Cold spray coating: review of material systems and future perspectives

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Cold gas dynamic spray or simply cold spray (CS) is a process in which solid powders are accelerated in a de Laval nozzle toward a substrate. If the impact velocity exceeds a threshold value, particles endure plastic deformation and adhere to the surface. Different materials such as metals, ceramics, composites and polymers can be deposited using CS, creating a wealth of interesting opportunities towards harvesting particular properties. CS is a novel and promising technology to obtain surface coating, offering several technological advantages over thermal spray since it utilizes kinetic rather than thermal energy for deposition. As a result, tensile residual stresses, oxidation and undesired chemical reactions can be avoided. Development of new material systems with enhanced properties covering a wide range of required functionalities of surfaces and interfaces, from internal combustion engines to biotechnology, brought forth new opportunities to the cold spraying with a rich variety of material combinations. As applications multiply, the total number of studies on this subject is expanding rapidly and it is worth summarizing the current state of knowledge. This review covers different material systems that have been studied up to now with an emphasis on potential innovative applications. This includes metallic, ceramic and metal matrix composite (MMC) coatings and their applications. Polymer (both as substrate and coating) and metal embedment in the polymer are also covered. CS has emerged as a promising process to deposit nanostructured materials without significantly altering their microstructure whereas many traditional consolidation processes do. Relevant material systems containing nanostructured powders are also considered. A critical discussion on the future of this technology is provided at the final part of the paper focusing on the microstructural bonding mechanisms for those relatively less explored material systems. These include MMCs involving more than one constituent, ceramics, polymers and nanostructured powders. Future investigations are suggested especially to quantitatively link the process parameters and the behaviour of the material systems of interest during impact.

Keywords: Cold spray, Metal matrix composite, Polymer, Ceramic, Nanostructured Powder

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Introduction

Cold spray technology: basic principles

CS is a process in which solid powder particles are accelerated over the sonic velocity through a de Laval nozzle with a convergent-divergent geometry. Particles have ballistic impingement on a suitable substrate at speeds ranging between 300 and 1200 m s^{-1}. The nozzle geometry as well as the characteristics of feedstock powders is fundamental to determine the final temperature and velocity of sprayed particles which is strictly related to coating microstructure, physical and mechanical properties. The temperature of the gas stream is always below the particle material's melting point. Therefore, CS could be effectively defined as a solid state deposition process. As the coating deposition is accomplished at the solid state, it has characteristics that are quite unique compared to other traditional thermal spray techniques.

There are currently two main types of CS systems: high pressure cold spray (HPCS) in which particles are injected prior to the spray nozzle throat from a high pressure gas supply;[1] and low pressure cold spray (LPCS) in which powders are injected in the diverging section of the spray nozzle from a low pressure gas supply.[2] LPCS systems are typically much smaller, portable, and are limited to 300–600 m s^{-1} particle velocities. They are used in the application of lighter

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materials and they generally utilise readily available air or nitrogen as propellant gases. High pressure systems instead, use higher density particles. They utilise higher pressure gases, are stationary and typically generate particle velocities of 800–1400 m s^{-1}. Lower weight gases, such as nitrogen or helium, are the preferred propellant gases for HPCS.

Both aforementioned systems have some limitations. For upstream (high pressure) powder feeding CS systems, in order to avoid powder back flow, a high pressure powder feeder running at a pressure higher than that in the main gas stream has to be used. The high pressure powder feeders are usually very big and expensive. Another major difficulty is related to nozzle clogging. This is more severe when the particle velocity and temperature are increased. To overcome the problem, a second particle population with either a larger average particle diameter or higher yield strength (hardness/elastic modulus) should be mixed with the first particle population.[3] Another disadvantage of HPCS system is the severe wear of nozzle throat due to particle erosion, which affects the nozzle operation and leads to large variations in operating conditions and deposit quality. This becomes worse when hard particles are being sprayed. On the other hand, the downstream (low pressure) powder feeding CS systems has simpler equipment. However, the nozzle design in this case is restricted to relatively low exit Mach number (usually <3). The inlet pressure is also restricted (normally <1 MPa) otherwise the atmospheric pressure will no longer be able to supply powders into the nozzle. As a result, only relatively low particle velocities can be reached through the downstream powder feeding technique.

With the development of the CS process, a number of studies were conducted to introduce the technology and its basic principles[4–6] and consequently potential applications of CS in different fields were explored.[7–10] More recently, some variations have been made to the CS technology. In this part we will also introduce different variants of the standard apparatus of CS.

The first method is called kinetic metallisation (KM), which is also a solid state process.[11] KM is a CS variant that uses a convergent barrel nozzle under choked flow conditions to achieve an exit gas velocity of Mach 1, with a slight divergence to compensate for friction effects. Most other CS systems (including low pressure cold spray) use a de Laval nozzle (convergent–divergent nozzle) to accelerate the process gas to supersonic velocity.

Another variation to CS set up is called pulsed gas dynamic spraying (PGDS).[12] This process heats up the particles to an intermediate temperature (still below melting temperature) which is expected to be higher than temperatures experienced in the CS process. Increasing the temperature will result in a decrease of the critical velocity which is of technological value. In addition, it leads to a higher level of plastic deformation while maintaining the same impact velocity. This process has also a discontinuous nature which exploits non-stationary pressure waves to generate simultaneously higher pressure and temperature than in CS process (where a continuous, stationary flow exists.).

Another variation to CS is called vacuum cold spray (VCS). In this process the specimen is placed in a vacuum tank with a pressure that is substantially less than the atmospheric pressure. The low pressure environment is provided by a vacuum tank coupled to a vacuum pump. The vacuum tank allows for gas recovery and for powder overspray collection.[13] It is worth noting that a similar design has been also disclosed which is called aerosol deposition method (ADM). In this process, nanoparticles are sprayed in a vacuum chamber using a propellant gas flow of helium or air. In this method, the propellant gas pressure is also below atmospheric pressure and the velocity reached is lower than that for CS. This process reduces the presence of the shockwave at the substrate or bow shock effect significantly, making it possible to deposit very small particles.[14] A schematic of different CS systems is shown in Fig. 1.

The main and more applicable categories of CS technology have been described. Nevertheless introducing all the patented CS apparatus is out of the scope of the present review and interested readers are referred to the available review on this topic.[15]

Impact phenomena and bonding mechanisms

Particles/substrate interaction during the CS deposition process and the resultant bonding, is of great importance in CS technology because of the effect on coating characteristics. Experimental studies and computational modelings have been performed to have a better understanding of the bonding process during CS.[16] They revealed that adhesion only occurs when the powder particles exceed a critical impact velocity which is specific to the spray material.[17] The predominant bonding mechanism in CS is attributed to 'adiabatic shear instability' that occurs at the particle substrate interface at or beyond the critical velocity. A strong pressure field is introduced as a result of particle impact on the substrate. Consequently, a shear load is generated which accelerates the material laterally. This causes localized shear straining which under critical conditions leads to adiabatic shear instability.[18–20]

The initiation of adiabatic shear instability is usually described by thermal softening in competition with rate effects and work hardening. During work hardening, the distortion of grain structure and the generation and glide of dislocations occur. The rest of the plastic work, which can be as much as 90% of the total, is dissipated as heat. Heat generated by plastic work softens the material. At a certain point, thermal softening dominates over work hardening such that eventually stress falls with increasing strain. As a result, the material becomes locally unstable and additional imposed strain tends to accumulate in a narrow band.[21] Consequently, an interfacial jet composed of the highly deformed material is formed. Experimental results show that the minimal particles impact velocity needed to produce shear localisation at the particles/substrate interface correlates quite well with the critical velocity for particle deposition by the CS process in a number of metallic materials. So far adiabatic shear instability is the most prevailing bonding theory in CS.[20] By explaining the bonding mechanisms one can see that both mechanical and thermal properties of the powder material are important in particle-substrate bonding.

The success of the CS process depends mainly on the correct choice of the process velocity which should be set to lie between the critical and erosion velocity. Erosion velocity is an upper limit for particle velocity beyond

which erosion occurs instead of adhesion. Assadi *et al.*[19] used finite element simulation to study the effect of various material properties on the critical velocity in CS. They also presented a simple formulation for the critical velocity estimation which expresses it as a function of impact temperature, particle density, melting temperature and ultimate tensile strength. The formulation was later modified by addition of the particle diameter effect by Schmidt *et al.*[22] They argued that the size effect in impact dynamics can have a significant influence on the critical velocity. The results obtained from copper and stainless steel 316L clearly demonstrated that the critical velocity decreases with increasing particle size. This can be attributed to the effects of heat conduction or strain rate hardening. Another finite element model was developed later based on the determination of the adiabatic shear instability, which resulted in the predicted critical velocity assessment close to the experimentally extracted values.[23] An important parameter which was not considered in previous models but has a significant effect on the critical velocity is particle porosity. As the oxygen content of feedstock increases, the critical velocity significantly increases.[24–27] An oxide accumulated at the particle/ substrate interface obstructs the adhesion between activated particle and substrate surface during impact. A hybrid approach containing finite element model and analytical solution was developed by Moridi *et al.*[28] to predict both critical and erosion velocities. Based on the results, the existing formulation was further developed taking into account the effect of particle porosity in calculation of critical and erosion velocities.

Conventional versus new material systems

The worldwide materials industry has experienced a revolution related to new materials and their commercial product applications. Advanced materials can be used as coatings to reduce material consumption. Following that, CS technology with its unique properties is a prime candidate. In the last decade, there has been a continuous trend toward spraying new materials for specific applications. At the beginning, CS technology was mostly conducted on selected metallic materials to understand the adhesion mechanism involved during the process. Soon it spread to other materials and currently a wide variety of materials has been successfully deposited to obtain surfaces with superior and possibly multifunctional properties. For instance one could mention successful deposition of brittle compounds in a ductile matrix and its commercial applications. The technology has emerged into polymers as well, but the area is still developing and there is a lot more to explore. Currently, studies in this field are expanding and the main purpose of this review is to summarize the current state of knowledge on various material systems, focusing on the most promising material systems under development. In this perspective, material systems involved in CS technology are divided into six important categories: metals, metal matrix composites, ceramics, polymers, nanostructured powders and finally nonmetallic substrates.

Material systems

Metals

Different material systems that have already been cold sprayed will be discussed. We will start with the material eligibility for CS process is first described. Although exceeding the critical velocity is necessary for successful bonding and coating formation, one can also rate material suitability for CS process. The suitability of materials depends mainly on their deformation properties. Different crystal structures have different dislocation systems. A systematic approach has been developed to determine the eligibility of materials considering the basic physical properties such as material hardness, melting temperature, density and particle velocity.[29] Materials with relatively low melting point and low mechanical strength such as Zn, Al, and Cu are ideal materials, as they have a low yield strength and exhibit significant softening at elevated temperatures. No gas pre-warming or only low process temperatures are required to produce dense coatings using these materials. It is worth mentioning that the deposition of Al is somewhat more difficult than other soft materials such as Zn and Cu. This is attributed to its high heat capacity which makes it more difficult to achieve shear instability conditions during impact, in spite of its low melting point and low yield strength. This classification is based on physical properties. Thermal properties of material are not taken into account although they can be important factors as well.

There are quite a number of studies available in the literature on depositing Cu and its alloys,[30–38] Al and its alloys[30,39–44] and Zn and its alloys.[45–47]

In contrast, for the majority of materials with higher strength such as Fe and Ni base materials, the low process temperatures generally do not provide enough energy for successful deposition. Although these materials are in general not ideal for CS deposition, this never inhibited the spreading of CS technology to deposit such materials. Several reports are available on deposition of titanium and its alloys,[48–53] stainless steel,[46] nickel and its alloys,[54–56] and tantalum.[57–60]

The available literature in this section mostly discussed the deposition of metal and metal alloy particles and their resulting microstructures. The effect of CS coating on different mechanical characteristics such as fatigue, corrosion, bond strength, hardness, oxidation, etc. has been investigated. These properties are all of industrial interests. Among these, fatigue accounts for about 90% of all mechanical failures. However, less attention has been paid to the fatigue performance of cold spray coating. The available literature on this topic presents controversial results. Some material systems showed improvement while the others showed deterioration of fatigue limit. The results could be interpreted as follows: if the coating remains attached to the substrate during the fatigue test; it can potentially increase the fatigue limit. Considering available data one might speculate that the level of improvement of fatigue limit depends on the amount of compressive residual stress in the coating and substrate and more importantly on the difference between the coating fatigue limit and the substrate fatigue limit. The coating should have higher fatigue limit to be able to increase the coating/ substrate system fatigue limit. The higher the difference, the higher the coating/substrate fatigue limit will be, in the case that coating remain attached. The influential parameters are gathered in a formula, which can predict the fatigue limit of CS system as a function of residual stress, coating hardness and stress gradient in the specimen.[61]

