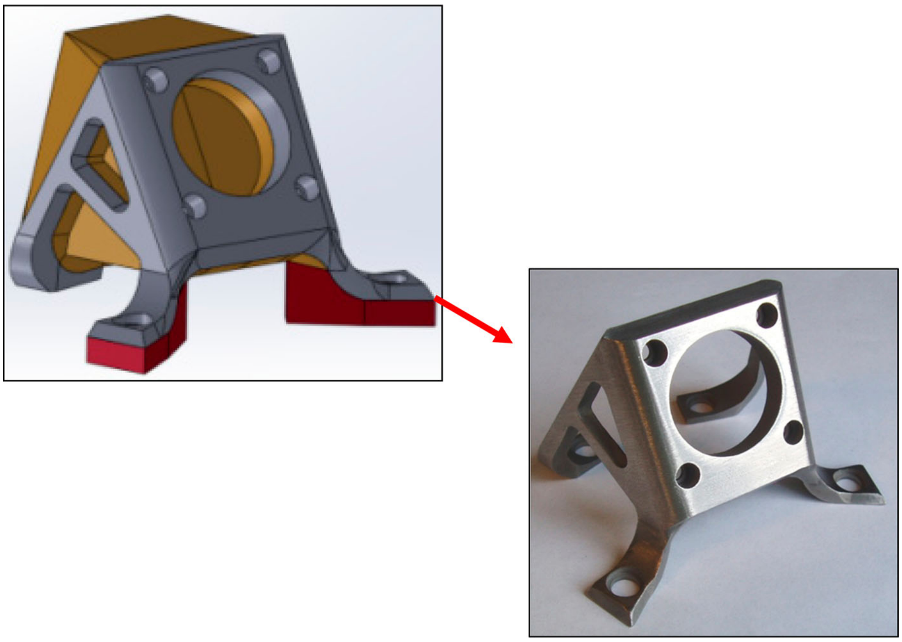
The influence of the process parameters, powder type as well as HAP to titanium ratio were investigated, and it was observed that dense composite coatings, containing up to 30% HAP can be deposited by this technique. XRD analysis indicated that the phase composition of the HAP in the deposit was identical to that of the powder. Tlotleng *et al.*[78] used laser-assisted cold pray to deposit matrices of Ti and HAPs. They were able to deposit 80% HAPs, 20% Ti.

It was demonstrated that HAP powders can be cold sprayed simultaneously with titanium to form thick biocompatible composite coatings, without compromising the phase constituents of HAP. Coatings deposited using this process hold potential for improving bone integration of a wide range of dental and orthopaedic implants.

Antimicrobial

Bacterial contamination on touch surfaces results in increased risk of infection. In the last few decades, work has been done on the antimicrobial properties of copper and its alloys against a range of micro-organisms threatening public health in food processing, healthcare and air conditioning applications; however, an optimum method of copper surface deposition and the resulting mass structure has not been identified.

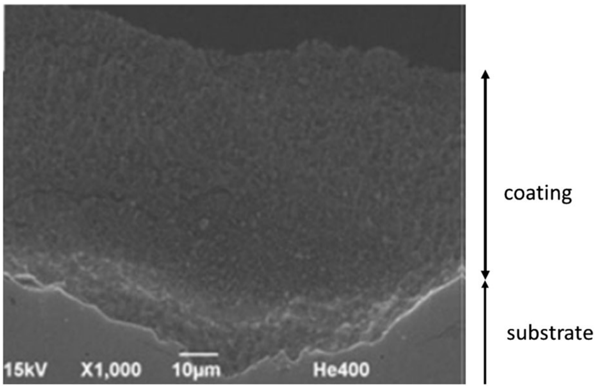
In order to identify ideal deposition methods and deposit characteristics the US Army Laboratory conducted a study of the disinfection effectiveness of three copper surfaces.[79] The surfaces were produced by the deposition of copper using three methods of thermal spray, namely, plasma spray, wire arc spray and cold



19 Bracket, first cold sprayed onto substrate, then released and machined

spray The surfaces were subsequently inoculated with methicillin-resistant *Staphylococcus aureus* (MRSA). After a 2 h exposure to the surfaces, the surviving MRSA were assayed and the results compared.