Besides, there were also some studies concerning microstructure evolution such as the effect of post annealing treatment on forming a diffusion bond and
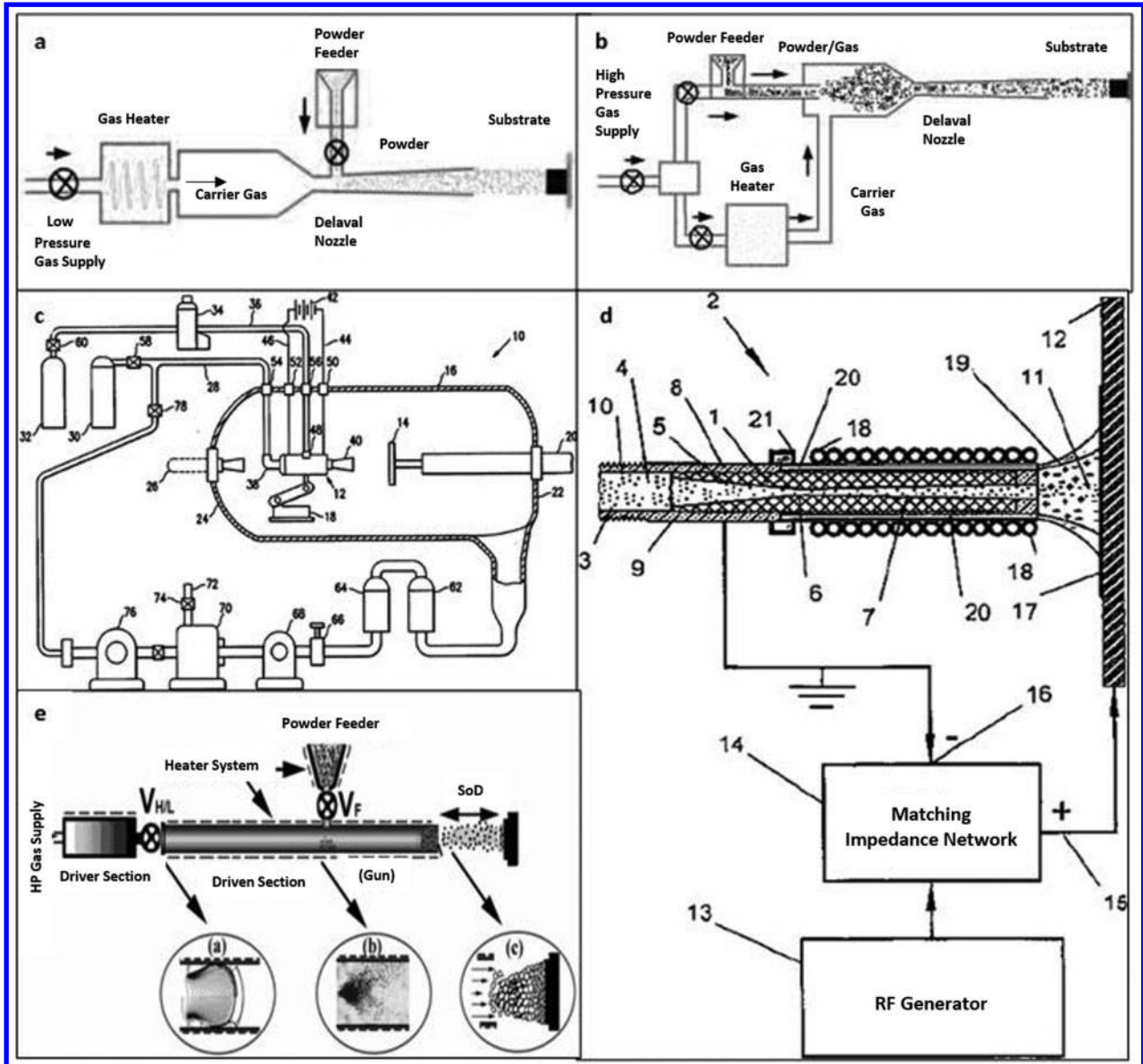
1 Schematic of different CS systems: *a* **low pressure cold spray;** *b* **high pressure cold spray;** *c* **vacuum cold spray;**[13] *d* **kinetic metallisation;**[11] *e* **pulsed gas dynamic spray**

making intermetallic compounds,[30,41] effect of vacuum heat treatment on the microstructure and microhardness,[36] phase stability,[62] and effect of quasi crystalline particles of submicrometre and nanoscales (<100 to 200 nm) on the deformation-induced structure.[63]

There were also quite a number of studies on cold spraying of thermal barrier coatings (TBC) which in some cases did not show significant improvement in functionality over high velocity oxy-fuel (HVOF) deposition method.[64,65] Increasing demands for higher gas turbine engine performance have led to the development of TBC systems applied to the engine's hot components. TBCs typically consist of an underlying MCrAlY bond coat with an yttria partially stabilised zirconia (YSZ) ceramic top coat.[66] The latter acts as a thermal insulator whereas the former promotes bonding between the part and the top coat and provides protection against oxidation and hot corrosion. In contrast to the generally accepted theory that the CS process does not lead to changes in the deposited

material's microstructure and phase, results of CoNiCrAlY coatings deposited using the CS system demonstrated the occurrence of notable microstructural and phase changes.[67] There are also some studies on nanostructured MCrAlY coatings as well, which will be discussed later in the section devoted to 'Nanostructured powders'.

Cross-sections of selected metallic cold spray coatings are illustrated in Fig. 2. The coating microstructure varies in different cases but, generally, dense coatings with small porosities are obtained by CS process.

Amorphous metals have also been deposited using CS. An amorphous metal (also known as metallic glass or glassy metal) is a solid metallic material, usually characterised by its lack of crystallographic defects such as grain boundaries and dislocations typically found in crystalline material.[68,69] The absence of grain boundaries, the weak spots of crystalline materials, leads to better resistance to wear and corrosion in amorphous metals. Therefore, they are potential candidates to form
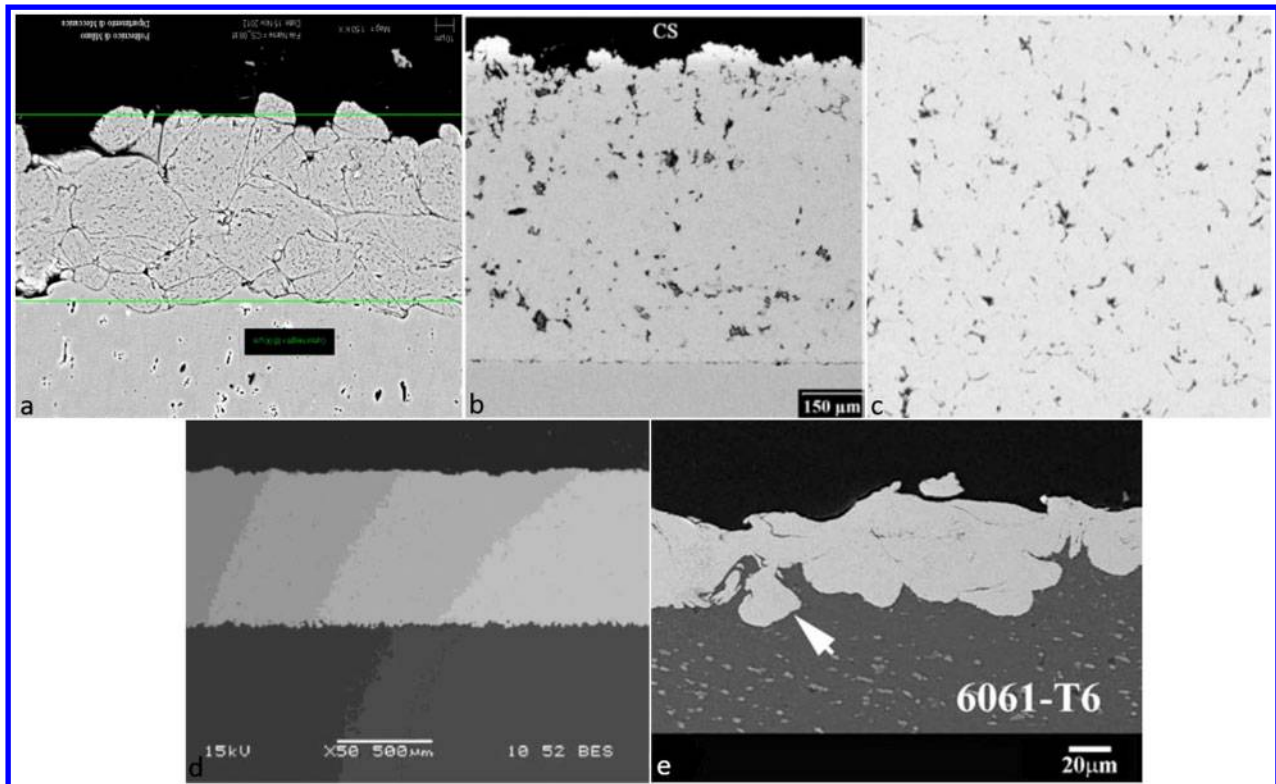
2 Cross-section of selected metallic CS structures: *a* Al 6082 on Al 6082;[44] *b* Ti on Ti6Al4V;[52] *c* Inconel 718 on Al alloy;[54] *d* Ta on Al;[57] *e* Ni on Al alloy[55]

a strong coating. Amorphous metals, while technically glasses, are also tougher and less brittle than oxide glasses and ceramics. In fact, they exhibit unique softening behaviour above their glass transition temperatures. There are several ways in which amorphous metals can be produced, including extremely rapid cooling, physical vapour deposition, solid state reaction, ion irradiation and mechanical alloying. More recently a number of alloys with low critical cooling rates have been produced; these are known as bulk metallic glasses (BMGs).[70,71] Perhaps the most useful property of bulk amorphous alloys is that they are true glasses, which means that they soften and flow upon heating.

Bulk metallic glasses display superplasticity within a supercooled liquid region (T_g to T_x; T_g is glass transition temperature where significant softening occurs and T_x is ductile–brittle transition temperature). However, the degradation of the properties of amorphous BMGs can occur due to crystallisation driven by external energy input through heating and mechanical deformation.[72,73] Also, it has been confirmed that thermal energy released through mechanical deformation can result in the nanocrystallisation of BMGs. There are a few records available in the literature on CS deposition of metallic glasses.[74,75] According to calculations and CS experiments, neither the glass transition temperature T_g nor the melting temperature T_m can adequately describe the required conditions for bonding. Thus, the so called softening temperature between the glass transition temperature and the melting temperature had to be defined to determine the critical velocity of metallic glasses.

The impact of BMG particles with different initial temperatures is shown in Fig. 3. The different deformability in super liquid region without any cracking can be easily seen in the figure.

Critical discussion

The literature on deposition of metallic materials via CS is rich. Metallic powders were the first class of materials being investigated for CS process. Since the invention of CS, there has been a number of fundamental studies in the field of gas dynamics of CS, the interaction of a high speed particle with the substrate and the related bonding mechanism. However, there are still some open questions such as the material behaviour under extreme deformation conditions including very high strain rates of up to 10^9 s^{-1}. In addition, less attention has been paid to the coating build up (particle to particle impact) mechanism and studies were more focused on the initiation phase of the coating formation (particle to substrate).

Another possible avenue to explore is finding the major parameters that may play a role in the adhesion during CS deposition of BMGs. Another missing chain in the field of CS is that there is not a standard way to quantitatively characterise CS coatings for comparing results of different deposited coatings. The progress in this aspect will be very helpful to reveal the strengths and weaknesses of different CS apparatus and CS conditions in comparison to each other. Some researchers suggest free standing coatings can be used to test the coating properties and compare coatings obtained by different technologies and parameters. Nonetheless there is an argument that it is crucial to capture the interaction of substrate and coating during experimental procedures.

Metal matrix composites

The limitation of material applicable as feedstock for CS comes from its bonding nature. Feedstock powders must have some degree of ductility at high strain rate in order
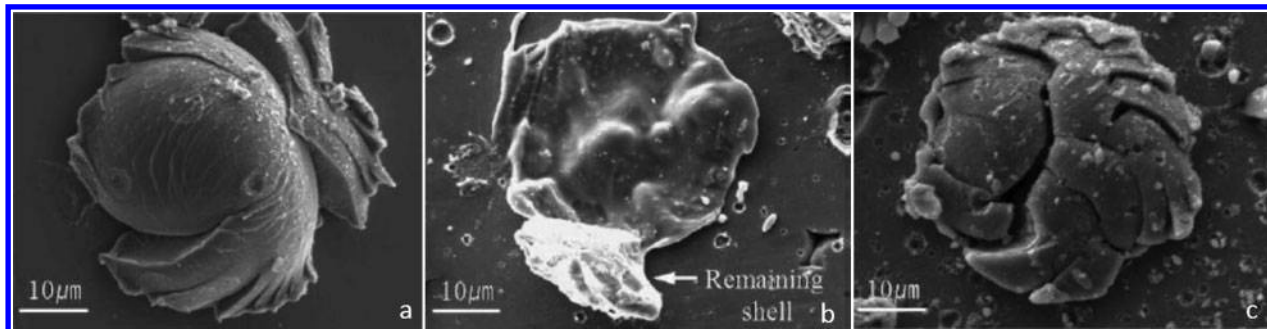
3 BMG impact particles with different initial temperatures: *a* room temperature; *b* between T_g and T_x; *c* above T_x (Ref. 75)

to form shear deformation on the contacting surfaces and consequently result in bonding and coating build up. Therefore, CS seems not to be so convenient for producing coatings made from brittle materials. On the other hand, by increasing demand for coating tribological properties, hard particles with enhanced hardness are needed. Because of their lack of ductility they cannot be deposited directly. In addition, intermetallic compounds (involving two or more metallic elements, with optionally one or more non-metallic elements in solid phase, whose crystal structure is different from the other constituents) are also generally brittle and have a high melting point which is not appropriate for CS. To solve the problem, addition of hard particles to deformable metallic matrix appeared to be an appropriate solution.[76]

The idea of metal matrix composite (MMC) was implemented to facilitate deposition of brittle materials. MMC is a composite material with at least two constituent parts, one being a metal and the other being a different metal or other material. MMC manufacturing techniques can be divided into three types: solid state, liquid state, and vapour deposition. In recent years, CS has emerged among solid manufacturing processes of MMC. Blending different powders and cold spraying them on the substrate is the widely applied method. Because of the low deposition temperature during CS, there are no significant reactions during the spraying of mixed powders. There are other advantages such as lower oxygen content and higher density for the obtained coating. These advantages help to reduce shrinkage during any subsequent heat treatment.

In case of two metals forming a MMC, a post deposition heat treatment can result in the formation of intermetallic compounds in a controlled environment. In case of a combination of metal with hard particles, metal acts as matrix allowing hard particles to be embedded and facilitating the development of high density or functional coatings.[77]

MMC, depending on the involved materials, has different applications which are summarised in this section. This section is divided into two categories. In the first group, the main components are metals and in the second group, metal and hard particles are deposited together. There is not an established criterion to ensure the success of CS process during deposition of composite materials. All numerical studies in the literature have focused on metal powder deposition and the critical velocity as a criterion for bonding. Since there are no criteria for successful deposition of composite powders, different studies in this field have used experimental tools such as optical, transmission and scanning electron microscopy (SEM), as well as micro hardness and bond strength tests to evaluate the coatings characteristics.

Metal-metal matrix composite

In this section we will review the available literature on the deposition of combination of pure metals, metal alloys and intermetallic compounds. Note that intermetallic compounds are different from alloys although they are both metallic phases having more than one element. In intermetallic compounds, different elements are ordered into different sites with different environment while in alloys, they substitute randomly in the crystal structure.

A reasonably dense material was produced by HPCS of Ti/Al.[77] A mixture of Al and Ti regions was found in the coating. The temperature during process was low enough preventing particles from being alloyed together. It was shown that post heat treatment can convert Ti/Al deposits into intermetallic materials. Subsequent post spray heat treatment at 630°C for 5 h was performed on co-deposited Ti/Al to prepare a novel TiAl$_3$–Al coating.[78] In the coating structure TiAl$_3$ phase embedded in the residual aluminium matrix. An interlayer about 10 μm was formed between the coating and the substrate. High temperature oxidation protection was proved for the base orthorhombic Ti–22Al–26Nb (at-%) alloy with no sign of degradation after being subjected to 150 oxidation cycles at 950°C. The microstructure analysis of the oxidised composite coating showed that an Al$_2$O$_3$ scale with a complex structure can be formed outside the interlayer during oxidation. No oxide beneath the interlayer was detected, which indicates that the complex continuous Al$_2$O$_3$ and the interlayer provided the protection of the substrate under the high temperature oxidation condition.

The most influential factor in compounding reaction is solid state diffusion. The defect generation during the CS process can have an effect on diffusion. The processing parameters, such as gas pressure, gas temperature, and powder feeding rate, etc., could influence the particle velocity and subsequently the coating properties such as coating density and defect density. The relationship between gas pressure and Al based intermetallic compound formation was investigated.[79] Spraying Al onto Ni substrate and Al + Ni onto Al substrate was investigated. Post annealing was performed on different samples at low temperature and intermetallic compound layers of Al$_3$Ni and Al$_3$Ni$_2$ were observed. The relatively soft Al has been coated under a low gas pressure condition (0·7 MPa) with severe plastic deformation owing to large peening effect.
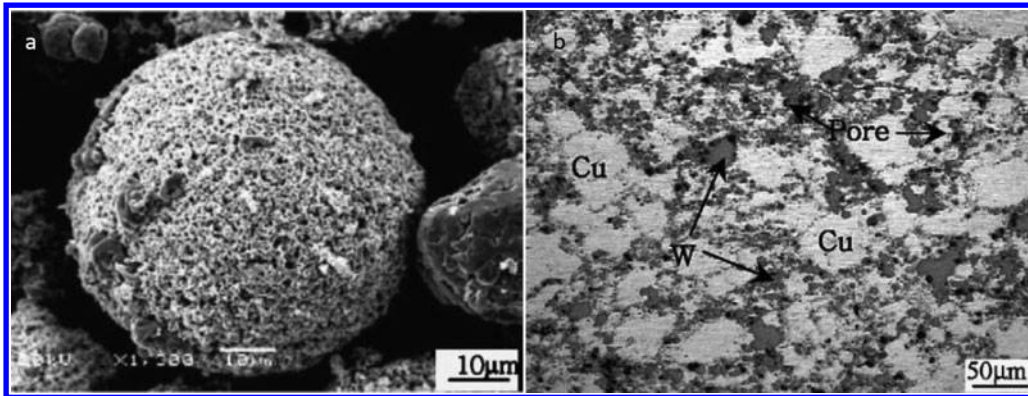
4 *a* W/Cu composite powder and *b* cross-section of resulting CS coating[82]

On the contrary, the Al particles coated at higher pressures (1·5 and 2·5 MPa) were not severely deformed. The pressure controlled peening effects could alter the main route of Al consumption during annealing: eutectic or compounding of intermetallics. The thin and continuous intermetallic compound layer was formed at the interface with the low pressure condition (0·7 MPa). On the other hand, the thick and discontinuous intermetallic compound layer was observed under the higher pressure conditions (1·5 and 2·5 MPa). Also, many eutectic pores were found in the Al–Ni composite coatings with the lower gas pressure condition (0·7 MPa). Far less pores were found with the higher pressure environment.

Co base refractory alloy [38·15Co–21Cr–31·2Ni–0·099Fe–7·60Al–0·065Y–0·11O (wt-%)] with and without the addition of Ni powders was prepared on a carbon steel substrate by CS.[80] About 250 μm thick Co base refractory alloy coating was deposited on a steel substrate. Particles had considerable plastic deformation during the deposition process. The elastic modulus of the coating was higher than 160–GPa and the nanohardness was more than 6–GPa. Addition of Ni powders into Co base refractory alloy reduced nanohardness and increased density of the coating.

Stainless steel 316L mixed with three different proportions of Co–Cr alloy L605 powders (by volume of Co–Cr, 25, 33·3 and 50%) has been HPCS-ed onto a mild steel substrate.[81] The porosity of the coating was low (about 0·9–1·5%) for both the 25 and 33·3% coating. However, much higher porosity (about 4·5%) was generated for 50%Co–Cr. Much poorer deposition rate in this case caused much thinner coating using the same processing parameters. The ductility of the annealed 25 and 33·3% specimens (from tensile test) reached approximately 20 and 18% respectively after annealing, but the 50% specimen was too thin to be tested. Potentiodynamic polarisation tests carried out in Hank's solution (A balanced salt solution made to a physiological pH and salt concentration) as an electrolyte showed that higher corrosion resistance was obtained for the metal–metal mixture with respect to the pure stainless steel.

Several types of Zn based coatings including Zn+(Al–Si) and Zn+Al+Si (tri-powder) were deposited using LPCS.[45] Metal coatings of Zn and Al, and the composite coatings of Zn+Al were also deposited for comparison. The effect of mass loading (the mass of the coating per unit area (g m^{-2}), which is determined by measuring the mass of a sample before and after deposition) of the coating as a function of the dwell time (i.e. the inverse of the traverse speed at which the substrate moves in front of the spray nozzle) was studied. The Zn coatings and Al coatings were observed to exhibit distinct loading behaviours, which, in turn, affect the coating formation and microstructure of the composite coatings of Zn+Al and Zn+Al+Si (Tri-powder). The microstructural inhomogeneity of these coatings, namely the preferential distribution of Zn particles near the coating substrate, was directly related to the different loading dependencies of Zn particles and Al particles. For composite coatings of Zn+(Al–Si) containing Zn powder and Al–Si alloy powder, the coating compositions invariably deviated from the starting powders. This was caused primarily by the different deposition efficiencies of Zn and Al–Si powders at the same spray condition, which depend on their respective hardness. With the proper post-spray heat treatments, (e.g. using induction or laser heating), the diffusion of Si, along with the Zn particles, can effectively lower the melting temperature of the coatings. In addition, a surface layer with Zn concentration gradients can be obtained on the Al substrates coated with composite coatings of Zn+Al+Si and Zn+(Al–Si).

Proper ratio of tungsten powder and copper powder [75W–25Cu (wt-%)] were ball milled in a stainless steel container with cemented tungsten carbide balls.[82] Agglomerated W/Cu composite powders (Fig. 4a) were deposited on mild steel substrate for electronic package applications by HPCS. Both CS and plasma spray have been used as deposition methods. Microstructural observation revealed that more pores are present in the vicinity of the tungsten rich regions of the final product. The level of porosity varied with the content of tungsten. Two processes have different oxidation levels. For the CS deposition no Cu oxidation was found. However, relatively high Cu oxidation was observed for the plasma sprayed deposition. The SEM image of composite powder and the resulting microstructure via CS deposition is shown in Fig. 4. Localised pores around the W rich regions are obvious in the figure.

$Nd_2Fe_{14}B$ powder was blended with Al powder to make mixtures of 20–80 vol.-%$Nd_2Fe_{14}B$. HPCS at temperature range of 200–480°C was utilised to obtain $Nd_2Fe_{14}B$ permanent magnet/Al composite coating.[83] The hard $Nd_2Fe_{14}B$ particles fractured when they
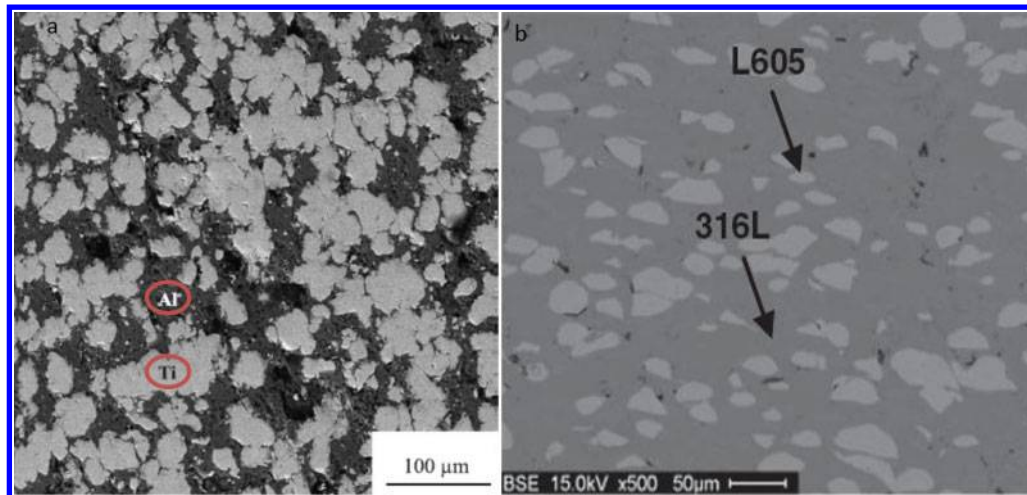
5 Cross-section of selected MMC coating containing two metallic parts *a* Al/Ti[77] and *b* stainless steel/Co–Cr alloy[81]

impacted the substrate while Al had severe plastic deformation. The deformation could remove pores and entrap $Nd_2Fe_{14}B$ within the coating. The magnetic properties of $Nd_2Fe_{14}B$ remained the same by the CS process. It was found that entrapping Nd_2Fe14B particles within the composite coating can be increased by higher spray temperatures and finer $Nd_2Fe_{14}B$ particle sizes. This fact could be explained by calculating rebound momentum and how process parameters affect it. The particle will rebound off the surface unless its momentum is small enough to be immobilised by later arriving particles and be entrapped in the coating.

Commercially pure Al and Al blended with 50 and 75 vol.-% of the intermetallic $Mg_{17}Al_{12}$ compound feedstock as reinforcement powders was deposited onto as cast AZ91D magnesium substrate using CS. Low working gas pressure and temperature were employed in the process.[84] The $Mg_{17}Al_{12}$ intermetallic particles are hard and can be considered as hard ceramic reinforcement particles in the MMC coatings. Less than 10 vol.-% of the $Mg_{17}Al_{12}$ particles were maintained in the coatings. However, they were able to increase the hardness from 47 ± 5 HV $(0.1$ kg$)$ to 58 ± 3 HV $(0.1$ kg$)$ and the bonding strength was significantly higher than the pure Al coating. The results suggest that adding hard particles into initial feedstock can reduce the porosity in the coating. Electrochemical corrosion experiments showed that the composite coating and bulk Al exhibited similar behaviour. Therefore, it can be used as an appropriate protective layer for AZ91D magnesium.

Selected microstructures of MMC coatings including metallic components are shown in Fig. 5.

Particle reinforced metal matrix composite

In order to have a successful coating with low porosity and good adherence, the particles should have a degree of deformability. They should undergo plastic deformation in order to result in adherent coating. Therefore, less deformable materials cannot be successfully deposited due to lack of plastic deformation. Producing CS coatings of ductile metals mixed with brittle ceramic materials would be a very useful achievement. Particle reinforced MMCs enable physical and mechanical properties to be tailored. However, ductility might decrease to some extents.[85]

Besides, this type of spraying has other advantages such as keeping the nozzle clean and eliminating its clogging. Hard particles can activate the sprayed surface by removing oxide layers, contamination and impurities. Moreover hard particles create microasperities that favour the bonding of the incoming particles and increase the contact area between the coating and the substrate. It was shown that the deposition efficiency can be improved by adding hard particles to a metal powder. The use of a ceramic metal mixture can enhance the coating quality by reducing porosity of the coating, peening of preexisting layers, removing poorly bonded particles and increasing bond strength of the coating to the substrate.[86]

The deposition efficiency of a cermet mixture depends strongly on the mass ratio between components and, under certain conditions; it can considerably exceed that of pure metals. It was also shown that the deposition efficiency of a metal ceramic mixture strongly depends on the ceramic particle granulometry.[87] There are several studies on this material system which will be briefly summarised. The majority of studies were on oxides and carbides of different metals and especially with Al_2O_3 as reinforcement particle. There were also some reports available on WC and diamond and their characterisation which we will go through consequently.