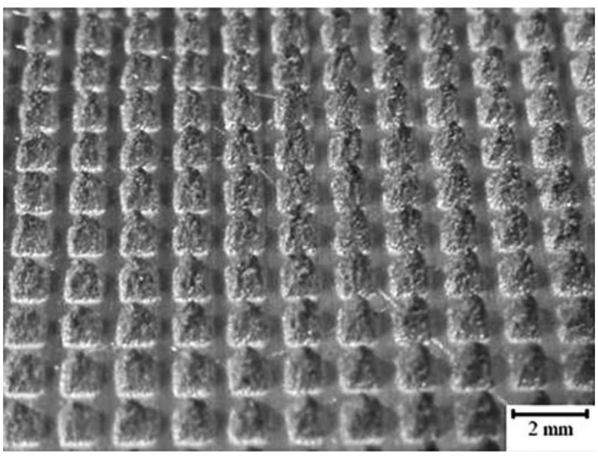
The cold spray deposition method was significantly more effective than the other methods, yielding greater than 99.99% microbial destruction after a 2 h exposure. It was determined that work hardening caused by the high-velocity particle impacts created by the cold spray technique results in a copper microstructure that enhances ionic diffusion, which subsequently improves antimicrobial activity. As an example of how these results can be implemented, Fig. 23 shows a hospital table, coated with cold-sprayed copper.



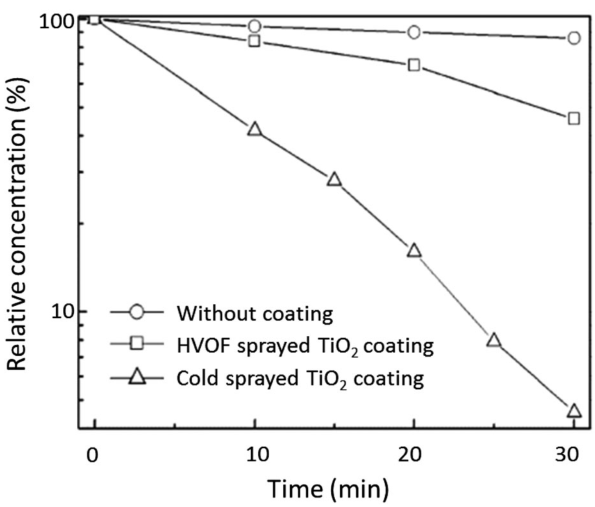
21 Photocatalytic TiO_2 cold sprayed onto steel

Antifouling

Biofouling is a problem which affects most submerged, man-made surfaces. Marine biofouling has enormous economic impact on shipping, offshore oil and gas rigs, power and desalination plants and aquaculture. The use of copper and copper alloy sheathing has been demonstrated to exhibit long-term antifouling activity on marine surfaces, but is not compatible with some plastic surfaces.



20 Finned heat exchanger produced by cold spray



22 The change of the relative concentration of acetaldehyde with time

23 **Hospital table coated with cold-sprayed copper**

Vucko *et al.*[80] have developed a cold spray method to embed copper particles into the surface of polymer structures as an alternative to copper plates and copper containing paints. Marine seismic streamers are candidates for this cold spray technique. The streamers are plastic, towed cables housing regularly spaced hydrophones. The hydrophones receive sonic pulses that have been reflected from the ocean bed.

This technique was applied to a half section of seismic streamer, with the remainder untreated.[81] Using cold spray, half the length of 600 mm samples of streamer jacket (Colex) was embedded with copper particles. This was deployed in the tropical waters of Townsville harbor, Queensland, Australia. After 220 h of exposure, no fouling was found on the copper-embedded section (Fig. 24).

Electronic and electromagnetic

Antennas

Large antenna arrays mounted directly on the surface of load bearing aircraft wings and structures permit implementation of future communications systems without the aerodynamic drag of protruding antenna. Current techniques for fabricating conformal antennas are difficult to apply to the shapes of high performance aircraft. Large, irregular, and doubly curved surfaces such as those found on the wings and tail of an aircraft are more difficult to populate with antenna substrates and radiating elements.

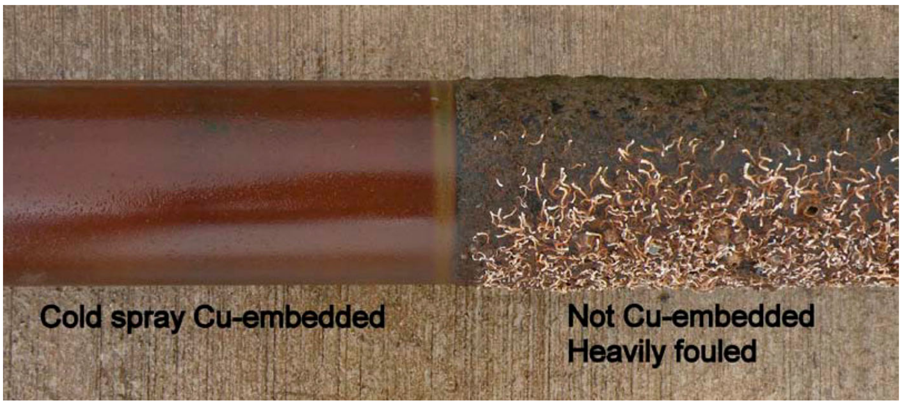
The Inovati Corporation has been developing a direct write method of fabricating metallic antenna structures onto doubly curved dielectric surfaces using the low temperature KM process.[82] The KM process is similar to cold spray in that it deposits high velocity particles, which have been accelerated in a nozzle. The technology can enable fabrication of low profile RF systems on current and planned airborne platforms.

In order to demonstrate the application of high quality RF conductor patterns in complex net shape geometries via KM, a doubly curved 4-element antenna array was fabricated with KM deposition of copper onto RO3003 dielectric (Teflon with fused silica composites). Figure 25 shows the completed antenna. RF testing performed with the KM copper coatings showed that the electrical characteristics of the conductor deposited using the KM process is similar to that made using conventional etched copper foil techniques on identical RO3003 dielectric materials.

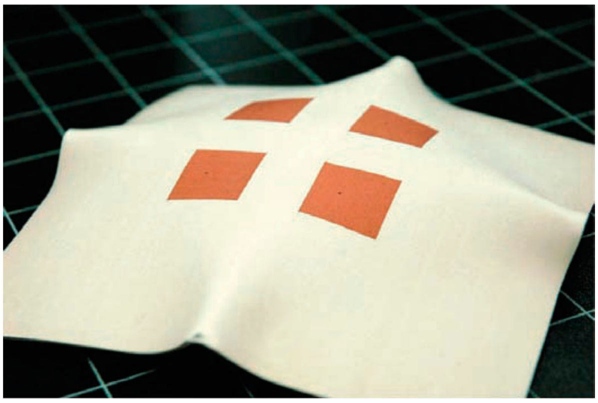
Electromagnetic shielding

There are two purposes for the shielding of electronics enclosures. The first is to prevent external electromagnetic sources from penetrating a sensitive environment containing electronic equipment, which is susceptible to interference from the unwanted signals. The second purpose for shielding is to prevent electromagnetic signals generated by equipment within the facility from being transmitted or conducted in sufficient magnitude to be received by external receiving and signal recovery systems.

The S-778, lightweight multipurpose shelter (LMS) is a transportable, rigid wall, tactical shelter, mounted on a high-mobility multipurpose wheeled vehicle. The LMS provides a lightweight shelter for a broad range of battlefield electronic systems. The LMS is constructed from 3 cm thick panels consisting of aluminium skins that encase a fibrous honeycomb inner core. The bonded panels contain many aluminium to aluminium seam



24 **Streamer jacket high-density sample after 210 days field exposure in Townsville Harbour, showing the interface between the sprayed and unsprayed area**



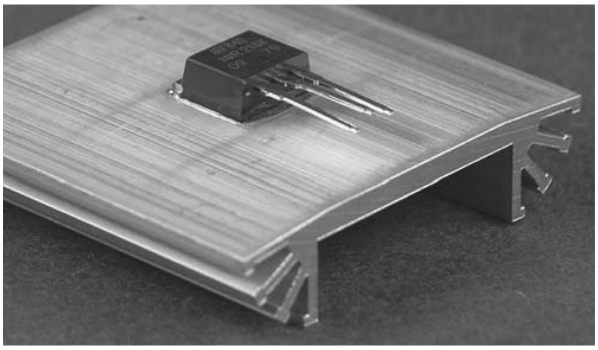
25 Four-element patch antenna array deposited on a doubly curved dielectric substrate

joints. Panels that have been bonded with adhesives present shielding problems, because electrical contact across the seam is lost due to the dielectric nature of organic adhesives. Conductively sealing the seams by means of flowing metal, such as brazing, cannot be done, because of the temperature limitations of adhesives.

Engineers at the US Army Research Laboratory have demonstrated that the cold spray technique for metal particle deposition can produce conductive coatings on seams in aluminium panels.[83] Since application temperatures are relatively low (<100°C), nearby adhesives are not damaged. While cold spray is often carried out with a stationary robot controlled system, the large panel size (3 m×3 m) and field application favoured the use of a hand-held portable system. This portable unit used shop supplied compressed air as opposed to the significantly higher pressures used by stationary units. The coatings produced by cold spray exhibited good bond strength to aluminium, and their density provided high resilience to vibrations. Figure 26 shows how a seam is filled with aluminium deposit by cold spray.