We start with studies on Al_2O_3 as reinforcement particles. Different studies vary according to the material systems involved (metal matrix and substrate) and the parameters chosen (particle shape, velocity, weight ratio of powder mixture).

Different compositions of $Al–Al_2O_3$ varied from $10:1$ wt-% to $1:1$ wt-% were successfully deposited on Si and Al substrates using LPCS.[88] Initial starting Al_2O_3 particles affected the crater formation between the coatings and substrate. Examination of $Al + SiC$ composite, pure Al, SiC, and Al_2O_3 coatings on Si substrates by the CS process[89] demonstrated that SiC and Al_2O_3 have been successfully sprayed producing coatings with thickness more than 50 μm with the incorporation of Al as a binder.

Two spherical aluminium powders with the average diameters of 36 and 81 μm were employed to study the coating build-up mechanisms and properties of cold
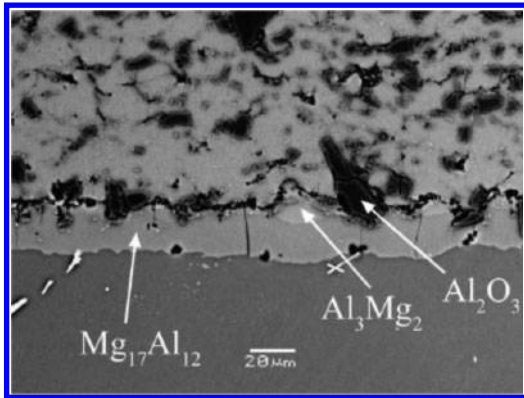
6 6061Al–50%Al$_2$O$_3$ coating after heat treatment of 400°C for 2 h (Ref. 90)

sprayed Al–Al$_2$O$_3$ cermets using LPCS.[86] Al$_2$O$_3$ fraction either in the starting powder or in the coating was found to play an important role in the resultant coating properties such as bond strength, wear, corrosion and hardness. Coatings with larger starting powders are likely to be harder than coatings made with the smaller size Al powder. This is due to the higher kinetic energy and consequently larger peening effect of the large particles. The coating deposition efficiency was improved by addition of Al$_2$O$_3$ to the Al powders. Al$_2$O$_3$ particles alone cannot form a coating due to the lack of deformability. However, they can be entrapped during deposition of blended Al and Al$_2$O$_3$ powders. The bonding between Al and Al$_2$O$_3$ is therefore weak. The abrasion resistance of composite coating is generally expected to increase by addition of hard phase. Nevertheless, the poor cohesion between Al and Al$_2$O$_3$ restricts possible improvement of the abrasion resistance of the composite coatings. In addition, the reduction in cohesion strength can ultimately result in fracture transition mode from adhesion (which is typical in case of ductile CS coatings) to cohesion. The adhesion of the coating on the substrate increased by addition of Al$_2$O$_3$ to Al powder. The hard ceramic particles create microasperities that assist the bonding of the incoming Al particles and also increase the surface area between the coating and the substrate. The inclusion of alumina particles in the aluminium coatings proved to have no detrimental effect on the corrosion protection of the substrate against alternated immersion in saltwater and against salt spray environment.

Similar results were also obtained for pure Al and 6061 aluminium alloy based Al$_2$O$_3$ particle reinforced composite coatings produced on AZ91E substrates.[90] Figure 6 shows the formation of intermetallic compound after heat treatment at the interface between coating and substrate.

The effect of adding reinforcement particles to a relatively hard matrix material was also studied by addition of Al$_2$O$_3$ to SS316 powders.[85] Although the deposition efficiency of Al$_2$O$_3$ was less than SS, the overall LPCS efficiency increased for the powder mixture deposition. Shear testing of the coatings was done on the composite coating. There was no significant change in bond strength as a function of Al$_2$O$_3$ content. However, the fracture mechanism clearly shifted from cohesive to adhesive fracture with higher Al$_2$O$_3$ contents in the coating. In contrast to adhesive failure of more

ductile matrices and coatings, the fracture mode in this case was cohesive. This could be attributed to higher porosity in the coating and lack of plastic deformation for relatively hard matrix material. The addition of Al$_2$O$_3$ to the coating induced larger plastic deformation, reduced the porosity and resulted in a coating with cohesive strength higher than the interface strength. Although the maximum Al$_2$O$_3$ addition increased the hardness of the coating by 30%, it reduced the wear rate by a factor of ten. The wear mode change to fully abrasive wear was the possible explanation for this observation. A shift towards the polarisation behaviour of bulk stainless steel with Al$_2$O$_3$ additions was also observed in the corrosion behaviour, examined by anodic polarisation tests.

The effect of different particle types of Cu powder and different amount of added Al$_2$O$_3$ particles on the microstructure, coating density, fracture behaviour, and mechanical properties, i.e. hardness and bond strength was evaluated.[91] 0, 10, 30, and 50 vol.-%Al$_2$O$_3$ were added to spherical and dendritic Cu particles. LPCS was used for deposition. The amount of Al$_2$O$_3$ inside the coating was far less than the initial mixture: 0·9, 1·5 and 3·6% for spherical powder and 0·7, 2 and 3·3% for dendritic powder. Hard particle addition improved the coating densities and particle deformation reflecting the densifying and hammering effect of hard particles. Furthermore, increasing the fraction of Al$_2$O$_3$ caused an increase in hardness and bond strength. Spherical Cu particles led to a denser and less oxide containing coating structure with respect to the other powder shapes. The reason is that the dendritic particles have more boundaries due to the finer particle size of the primary particles. Therefore, there are more possibilities for them to have weak bonds between the particles due to the higher amount of oxidised particle boundaries.

Al–Al$_2$O$_3$ composite coatings was deposited on AZ91D magnesium alloy substrates using KM.[92] KM, as introduced before, is a special type of CS which accelerates particles up to sonic velocities. Similar results concerning mechanical properties and deposition efficiency were obtained using KM instead of CS system. Results of bond strength tests and SEM observations revealed that higher Al$_2$O$_3$ contents caused an adhesive to cohesive failure mode transition as we mentioned earlier.

The effect on the resultant coating with different ceramic particle velocities during CS process of a composite coating was analysed.[87] Different amount of Al$_2$O$_3$ and SiC were co-deposited by HPCS with Cu and Al powders as metal components. Ceramic particles were injected into different zones of the gas flow to obtain different velocities. The subsonic and supersonic parts of the nozzle and the free jet after the nozzle exit (see Fig. 7) were chosen as injecting sites. Results showed that ceramic particles that have high enough velocity can penetrate into the coating. In contrast, low velocity ceramic particles rebound from the surface. The study revealed the importance of the ceramic particle velocity to have a successful and stable CS process.

Composite coatings of an aluminium bronze metal matrix and a hard ceramic alumina phase were sprayed by CS technique in order to increase the tribological
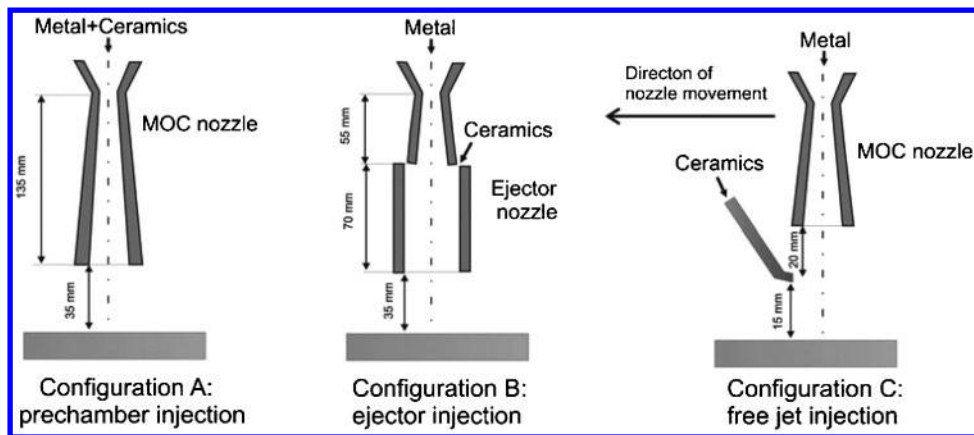
7 Schematic of powder injection in different parts of nozzle[87]

properties of the pure bronze coatings.[93] Results confirmed that the hard ceramic phase increases the tribological properties compared to the original bronze coating.

Several metal feedstock compositions (combinations of Al, Zn atomised powders, and Al_2O_3 fine particles) were deposited on AA2024-T3 Alclad substrate using LPCS.[94] Result confirmed the possibility of utilising LPCS process to deposit corrosion protective coatings of light alloys as well as repairing Al and Al cladding structures during overhaul maintenance schedule in industry.

After the overview of material systems utilising Al_2O_3 as reinforcement particles, we will go through other studies with the aim of increasing coating tribological properties by using hard particles other than Al_2O_3.

Because of the unique properties of tungsten especially for wear resistant applications, compounds of W have been noteworthy for CS deposition. WC/Co composite coating with different ratios has been studied. WC–12–17%Co powders with nano and microstructures were deposited by HPCS process using nitrogen and helium gases.[95] No phase transformation and/or dec-arburisation of WC were noticed after CS deposition. It is also observed that nano-sized WC in initial powder is maintained in the CS coatings. It seems that the agglomeration of nanoparticles into microscopic particle is advantageous over micro-sized particles for CS deposition as higher particle velocity can be obtained in this case with the same gas velocity. Nanostructured WC–Co coating was successfully fabricated with high density and very high hardness (2050 HV) by CS deposition with appropriate powder preheating.

The same composition with a different weight percent ratio was also studied. Two types of cermet powders, the nanocrystalline (WC–15Co) and the conventional (WC–10Co4Cr) powders were deposited using HPCS and pulsed gas dynamic spraying (PGDS) for wear resistant applications processes.[96] Similar to the previous studies, no degradation of the carbide phase occurred. However, this study reported that CS process had difficulty in forming dense coatings without major defects. PGDS process was found to be capable of depositing thick composite coatings from both conventional and nano-crystalline powders. This was achievable only when the powder was heated above 573 K. The resultant coating microstructure via conventional CS and the new PGDS is shown in Fig. 8. It is obvious that the coating microstructure is much better and has fewer defects with PGDS deposition method.

WC–25Co cermet powders were also deposited on carbon steel and aluminium alloy Al7075-T6 substrates using HPCS.[97] Thick, dense and hard WC–25Co coatings on both substrates could be obtained by CS process. Coating showed excellent tribological and electrochemical properties.

The potential of the HPCS process in deposition of Cr_3C_2–25 wt-%NiCr and Cr_3C_2–25wt-%Ni coatings on 4140 alloy steel was also explored.[98] This composition improved the tribological properties and has a wear resistant application. A number of parameters such as powder feedstock characteristics, powder feedrate, standoff distance and gun traverse speed together with nozzle design parameters were changed to optimise deposition conditions. The goal was to improve the resultant average Vickers hardness compared to that obtained through conventional thermal spray processes. CS process optimisation resulted in increased hardness and improved wear characteristics with lower friction coefficients. The improvement in hardness is directly associated with higher particle velocities and increased densities of the Cr_3C_2 based coatings deposited on 4140 alloy at ambient temperature. The combination of CS process with the laser glazing technique was also studied. Results showed the highest HV (0·5 kg) of approximately 1015. The maximum hardness of 853 HV (0·5 kg) was obtained without hybrid treatment. The results revealed that laser glazing post treatment could significantly improve the quality of CS coatings.

Blend of SUS304 powders with 10 and 20 vol.-% diamond particles were used to prepare SUS304/diamond binary composite coatings on Al alloy substrate by CS process with *in situ* powder preheating.[99] Since the deposition efficiency of the diamond and SUS304 during the CS process is different, the fraction of the diamond in the coatings is about 30–60% of the original mixtures. Diamond particles have high impact velocity. This subsequently results in their fracture which was obvious in the composite coatings. Fracturing of diamond particles is mitigated by using higher toughness and smaller diamond particles. Since diamond fracture may occur during impact, applying a protective film on diamond powders may be beneficial. Diamond fracture might be avoided in this case because the impact energy is mostly absorbed by the outer protective film. Ti coated diamond did not present
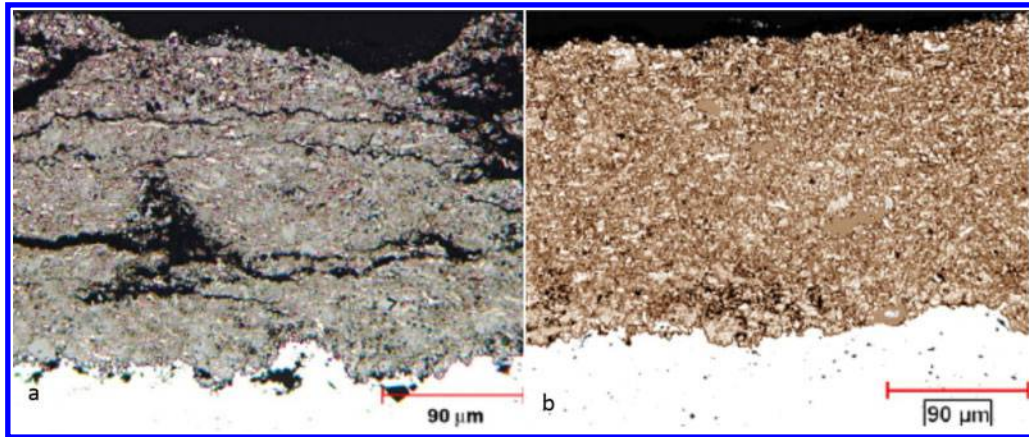
8 Cross-section of WC–Co coating using conventional powder deposited by *a* cold gas dynamic spray showing defects and *b* pulsed gas dynamic spray having dense microstructure[96]

significant difference in diamond fracture behaviour. However, results of another investigation on nickel coated diamond/bronze composite coating using HPCS shows that diamond fracturing was successfully avoided.[100] The uniform distribution and deposition efficiency of diamond particles in the coating layer could also be achieved by tailoring the physical properties (density, size, etc.) of the feedstock. Finite element simulation results also demonstrated a decrease in impact energy by applying a protective coating that can consequently protect diamond particles from fracture in CS process. Size distribution and deposition efficiency of diamond particles in the composite coatings were analyzed through SEM and image analysis methods.