Solder surfaces

The superior electrical and thermal conductivities of cold-sprayed copper and copper alloy deposits make cold spray well suited for electronics manufacture. In addition, cold spray allows the placement of lead-free connectors. Cold spray application to power electronics is of particular interest, since ceramics are often used as insulating substrates. Rastjagaev *et al.*[84] seek to replace a sandwich of copper-alumina-copper, normally utilising direct copper bonding (DBC), with cold-sprayed copper on alumina. They found that cold-sprayed copper, preceded by a cold-sprayed aluminium base on the alumina ceramic, closely matched the characteristics of DBC.



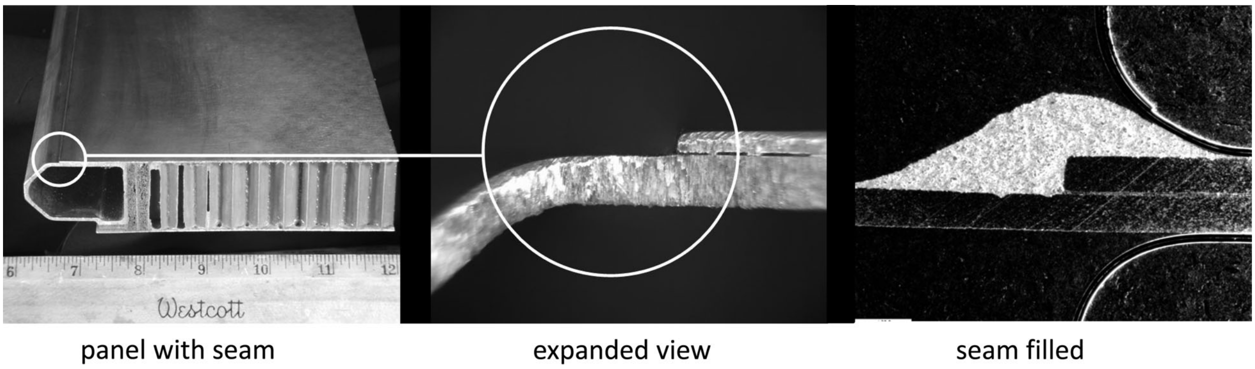
27 Power transistor soldered onto an aluminium heat sink covered with a cold-sprayed copper layer

Cold-sprayed copper can provide a solderable surface onto substrates that do not accept wetting by solders. Aluminium with oxides present is such a substrate. Marx *et al.*[16] show that copper can be cold sprayed onto an aluminium heat sink, allowing a power transistor to be soldered to the copper layer, see Fig. 27. The cold-sprayed copper layer removes the natural oxide film and provides a solderable surface for the tin- or copper-plated area of electronic parts. In addition, the copper layer conducts the heat very rapidly from the electronic part to the heat sink.

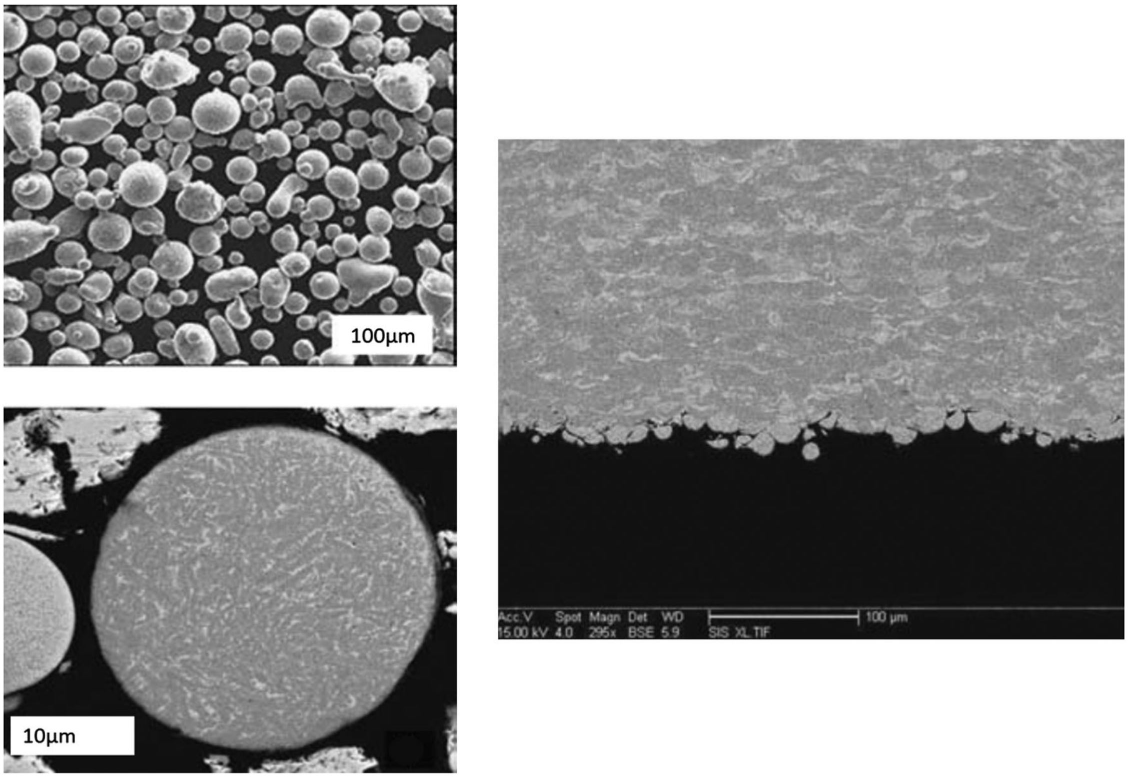
Powder development

Amorphous materials

The ability to retain the characteristics of initially amorphous powders subsequent to cold spray deposition has been demonstrated by several investigators. Since cold spray maintains the powders at relatively low temperatures, it is possible to retain the amorphous nature of the materials during cold spray deposition. Amorphous iron-based alloys,[85,86] copper based alloys,[87] and aluminium-based alloys[88] have been investigated. The results of all studies show that the amorphous characteristics of all the powders remain relatively unchanged after cold spray deposition. Figure 28 shows the iron-based (Fe–Cr–Mo–W–C–Mn–Si–Zr–B) powder and the resulting deposit by cold spray. The feedstock powder was prepared by gas atomisation (SHS727 powder, The NanoSteel Company, Maitland,

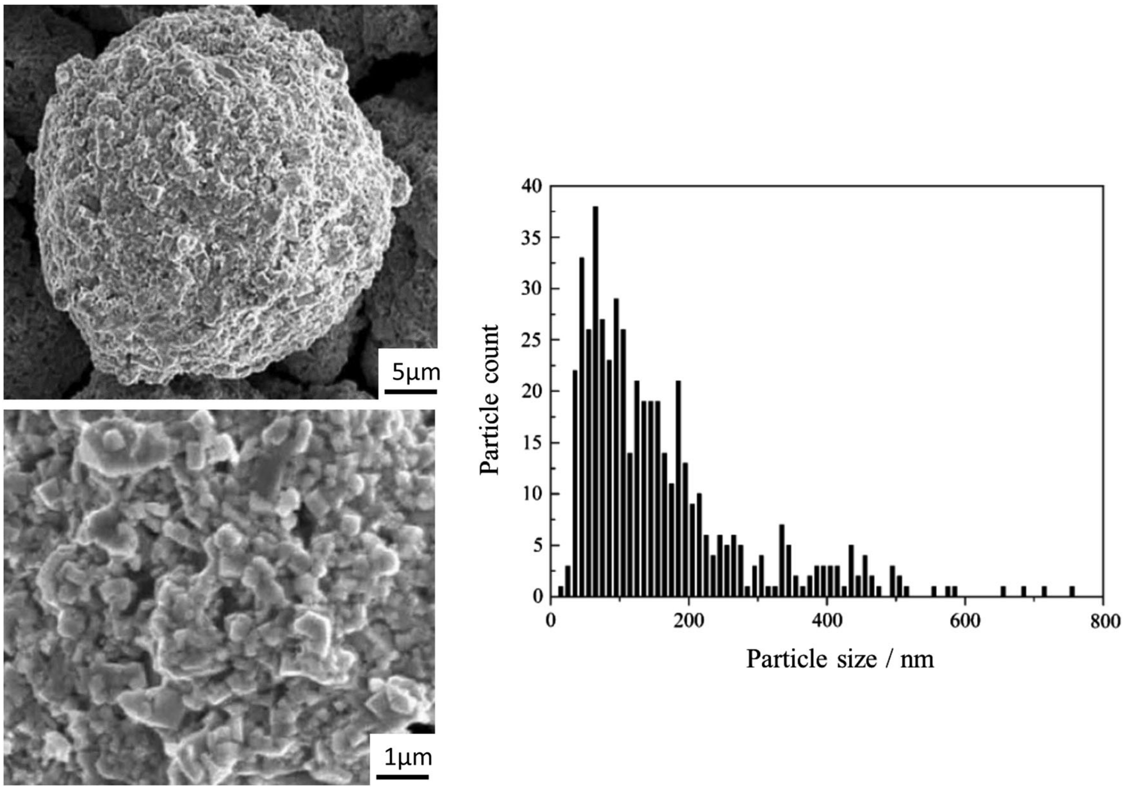


26 The potential EM leakage through the seam of an equipment enclosure sealed by cold spray



28 Iron-based amorphous powder on left and deposited on right. Light grey corresponds to crystalline regions and dark grey corresponds to fully amorphous regions

FL, USA). The deposit shows negligible porosity and excellent interfaces with the substrate material. The microstructure of the feedstock powder was retained after the spray process, fine particles (completely amorphous) remained amorphous after the impact, and the larger and crystallised particles also retained their initial microstructure.