The Cu–Cu$_2$O anti fouling coating was deposited by HPCS and rotating ring disk electrode was applied to study the corrosion behaviour of the coating in 3·5%NaCl solution.[101] Results indicate that both diffusion process and electrochemical reaction control the corrosion behaviour of the Cu–Cu$_2$O coating in Tafel region (region of strong polarization). Based on the reaction mechanism, a mathematical model for anodic Tafel polarization of the Cu–Cu$_2$O coating was established that agreed well with experimental results.

Reactive materials consist of intermetallic or thermite mixtures and have large energy contents. The energy involved in the alloying reaction of intermetallics results in very high reaction temperatures; while thermites, typically Al fuel oxidised by a metal oxide, may give rise to significant gaseous evolution, making them attractive in propellant applications. Investigation of this type of materials showed that HPCS process can be used to deposit reactive materials with high density and controllable shapes.[102]

Al/CuO thermite mixture was successfully deposited using CS deposition method without initiating the thermite reaction. Results showed that the flame propagation velocity is related to porosity of the coating. Increasing porosity increased the flame speed from nearly 150 mm s^{-1} at 100% up to 1400 mm s^{-1} at 20% density. This indicates a transition of energy transfer mechanism with porosity variation. At low porosities, convection is the dominant energy transfer mechanism while at vanishing porosities conduction becomes more important.

Deposition of B$_4$C/Ni composite coating[103] is different from other case studies found in the literature since B$_4$C/Ni exhibits a density ratio (ceramic/metal) that is drastically different from all other case studies. In this study combination of a lightweight ceramic co-deposited with a heavyweight metal was investigated. Various B$_4$C content (54 to 87 vol.-%) with fine or coarse particles was blended with Ni powder. Fine B$_4$C was also used as core particle and was subsequently Ni coated with chemical vapour deposition (CVD) method. Three batches with different B$_4$C contents were synthesised. The microstructure of the composite coatings obtained by HPCS with blends or CVD Ni coated powders was investigated (see Fig. 9). Fragments of B$_4$C particles were present in both types of CS coatings but coatings with CVD coated powders had less fragmented particles. In case of the CVD coated powders, more B$_4$C (44·0±4·1 vol.-%) particles were present in the coating and subsequently the coating microhardness (429±41 HV0·5) was higher. However, the highest microhardness was not obtained from the coating with the highest B$_4$C content (44·0±4·1 vol.-%). Instead it was obtained from the specimen with 32·7±1·3 vol.-%B$_4$C content. This is a perplexing result and shows that microhardness measurements on ceramic/metal composite by CS may cause controversy and is not well understood. Therefore, a more reliable study of the microhardness could help, for instance, through observation of the indentation area in order to better estimate the local mechanical behaviour of such metal/ceramic composite coatings.

Recently CS has found its way in various technologies even in medical applications. Plasma spray technique has been used to deposit bioceramics such as hydroxyapatite (HA).[104] However, due to high deposition temperature in this process, it has some drawbacks such as evaporation, phase alteration, residual stress, deboning, gas release, etc. In this regard, CS can be a good alternative for coating deposition at temperatures well below the melting point. HA coatings have been used as surface coatings on metallic implants mainly for two reasons: more rapid fixation and stronger bonding between the host bone and the implant; and increased uniform bone ingrowth and/or ongrowth at the bone/implant interface.

Composite powders of titanium and HA have been deposited on Ti and Al substrate using HPCS system.[105]
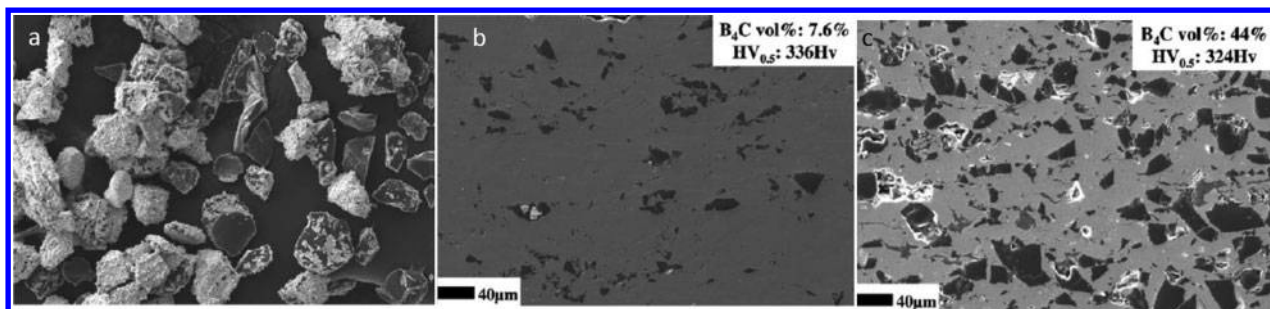
9 *a* CVD Ni coated B_4C composite powders, *b* cross-sectional images of B_4C–Ni composite coatings by CS from blend 78% mixed fine powder and *c* composite coating by CS Ni coated 78%B_4C composite powders[103]

Microstructural observations showed that dense composite coatings can be obtained. Up to 30%HA was present in the microstructure which was less than initial powder mixture. The reason is that HA and Ti powders have widely different physical characteristics and their adhesion mechanisms are different. No phase transformation of the HA occurred as indicated by XRD analysis. Furthermore, CS coating had comparable bond strength with respect to the plasma sprayed HA. Promising results revealed that CS can be a good alternative to improve surface properties of dental and orthopedic implants.

Another recent paper in this series is slightly different from previous studies and it was on embedding carbon nanotubes (CNTs) into some form of metal matrix. Many of the outstanding properties of CNTs, such as superior strength, elastic modulus, stiffness, and high thermal and electrical conductivity, will improve coating performance by incorporating CNTs into metal matrix. CNTs are allotropes of carbon with a cylindrical nanostructure. They have unique properties which are valuable for different technologies. CNT based systems are especially applicable as heat sink materials in electronic devices due to their very high axial thermal conductivity and low coefficient of thermal expansion.

Multiwalled carbon nanotube (MWCNT) reinforced copper (Cu) nanocomposite coatings were deposited on Al substrate by CS process at low pressure.[106] MWCNTs grown by the catalytic chemical vapour deposition method were employed. MWCNTs had highly crystalline thick walled structure with a narrow, hollow central part. The microstructure and the Raman spectrum showed structural damage to MWCNTs. However, the they kept their tube structure was retained. In comparison to pure Cu coated Al, MWCNT–Cu nanocomposite coated Al had higher thermal diffusivity and a comparable hardness. The reason is that high compressive stress during CS, resulted in scattering of MWCNTs within the clean and closed CNT/Cu interfaces and resulted in higher thermal diffusivity of the coating.

A selection of microstructures of MMCs with reinforced particles is shown in Fig. 10.

Critical discussion

MMC has attracted considerable attention in recent years and there are several studies with different combinations of materials available in the literature. The common feature of all studies is that no alloying, phase transformation or onset of thermite reaction (for reactive materials) occurred during CS deposition. Presence of ceramic particles in feedstock have several advantages including reinforcement of the coating by creation of a composite structure, densification of the coating and improvement of process stability, etc. Different strategies have been used to deposit MMC coatings. Blending powders together, feeding powders into different parts of the nozzle, milling powders to obtain nanostructure and finally metal coated particles have been studied so far. Among these methods, metal coated particles had promising results obtaining dense coating, entrapping more hard particles in the coating and decreasing hard particle fragmentation. However, an additional procedure of particle coating is necessary in this method.

Unfortunately, fundamental studies on co-deposition of different materials through CS have not been quantitatively conducted yet. There are still a lot of open questions that should be addressed. Case studies are available but generalising the results to be able to predict the effect of granulometry, mass ratio of powders, powder characteristics, etc. on deposition efficiency, porosity and bonding of coating to substrate has not been systematically done. The relation between the percentage of hard particles in the initial powder mixture and the resultant percentage in the sprayed coating is an important avenue to be fully understood. The fraction of reinforced particles present in the coating has a significant influence on bonding, wear, corrosion and hardness. There are some general trends such as fine particles and higher temperatures could help entrapping more particles in the structure or using deformable shell to encapsulate hard particles can absorb the impact energy and mitigate particle fragmentation. However, a generalised quantitative understanding is not yet available. Another problem is the characterisation of MMCs. Interpretation of micro hardness results for MMC materials should be treated with caution. The presence of reinforcement particles, their size and size distribution may influence coating hardness which has been ignored in some studies. The indenter may hit a reinforcement particle or the metal matrix which can cause differences in hardness values. Comparing results of different studies without these precautions could be misleading.

Results of some studies reveal that a higher content of reinforcement particles does not necessarily lead to a higher hardness. In addition, there was a report that even though the hardness increased by increasing the hard phase in the coating, the wear properties decreased because of a wear mode change. Besides, increasing the reinforcement particle content of the coating could also change the fracture mechanism. The fracture mode can
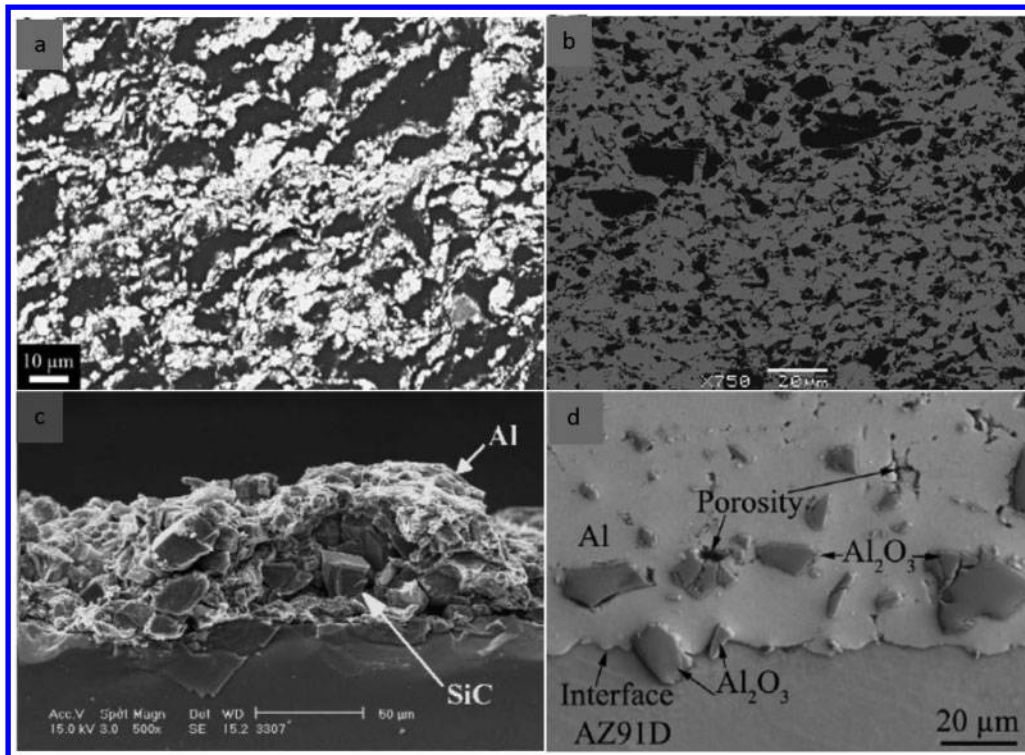
10 Selected cross-section SEM observations of MMC with reinforced particles: *a* Al/CuO;[102] *b* SS316/Al$_2$O$_3$;[85] *c* Al/Sic on Si;[88] *d* Al/Al$_2$O$_3$ on Mg alloy using KM (Ref. 92)

change from adhesive to cohesive by increasing the hard phase percentage in ductile matrices. This is due to the increase in the number of weak bonds between matrix and reinforcement particles. On the other hand, in case of relatively hard matrices the reinforcement particles can enhance the plastic deformation and increase the cohesion strength by reducing the porosity. Most often considerable attention was given to increasing the amount of hard particles in the final coating unaware of its possible drawbacks. Optimisation principles are crucial consideration for each specific application.