29 Nano-structured, agglomerated WC–12%Co particle on left and the particle size distribution found in the cold-sprayed deposit on right

Nano-scale

Individual nano-scale particles cannot be deposited by cold spray because their forward momentum is not large enough to overcome aerodynamic force turning them away from impact. As a result nano-scale particles are cold sprayed as agglomerate clusters, thus behaving aerodynamically as larger particles. The nano particles retain their dimensional characteristics after deposition. High temperature thermal sprays do not maintain the nano-structure of agglomerates as particles are melted. WC–Co nano-structured cermets have been successfully cold sprayed.[89,90] Figure 29 shows A WC–12%Co feedstock powder and the resulting particle size distribution of the cold-sprayed deposit. A commercial nano-structured WC–12Co powder (Inframat) was employed in this study. It was made from agglomeration of nanosized WC with cobalt followed by partially sintering. The powder particles had a size range from 5 to 44 μm. The nominal WC grain size was 50–500 nm. It was found that the size of most WC particles in the resulting deposit ranged from about 50 to 300 nm. In addition, there is no detrimental phase transformation and/or decarburisation of WC by cold spray deposition. The resulting deposition achieves hardness values exceeding 1800 HV, equivalent to sintered nano-WC.

Equipment evolution

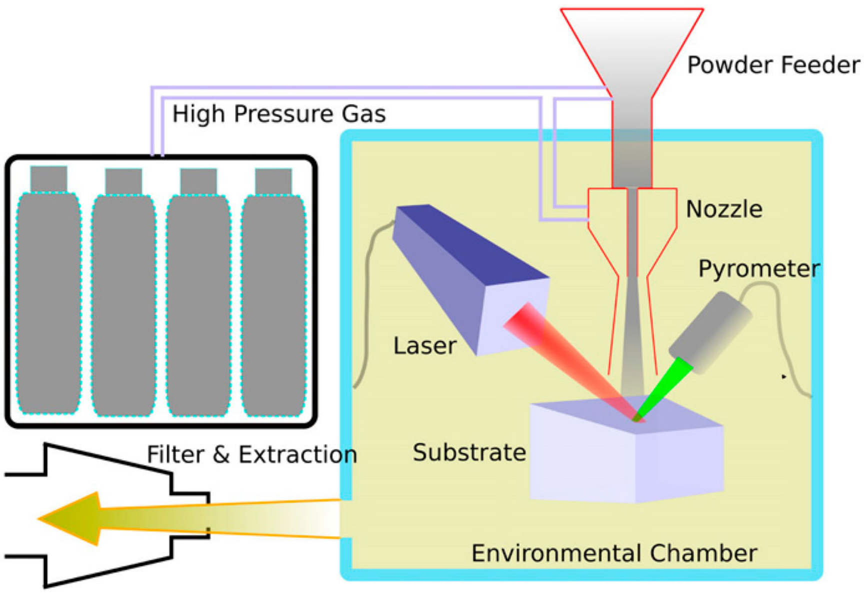
Improvements to cold spray systems have generally been directed toward higher particle velocity capability and hence the ability to spray harder, less ductile materials. Early systems were capable of inlet chamber pressures up to 3 MPa and temperatures up to 500°C, new systems can now operate at 5 MPa and 1000°C, yielding a 30% increase in particle velocity and an almost doubled particle temperature.[5–7,91]

Helium is often used as the accelerating gas due to the much higher attainable velocities relative to those when nitrogen is used. Because of its scarcity and non-renewable status, it is much more expensive than nitrogen and, when used, becomes the highest cost contributor to the cold spray process. After leaving the cold spray nozzle, helium can be recycled through capture, purification and recompression. The gas separation system removes impurities from the helium by means of a pressure swing adsorption process.[92,93] Very few current systems now possess helium recycle capability, and more utilisation of these systems should be a priority.

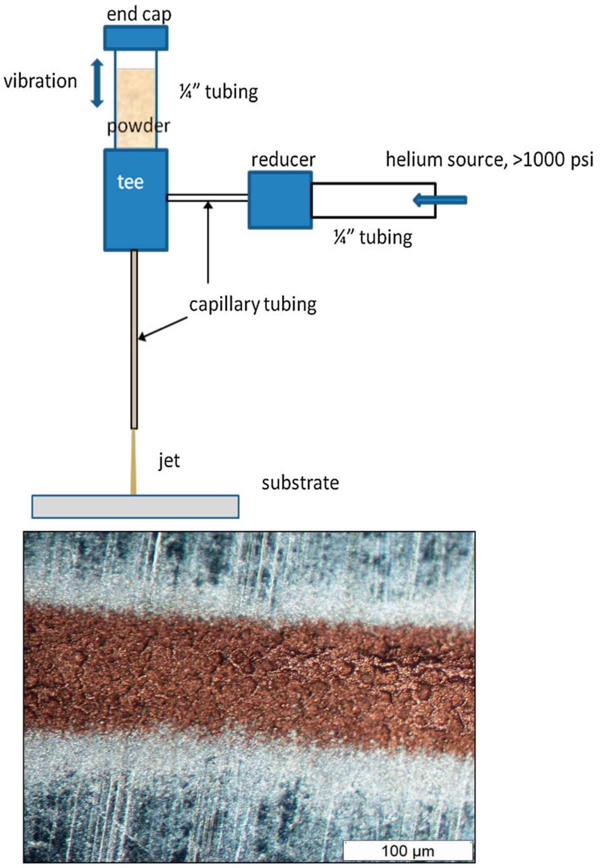
Lasers have recently been used in simultaneous combination with cold spray deposition. Called laser-assisted cold spray,[94] it is applied for both predeposition surface preparation,[95,96] and post-deposition conditioning.[50] Pre-preparation is used to condition the substrate surface prior to cold spray deposition in order to improve adhesion. Post-deposition is used to decrease porosity and improve the cohesion of the deposit. In an experiment to apply the laser at the deposition site, Bray *et al.*[97] utilise a 1 kW diode laser to heat the deposition zone in the arrangement shown in Fig. 30. They find that titanium can be readily deposited on stainless steel using unheated nitrogen gas when the deposition target is laser heated. The density of the deposits is equivalent to that of deposits produced by cold spray utilising heated helium as the driving gas.

Efforts at miniaturisation of cold spray systems are underway.[98] It has been recently demonstrated that replacing the conventional cold spray nozzle with a 100 μm diameter capillary can produce tracks of that same width.[99] Figure 31 shows the concept. The one-step process, utilising particle acceleration by means of flow through a capillary, directs a high velocity stream of copper particles within a helium carrier onto a ceramic substrate. Upon impact the particles deform and adhere to the substrate and to previously deposited particles, as for conventional cold spray. The use of a capillary tube as the flow nozzle restricts the jet and the resulting deposited copper to micron scale dimensions. The deposited copper is dense, with near zero porosity. Robot control of the jet position can yield precise conduction lines and component connections. When fully developed, such a device can yield micro circuitry.

Small cold spray nozzles that are oriented 90° relative to the supply lines are being developed for deposition