Moreover, the differences in material properties of matrix and reinforcement particles are likely to affect the final results of the obtained coating. The velocity of reinforcement particles before impingement on the substrate is also playing an important role. Wide range of reinforcement particles from tungsten to carbon nanotubes have been co-deposited with different metallic materials. Systematic studies on how these material property differences can affect the final results could be of great value.

Certainly both experimental investigations and theoretical studies are very important. However, fundamental studies have been underrepresented at this point. With the whole range of experimental observations available in the literature, more theoretical studies for optimizing coating properties and identifying influential parameters will help the field move forward.

Ceramics

Although cold sprayed coatings of ceramics have been tested and will be discussed in this section, ceramic particles are only able to be embedded in the substrates to form a thin layer (see Fig. 11). This is due to the lack of deformability of ceramic particles. Deformability is essential for CS coating build up. In this section we will summarise studies on deposition of ceramic particles and especially metal oxides and carbides. Consequently we will see a modification to the CS process, called VCS, which was developed because of the urgent need for ceramic coating fabrication at room temperature.

Several studies considered WO$_3$ and TiO$_2$ coatings deposited by CS. WO$_3$ and TiO$_2$ are semiconductor materials with a band gap at around 3 eV with good chemical stability in aqueous solutions. They present specific characteristics in order to be used as photoelectrodes. WO$_3$ can be used as efficient photo anode for water splitting under visible light illumination or for gas detection. Moreover, WO$_3$ thin films are also interesting electrochromic materials due to the nanocrystalline nature and open and porous structure. TiO$_2$ coatings have also potential applications in biomedical implants.

Deposition of WO$_3$ films on a silicon substrate was studied using LPCS.[108] The coating was dense and had a good adherence to the substrate. This is a ceramic on ceramic deposition so there is no plastic deformation or crater formation as normally seen in metallic coatings. The bonding mechanism was mainly due to the destruction of a relatively large size agglomeration of feedstock powder particles upon impact on the substrate. As a result very fine secondary particles were present in the microstructure and a surface with high roughness was formed. Surface roughness provided good interlocking and voids reduction among the particles in the coating. High resolution images showed that good adhesion was obtained between coating and substrate and particles had good interlocking. Therefore, particle impact onto the first layer of the coating can improve adhesion to the substrate mechanically and/or chemically.

Nano porous titanium dioxide (TiO$_2$) photocatalytic film was also deposited by HPCS using an agglomerate
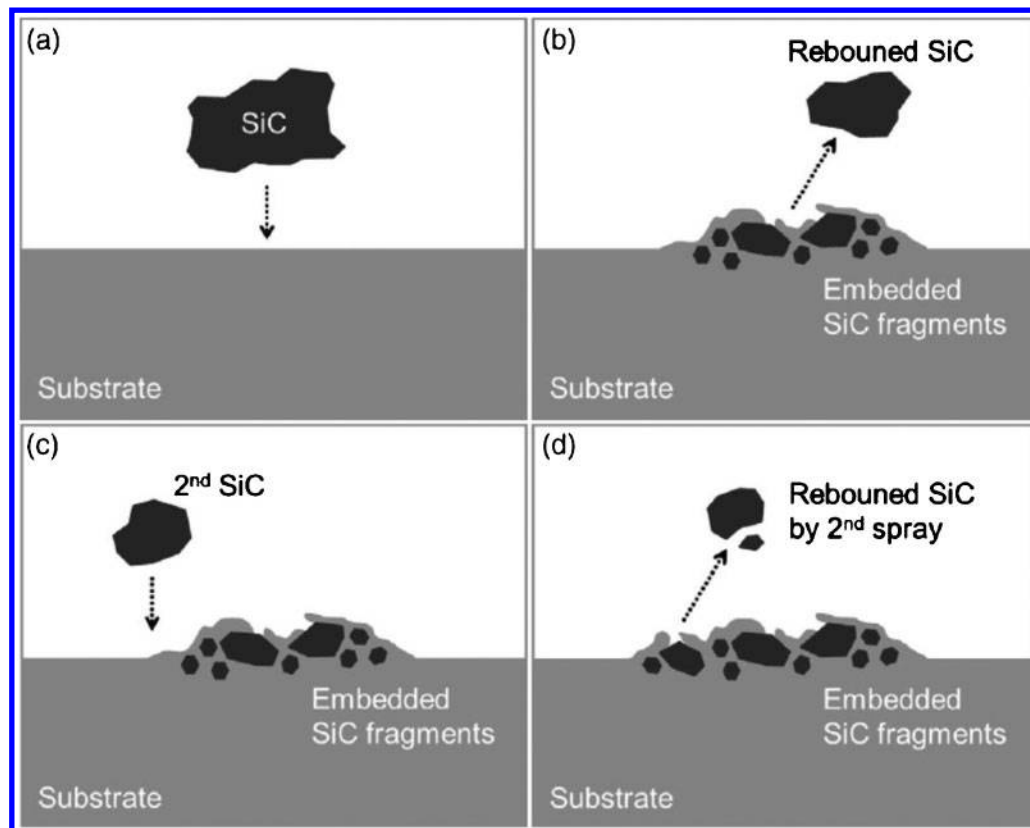
11 Schematic of SiC particle deposition on Inconel 625 substrate by CS: *a* before SiC particle impingement onto substrate; *b* after first SiC particle impingement, substrate deformed by SiC particles covers around crushed particle; *c* second SiC particle impingement; *d* substrate deforms plastically and covers around SiC fragments and subsequently SiC coating forms on substrate surface matrix[107]

anatase powder with a primary particle size of 200 nm.[109] The TiO$_2$ film had a mean thickness of 10–15 μm evenly deposited on stainless steel substrate surface. SEM examination was performed on coatings and showed a rough surface and porous structure. High photocatalytic performance was presented by coated microporous film due to its large surface area. As a result of low temperature of the spray material during CS process, the crystalline structure of the spray powder was completely retained in the film.

The formation of TiO$_2$ coatings on Al, Cu, Ti, and steel substrates using HPCS was also investigated by SEM, TEM, XRD, and Raman spectroscopy.[110] The results showed that the deposition efficiency depends on spray temperature, powder properties, and in particular on substrate ductility. This holds even for impact of ceramic particles during a second pass over already coated areas. Ceramic particles bond to metallic substrates showing evidence of shear instabilities. High-resolution TEM images revealed no crystal growth or phase transitions at the ceramic/metal interfaces.

Process gas condition effect on the coating formation of TiO$_2$ was also studied.[111] Low pressure was used for this study. Different gases (helium or nitrogen) were utilised but the results showed that the process gas is not an important factor to fabricate this coating. On the other hand, the thickness of the coatings increased with increase in process gas temperature. It indicates that the deposition efficiency of the sprayed particles can be enhanced by controlling the spray conditions.

The effect of the stand-off distance (SoD), which is an important process parameter and can be easily controlled

during fabrication, was evaluated for deposition of Al$_2$O$_3$ on Al$_2$O$_3$ (sapphire wafer) substrates.[112] The applied method was nanoparticle deposition system (NPDS). NPDS is a fabrication method for both metallic and ceramic coatings. The SoD varied from 1 to 7 mm in 2 mm increments. SoDs longer than 7 mm were not evaluated because the width and the thickness of deposited layer were not suitable for patterning. Numerical analysis showed that the impact velocity of particles increased with increasing SoD and subsequently enhances the mechanical properties of the deposited layer within the range of SoD tested.

In the next study SiC coatings were applied on Ni–Cr based super alloy Inconel 625 (58Ni–20Cr–8Mo–6Fe–3·15Nb–1Co) substrates using LPCS to improve their oxidation resistance at high temperatures.[107] The material system involves a ceramic particle and metallic substrate and the coating has been formed by fraction of particles and plastic deformation of the substrate (see Fig. 11). The super alloys form a well adherent oxide scale if they are exposed to high temperatures. The oxide scale protects the underlying substrate against further oxidation. Depending on alloy composition, Al$_2$O$_3$ or Cr$_2$O$_3$ oxide scales form on the surface. Silicon based ceramic coatings, such as SiC, are also attractive materials for anti-oxidation at elevated temperatures because of their thermophysical properties, as well as the formation of a thin amorphous SiO$_2$ scale with simultaneous low oxidation rate. The outward chromium diffusion was found to be decreased in SiC coated specimen. Therefore, the coating can sustain the elemental content of the substrate and prevent its

alteration. During oxidation process, relatively thick and porous chromia (Cr_2O_3) scales on the surface of uncoated Inconel substrate are typically formed while the chromia scales in the case of SiC coated specimen appeared to be more dense. A nearly uniform bright grey layer was observed beneath the chromium oxide layer which consists of Cr depletion from energy dispersive X-ray (EDX) mapping results. This region is believed to consist of very sparse chromium content and higher molybdenum content. From overlapping of O, Mo and Si elements, thin and almost homogenous layers of $MoSi_2$ and SiO_2 were observed beneath the chromia layer, which was also confirmed by EDX line scan and XRD analysis. $MoSi_2$ and SiO_2 layers play an important role in reducing the oxidation rate at elevated temperatures. Scratch adhesion tests were performed on coated specimens. The coating delamination occurred at 3·7 N which according to the authors is considered almost high for ceramic coatings on metallic substrates. Performing four point bending tests on specimens showed that oxide scales have strong adhesion, which is necessary for sustained oxidation prevention.

A simple modified CS process using high pressure cold air nozzle spray was designed. The AZ51 substrate was preheated to 400°C and sprayed with HA. Biocompatible coatings with 20–30 μm thickness were obtained.[113] The coatings have an average modulus of 9 GPa. Simulated body fluid (SBF) was used to test the biodegradation behaviour of HA coatings. Control samples showed heavy Mg corrosion but no Al corrosion. HA coatings started dissolving after 1 day. After 10 days they showed signs of regeneration. The HA coated samples were able to slow down the biodegradability of Mg alloy. This attributed to the dissolution and re-precipitation of apatite showed by the coatings as compared to the control samples.

Although there are records available on deposition of ceramic coatings, they are in general not the best option for CS. Moreover, there is an ever increasing need for ceramic coating fabrication at room temperature. This was the motivation of inventing VCS which we described earlier in the introduction section.

Titanium nitride (TiN) coatings are extensively used for machining tool protection, decoration and diffusion barriers due to their superior properties, such as high hardness, good wear and corrosion resistances and unique electrical characteristics. Titanium nitride (TiN) coatings were fabricated on α-Al_2O_3 substrates by VCS process at room temperature with nano-sized starting powders (about 20 nm in size).[114] The results showed that with increasing coating thickness, the sheet resistance of coatings was significantly reduced from 13565 to 127 Ω. A minimum electrical resistivity of $1·8 \times 10^{-3}$ Ω m was achieved. The results show that one can have control over the coating resistance by controlling the coating thickness. The VCS TiN coatings with high porosity ranging from 58·3 to 67·6% exhibited low hardness of 279–490 HV and relatively good fracture toughness of $\sim 3·12$ MPa m$^{1/2}$.

The last two studies we review in this section are on deposition of MAX phase particles by CS. MAX phases are a family of ternary carbides and nitrides ('X') of transition metals ('M') interleaved with group 12–16 elements ('A', e.g. Al or Si). They have gained much
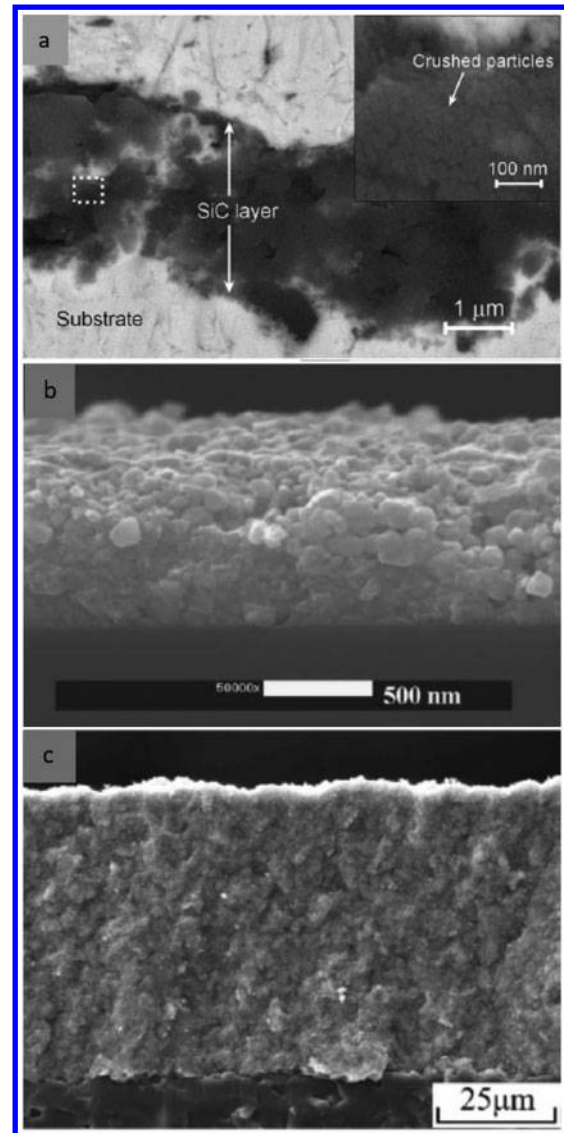
12 Cross-section of some selected ceramic coatings: *a* SiC on Inconel 625 using conventional CS system;[107] *b* WO3 on Si using conventional CS system;[108] *c* TiN on Al$_2$O$_3$ using VCS[114] (notice that magnifications are significantly different and coating obtained by VCS is much thicker than the other two)

interest in the last 15 years because of their interesting combination of ceramic and metallic properties. To avoid adding a new section we insert these studies in the ceramic section although these phases have characteristics between metals and ceramics. These coatings are resistant to oxidation and corrosion, elastically stiff, machinable and thermally and electrically conductive.