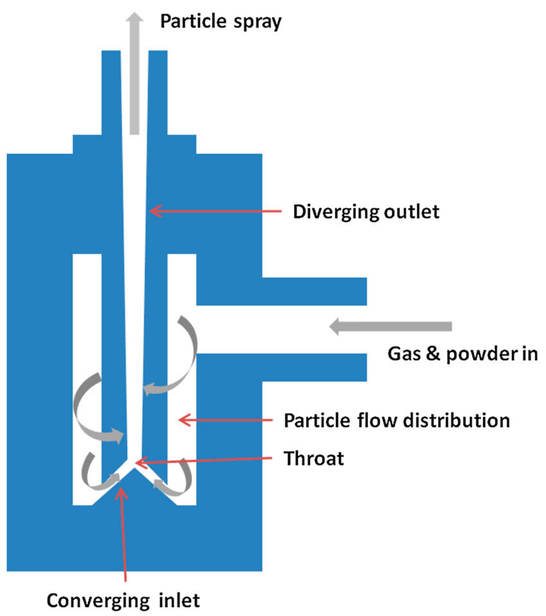


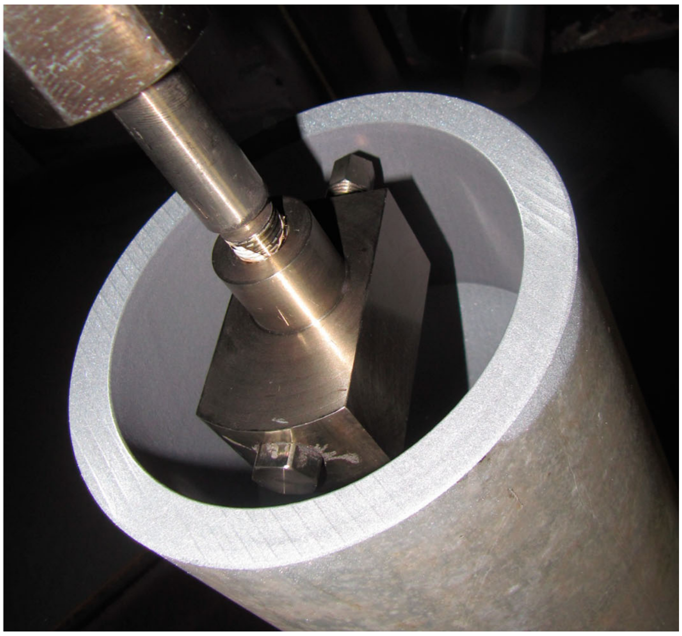
30 Laser heating of the deposit area, synchronised with cold spray



31 Miro-scale cold spray system with a representative copper deposit

on tube interiors and enclosed spaces.[100] Tube diameters to be coated are limited to approximately 75 mm, because particle acceleration requires an adequate nozzle length. Figure 32 shows an example of such a nozzle,[101] applying a tantalum coating inside a 100 mm aluminium tube.





32 Interior tube wall deposition by a 90° cold spray nozzle

Future directions

Development

Many ductile powders (for example aluminium) can attach to and build up on nozzle walls resulting in restricted gas flow. This can occur in as little as ten minutes of use. Plastic, or PBI, nozzles can resolve this problem at the cost of accelerated nozzle wear and frequent replacement. Plastic nozzles also limit the maximum allowed temperature. A better solution to this chronic cold spray problem would be helpful, especially when big jobs and long spray times are carried out.

Powders for cold spray use are often obtained from suppliers of general thermal spray powders. Successful cold spray operation depends more critically on powder characteristics than do high temperature thermal sprays and powders should be tailored specifically for cold spray use. Some equipment vendors offer powders developed specifically for their cold spray systems, but uniformly applicable specifications should be developed for cold spray powders. The first such specification is found in MIL-DTL-32495, covering some aluminium alloys. Similar specifications are needed for all regularly used cold spray powders.

Cold spray repairs generally need to be machined after deposition in order to meet specific dimensions. This is because deposition by cold spray (and all thermal sprays) is somewhat irregular and imprecise, and the deposit surface is rough. All of the case studies shown above required post-deposition machining. Refinement of cold spray powder feeds and nozzle traverse speeds can result in smoother, more predictable deposits and in some cases may do away with post-deposit machining.

Commercialisation

The cold spray applications described here represent a small percentage of the new application efforts currently being carried out worldwide. Much new work is proprietary in nature, and is not public. Research level work was presented, as well as applications that are near commercial use.

Fifty-five individual efforts to produce products were referenced, with 25 of these described in some detail. The wide range of applications possible with cold spray technologies is evident – from medical implants to radiation shielding. The scope of these efforts is indicative of the confidence of the cold spray community of a promising future. The efforts demonstrate the unique abilities of cold spray, which cannot be achieved with conventional thermal sprays. Some of these unique abilities are:

- Can be applied to heat-sensitive substrates
- Produces non-porous, impervious coatings
- Can produce composite deposits
- Can create 3-D structures
- Prevents heat-related crystalline transformations
- Nano-structured particles remain nano-structured after deposition
- Amorphous particles remain amorphous after deposition

While cold spray abilities have been demonstrated as shown above, significant commercial implementation has not yet occurred. There are many reasons for this hesitancy. Any new technology requires time for general acceptance. There needs to be commercial cold spray shops available to carry out the work, and until there is a demonstrable demand for repair by cold spray, new repair shops will not be opened.

The major justification for the commercialisation of anything is of course economic. Alternative manufacturing methods are available for most of the applications described above. Preferably, cold spray can yield superior products at the lowest prices. Generally, cold spray yields superior products but not at the lowest price. And sometimes cold spray is the only viable method to use at all, regardless of price.

Important steps for the commercialisation of cold spray include:

- An economic argument must be promulgated for each application.
- Efforts to identify opportunities should continue and cost-minimising operating procedures should be developed for each opportunity.
- The superior characteristics of cold spray deposits over those of other metal replacement technologies must be made clear.
- Success stories of manufacture by cold spray must be publicised.

The cold spray process is clearly available and successful. It is often one of few possibilities for the fabrication or repair of a part when high temperatures are not allowed for sensitive substrates or powder feedstocks. The commercial application of fabrication by cold spray will surely be developed, and it is the task of the community of cold sprayers to expedite the process.

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