In the first study using HPCS, single impacts of Ti_2AlC on Cu and SS304 were studied by SEM.[115] Deformation and shear instabilities occurring at substrate sites were revealed to be the reason for bonding of the first layer. However, the splats appeared more flattened by the impact comparing to initial feedstock. This deformation seems to be attributed not only to local internal shear but also to internal fracture. Ti_2AlC coatings with thicknesses of about 110–155 μm were achieved by applying up to five passes under optimised spray parameters. Results of XRD analysis showed that the crystallographic structure of the feedstock was

retained. The microstructure showed several cracks between subsequent layers but it had low prosity (<2%). Successful build-up of more than one layer can probably be attributed to local deformation of the highly anisotropic Ti_2AlC phase.

In the other study on the same feedstock, basic spray parameters were varied to study their effects on the microstructure of the coatings onto AA6060 aluminium alloy and 1·0037 steel substrates.[116] Gas temperature and pressure were 600°C and 3·4 MPa respectively for obtaining adherent and dense 50–80 µm thick Ti_2AlC coatings. Comparable results were obtained on harder 1·0037 steel by using higher temperature (800°C) and pressure (3·9 MPa).

Thermal spray methods such as HVOF have also been utilised to spray coatings from Ti_2AlC powders.[117] The coatings predominantly consist of Ti_2AlC but they contained inclusions of Ti_3AlC_2, TiC, and Al–Ti alloys. By CS instead, any phase transformation and oxidation of the Ti_2AlC feedstock were avoided. However the problem with CS is that the coatings showed cracks and internal delamination. Currently the quality of the coatings is not good enough to be used in practical applications.

Selection of microstructures of ceramic coatings is shown in Fig. 12. Note that coating thicknesses varied from less than 1 µm to more than 50 µm in different cases.

Critical discussion

Reviewing the available literature on ceramic particles reveals that different mechanisms for particle bonding exist. In the case of ceramic on metal deposition, on the one hand it is reported that there is little coating build up and particles are only being embedded near the surface of substrates; on the other hand, shear instability on the substrate side is interpreted to be the predominant phenomenon for bonding. Both phenomena of embedment and shear instability have been reported for ceramic coating build up on metals. For ceramic on ceramic instead, particle fragmentation to smaller size and mechanical interlocking were considered to be the main bonding mechanism. Different explanations are evidences that the ceramic bonding mechanism is not fully understood yet.

What we have known from investigations on metals is that density, melting temperature and material tensile strength play important roles in determination of the critical velocity which is believed to be the master parameter in CS. What is obvious is that metals and ceramic have far different properties so they undergo different phenomena during impact. In depth studies on the impact behaviour of ceramics are needed to better understand the involved mechanisms. This can also help us to further understand coating build up in MMCs. Ceramic material deposition is still in its initial stage and it is valuable to perform fundamental studies at this phase.

VCS was invented mainly to accommodate ceramic deposition. A few studies are available which gave more promising results in comparison to conventional CS method for ceramic deposition. What made this method successful is perhaps the ability of depositing smaller particle size and consequently obtaining higher velocities. The reason can be uncovered in more details once some additional steps are taken toward understanding the mechanisms involved in ceramic deposition and the onset of shear instability.
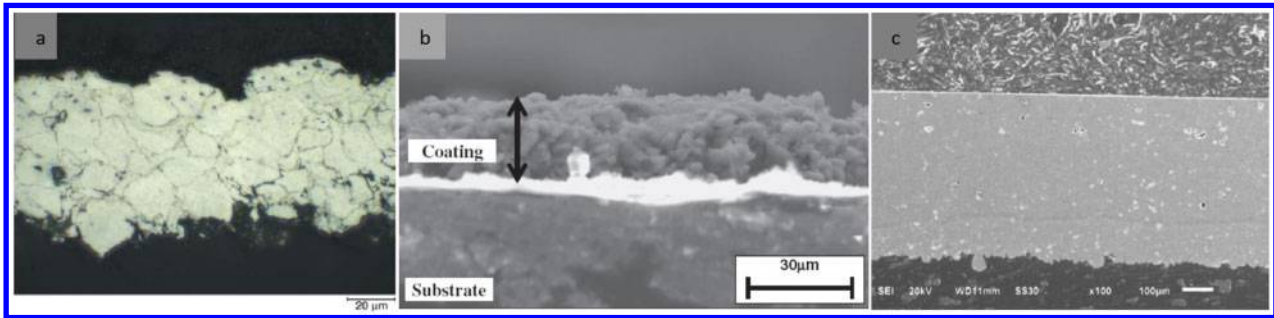
Polymers

Polymers have wide variety of applications that far exceeds that of any other class of available materials. Current applications extend from adhesives, coatings, foams, and packaging materials to textile and industrial fibres, composites, electronic devices, biomedical devices, optical devices, and precursors for many newly developed high tech ceramics. Because of the knowledge in polymer synthesis, there is control over the properties of bulk polymer components. However it is important to study surface interactions of polymer substrates because of its importance in biotechnology, nanotechnology, etc. Only recently researchers have studied material systems involving polymers for CS deposition. We divide this section into three parts: polymer as a coating, polymer as a substrate and metal embedment into polymer.

Coating build up on polymer substrate

Of particular interest for engineering applications are metallic coatings on surfaces such as plastics, fabrics or composite materials. Polymer matrix composites (PMCs) are widely used in the aerospace industry and in the military applications because of their low density, high specific strength and stiffness, and other unique properties such as ease of formation and machining. The surface metallisation of a PMC substrate is considered to be an effective technique for improving the surface property and extending PMCs' applications. Some special characteristics such as electrical conductivity, thermal conductivity, electromagnetic shielding, erosion and radiation protection can be achieved through the surface metallization of PMCs. The nature of such a substrate makes the process of metal deposition particularly difficult. Current coating technologies such as plasma spray, HVOF or laser cladding involve the delivery of molten materials during the deposition process. However, such techniques are not well suited for the deposition of metallic coatings on polymers and composites. CS has attracted much industrial interest over the past two decades. Studies showed that this process enables deposition of metallic coatings on non-metallic surfaces such as polymers and composites for engineering applications with reasonable bonding. In this section we will summarise the available literature of coating deposition on polymer substrates.

Powders for general engineering applications, such as commercial copper, aluminium, and tin have been sprayed onto a range of plastic materials such as PC/ABS, polyamide-6, polypropylene, polystyrene and a glass fibre composite using HPCS.[118] Among these three metallic powders only Sn was successfully deposited on a variety of plastic substrates after selecting a suitable nozzle type. Results of the study showed that materials like Cu can generate high impact energy once travelling at deposition velocities. This excessive energy will result in surface erosion rather than coating build up. On the other hand, Al has low specific weight so that the critical velocity could not be achieved with the CS system used in the experiments. In the case of Sn coating, the thickness varied between 45 µm and nearly 100 µm, while the average critical velocity was estimated through a CFD analysis to be 310 m s^{-1}.

13 Cross-section of metallic coatings on polymer substrates using CS: *a* Sn coating on polypropylene;[118] *b* Al on CFRP;[120] *c* Al coating on PEEK450CA30[121] (thicknesses vary in different cases)

In a similar study Cu, Zn, Pb and Al were selected to be cold sprayed on polypropylene and 30% carbon fibre reinforced polyetheretherketone (PEEK450CA30). Among those, a well adhered coating was achieved only between the Al powders and the PEEK450CA30 substrate.[119]

The next study is on metallization of carbon fibre reinforced plastic (CFRP) using LPCS. It has a great potential for applications in aircraft fuselage due to its light weight, high specific stiffness and high specific strength. It is crucial to coat the CFRP surface with an electrically conductive material to avoid the damage from lightning strikes. An interlayer was used to deposit an aluminium coating on the CFRP substrate since direct deposition was difficult.[120] Small size aluminium particles could be deposited on the CFRP but the coating was detached when the thickness was around 30 μm. In this study, a thin Al interlayer was deposited by plasma spray technique to assist the subsequent deposition of aluminium particles by CS. The interlayer enhanced the plastic deformation of CS particles and led to a thicker coating build up.

HA was cold sprayed on the PEEK hybrid material and its osteointegration in vitro and in vivo was evaluated.[121] CS was able to deposit a homogeneous and adhesive coating. The material was tested in vitro and HA coated implant showed early cell adhesion and viability improvement. The implant showed higher alkaline phosphatase (ALP) activity and calcium concentration. In addition, the expression of osteoblast differentiation markers, such as ALP, bone sialoprotein and runt related transcription factor 2, increased in these cells. Subsequently for in vivo tests, HA coated PEEK cylinders were designed and implanted into a rabbit ilium model by the press fit method. Results show that HA coated implant improved biocompatibility in vitro and osteointegration in vivo.

Ti particles were deposited onto PEEK substrates using HPCS technology.[122] By means of micro-Raman analysis, it was observed that the polymer was not degraded during the process even though the nitrogen gas stream was used. X-ray diffraction analysis also confirms that the composition of the metallic particles was not affected. The results showed that it is possible to coat biocompatible polymer implants with Ti leading to thick, homogeneous and well adhered coatings.

Figure 13 shows cross section of some of the material systems studied in the deposition of metallic coatings on polymer substrates. Different studies obtained various coating thicknesses and different microstructures. It is worth mentioning that the mechanism of coating build-up on polymeric substrates is still unclear.

Polymer coating

There are not many studies available on the CS of polymeric powders. Since polymers are generally softer than metals, they need less velocity to have plastic deformation. Conventional CS needs some alterations to deposit polymer coatings. We will go through two different studies to see their approaches and the necessary variations to the CS technology for polymer deposition.

The LPCS deposition of polyolefin powder has been investigated, at substantially lower velocities (up to 135 m s^{-1}) than those used in the CS process for metals.[123] Cylindrical nozzle instead of the conventional convergent divergent nozzle was used. The deposition was performed at room temperature and air was used as the carrier gas. Both metallic and polymer substrates were experimentally investigated (polyethylene and aluminium). The critical impact velocity for coating build up was 100 m s^{-1}.

The experiments with polymeric and metallic substrates showed marked differences in the initiation and development phase of the deposition. In case of polyethylene substrates deposits were formed and built up steadily at room temperature from the start of the spraying process. This suggests that deposition was propagation controlled rather than initiation controlled. In contrast, deposition on aluminium was much more difficult. It was essential for the aluminium substrates to be heated above the melting point of the polymer for deposition to be initiated. The initiation of the deposition represented the critical step in the process. Deposition then continued when the substrate surface and the growing deposit were cooled by the air flow. The deposition efficiency was much lower than the values typically seen in CS for metals.

The main difference between polymer deposition and metallic deposition is the critical velocity. Polymers need far lower velocities for deposition. To obtain lower particle impact velocities, a diffuser was located near the nozzle exit into the carrier gas flow.[124] Computational fluid dynamics (CFD) models were done for different nozzles to choose the diffuser place. A Schlieren optical system was used to visualize the density gradients and flow characteristics in the free jet impingement region. The diffuser also provides an appropriate application of compression heating of the particles to produce the conditions necessary at impact for successful coating adhesion of these materials. Polyethylene powders were
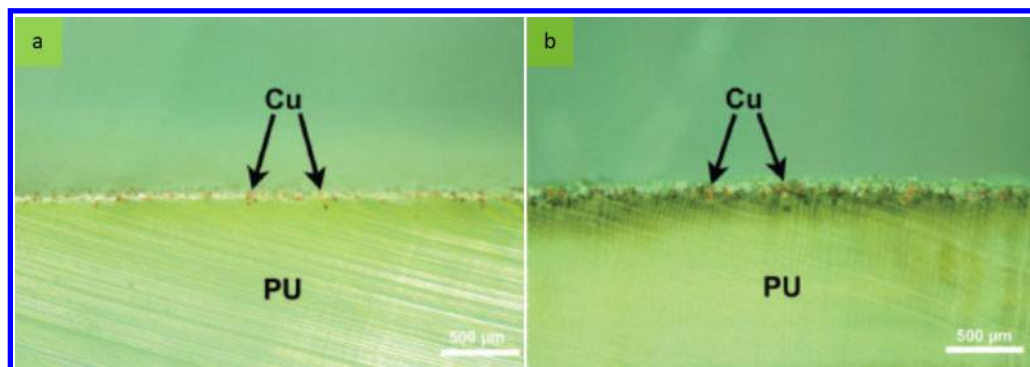
14 **PU streamers embedded with copper particles using CS technology:** *a* **low density Cu embedded showing embedment depth and** *b* **high density Cu embedded showing embedment depth**[127]

successfully deposited on a 7075-T6 aluminium substrate. The air was used as a carrier gas and the critical velocity for coating build up was 191 m s^{-1}. Melting of polymer particle was not observed.

Metal embedment into polymer

Fouling can hinder functionality of man-made devices that have interaction with water. It decreases the efficiency of vessel movement through the water and increase fuel consumption. It restricts water exchange in finfish aquaculture cages and consequently reduces water quality and increases disease transmission. It can also cause deformation and structural fatigue to the cage. It has also detrimental effects on the function of oceanographic equipments.

Some preliminary studies have shown that CS coating for metal embedment in polymeric substrates can be an alternative anti-fouling (AF) technology to standard AF coatings. It is specifically applicable for polymers which have difficulties to be coated with standard AF coatings. The embedding technique without any coating build up retains the flexibility of the polymer. The interaction between the CS metal and the polymer substrate is critical and determines the efficacy of the method. It affects particle embedment depth, and subsequently, the release of copper ions. Nowadays, anti-fouling paints are formulated with toxic copper, organotin compounds, or other biocides (special chemicals which impede growth of barnacles, algae, and marine organisms).

Copper powder was used to metallise two polymers, high density polyethylene (HDPE) and nylon using HPCS technology.[125] After 250 days in the field, Cu embedded HDPE and copper plate controls were completely free of hard foulers. However Cu embedded nylon and polymer controls were heavily fouled with both soft and hard fouling.

The same group extended the study to six different polymers, polyurethane, high density polyethylene, polypropylene, nylon 6, polytetrafluoroethylene and polycarbonate, without coating buildup.[126] The particles were captured by the surface upon impact. Polymer flew around the impact zone and particles penetrated into the substrate. The effects of different parameters such as spray temperature, traverse speed on particle penetration, sample weight gain cold polymer deformation were studied. Cross-sections of the treated materials were used to measure average embedment depth. Over 50 μm was measured in high density polyethylene and polyurethane (PU).

PU seismic streamer skins, which are used in geophysical exploration, were also studied. The AF efficacy of low (22·1 + 4·8 g m^{-2}) and high (101·1 + 10·8 g m^{-2}) densities of copper particles embedded were quantified.[127] The cross-sections of the aforementioned coatings are shown in Fig. 14. The failure criterion for treated specimens was defined as settlement of hard foulers. Low density streamers failed after 42 days while high density streamers failed after 210 days.

Critical discussion

Depositing polymers or using them as a substrate is rather new in the field of CS. CS can be performed at room temperature which is fine for polymers since they have low melting temperatures. However, previous studies found difficulties in bonding between polymer and metallic counterpart.

Supposing the shear instability formation is necessary for successful polymer coating build up like what occurs in metallic materials, this condition for polymers can be obtained at lower velocities in comparison to metals. The reason is attributed to thermal diffusivity which is far less for polymers comparing to metals. This will cause the material to switch from isothermal to adiabatic condition at a lower strain rate which means at a lower velocity.

In this regard, modifications have been done to CS with the aim of decreasing the impact velocity. So far using cylindrical nozzles (instead of a De-Laval nozzle) and placing a diffuser at the end of the nozzle have been proposed. Among different combinations of material systems, some were successfully coated while others were not. An interlayer may be useful in some cases to accommodate the coating build up. However, there is not yet a criterion available to predict deposition of polymers or coating buildup on polymers. Since the beginning of CS technology, early fundamental studies were done on metallic materials. Later CS technology developments produced encouraging experiments with the emergence of new material systems, while fundamental understandings are far from sufficient. Finding more reliable methods to coat polymers or make coatings on polymers can expand their applications in different industries.

Nanostructured powders

Following the visionary argument made by Gleiter,[128] that if metals and alloys are made of nanocrystals they would have a number of appealing and outstanding physical, mechanical, thermal and electrical properties, nanocrystalline materials have been the subject of widespread research over the past three decades.[129,130] They have high grain boundary content which results in
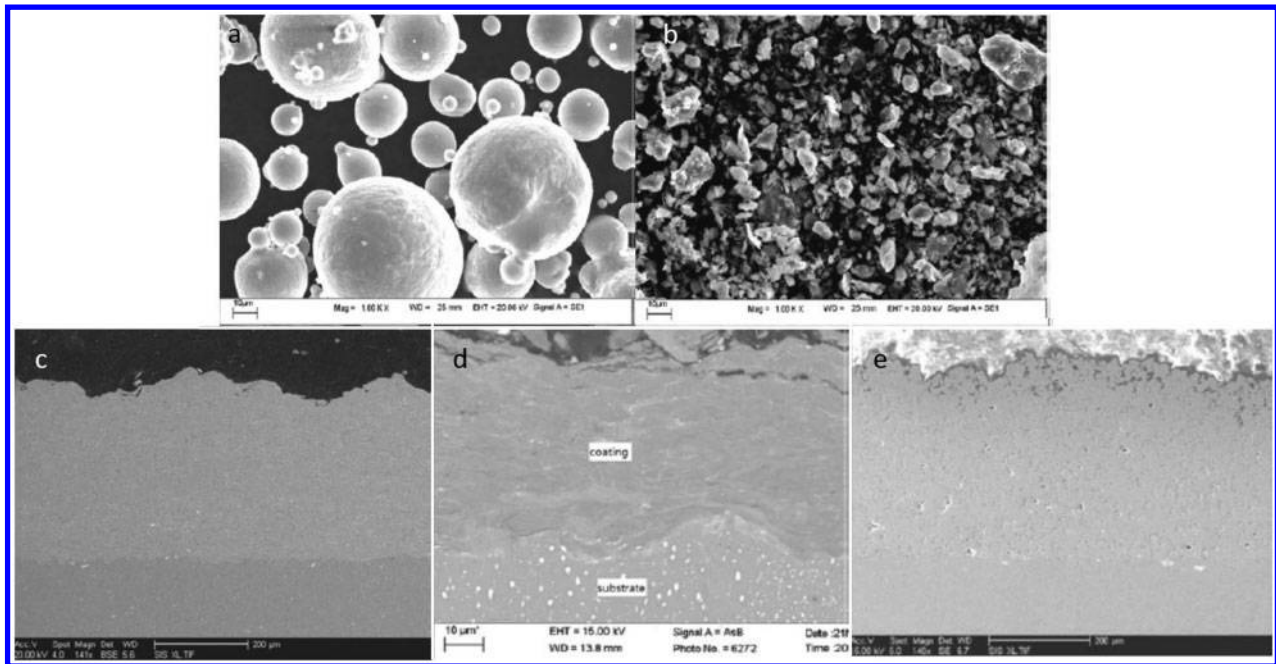
15 Morphologies of Al–Cu–Mg–Fe–Ni alloy powders: *a* as atomised; *b* as cryomilled; microstructure of coating obtained by *c* as atomised powders,[134] *d* mixture of as atomised and as cryomilled powders;[76] *e* as cryomilled powders[134]

grain boundary properties contributing significantly to the bulk material properties. Of their outstanding mechanical properties, one could mention high strength, increased resistance to tribological and environmentally assisted damage, increasing strength and/or ductility with increasing strain rate, and potential for enhanced superplastic deformation at lower temperatures and faster strain rates.[129] Many techniques have been developed for preparing nanocrystals including inert gas condensation, precipitation from solution, ball milling, rapid solidification, and crystallisation from amorphous phases. Many of these techniques result in either free standing nanocrystals (precipitation and inert gas condensation) or micrometre-sized powders (ball milling) containing nanocrystalline microstructures.

Ball milling, is a well proven technique that exist for preparing nanocrystalline powders. Mechanical alloying (MA)[131] in particular is a solid state powder processing technique involving repeated cold welding, fracturing, and re-welding of powder particles in a high energy ball mill. Ball milling is performed with a single phase constituent while for MA at least two constituents should be present.

What remains challenging and limits the use of nanocrystalline metals is to make sure that the consolidation process can retain the nanostructure. CS appears to be an appropriate spraying technique for depositing nanocrystalline powders because of its low deposition temperature. Therefore, the combination of CS and the ball milling process provides the opportunity to produce a complete nanostructured coating. Deposition of different nanostructured powders including two different categories of metallic and composite powders will be discussed in this section.

Nanostructured metals and alloys

Aluminium 5083 powder was mechanically milled under liquid nitrogen to achieve a nanocrystalline grain size in the range of 20–30 nm.[132] The nanocrystalline grain structure of the cryomilled feedstock powder was proved to be retained after the CS process by TEM analysis.

Comparing the nanocrystalline coating with cast, cold worked, Al-5083 showed a significant increase in hardness from 104 to 261 ± 8 HV(300 g).

A Similar study using a larger initial grain size (250–400 nm) on gas atomised 6061 and 5083 aluminium was carried out.[133] The final grain size shown by TEM analysis was 30–50 nm. The observation reveals that the HPCS process can cause considerable grain refinement after deposition.

Cold spraying of conventional and nanocrystalline 2618 (Al–Cu–Mg–Fe–Ni) aluminium alloy containing scandium (Sc) was studied using HPCS system.[134] This work showed that Al–Cu–Mg–Fe–Ni–Sc coatings with a nanocrystalline grain structure were successfully produced. It was claimed that this is the first time a hardness value of 181 HV has been reported for this specific alloy.

Generally coatings obtained by deposition of nanocrystalline powder have more porosity in comparison to as atomised powder. A possible way to increase the coating density and yet having improved properties is using a mixture of as atomised and as cryomilled powders.[76] A mixture of 30 wt-% as atomised aluminium alloy 2009 powder and 70 wt-% as cryomilled powder with grain size ranging from 5 to 30 nm was sprayed onto the aluminium substrates using HPCS. High density coatings were attained by use of this kind of mixture.

The oxidation behaviour of conventional and nanocrystalline CoNiCrAlY produced using the HPCS process was investigated.[135] Cryogenic milling process was utilised to produce nanocrystalline feedstock powder from the conventional feedstock powder. The nanocrystalline coatings had a larger porosity level but they still showed a slower oxide growth rate. The reason is that alumina scale is formed in the early stages of oxidation because of high diffusion rate of Al at the grain boundaries.

Mechanically alloyed Cu–Ni–Fe powders deposited via HPCS were evaluated for the production of inert anodes for Al electrolysis.[136] An attritor was used to
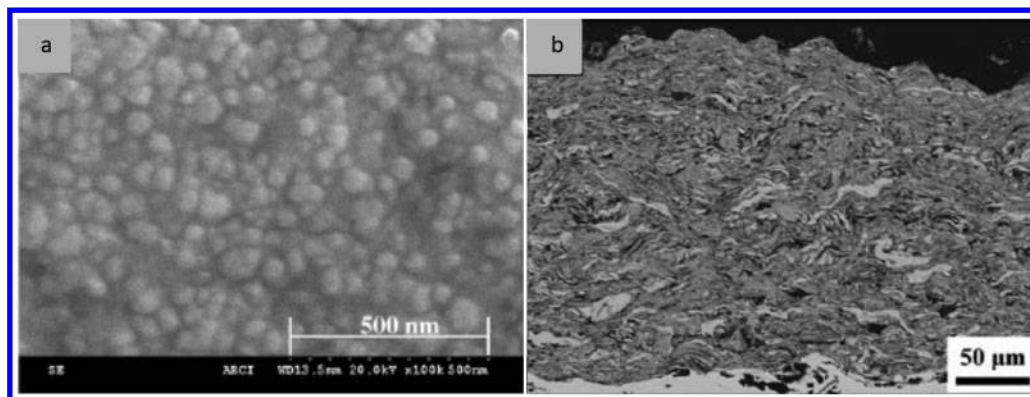
16 Cross-section microstructure of selected composite coatings: *a* copper alumina coating; *b* Fe/Al coating

prepare $Cu_{65}Ni_{20}Fe_{15}$ (in wt-%) alloy from elemental Cu, Ni, Fe powders. A nanocrystalline and monophasic Cu(Ni,Fe) solid solution was formed after 40 h of milling. It was shown that with the addition of stearic acid to the initial powder mixture the particle size of the milled powder can be controlled. In a second step, in order to maximise the impact velocity of the $Cu_{65}Ni_{20}Fe_{15}$ particles on the substrate, the CS parameters (pressure and temperature of the carrier N_2 gas) were optimised. Then, thick (1100 µm), dense (1–2% porosity) and adhesive (15 MPa adhesion strength) coatings of $Cu_{65}Ni_{20}Fe_{15}$ on C63000 substrate (nickel aluminium bronze alloy) were produced. No structural changes of the $Cu_{65}Ni_{20}Fe_{15}$ alloy were observed during CS processing.

As an example, the morphology of conventional and milled powder of aluminium alloy is shown in Fig. 15*a* and *b*. In addition the microstructure of the CS coating by spraying conventional, as milled and mixture of these two powders is illustrated for comparison in Fig. 15*c*–*e*. The higher porosity level in coating microstructure of as cryomilled powder in comparison to other two coatings can be observed.

Nanostructured metal matrix composites

As mentioned earlier, composite coating attracted considerable attention for obtaining coatings with enhanced properties. Producing composites with nanostructured reinforcement is not straight forward. In powder metallurgy, high energy mechanical milling could segregate nanoparticle agglomeration. In addition it can disperse reinforcement homogeneously and reduce the grain size significantly. However, consolidating milled nanocrystalline powders turned to be challenging.[137] In this section we will summarise studies concerning consolidation of nanocrystalline composite powders by the CS deposition process and the resulting characteristics.

Nanocrystalline copper alumina coatings were deposited on copper substrates using HPCS for potential use in high strength, high conductivity applications.[138] Cu/Al_2O_3 coatings are resistant to grain growth and softening even upon heat treatment at 950°C which is close to the melting point of copper (1083°C). The reason is the presence of fine alumina particles. Hall–Petch hardening was regarded as the predominant strengthening mechanism in CS Cu–Al_2O_3 because of the fine grain size in the coatings.

Milled Al and Al_2O_3/Al nanocomposite powders as well as the initial unmilled and unreinforced Al powder

were consolidated by LPCS process.[137] The hardness of Al powder increased after milling process and it was retained after CS. Low porosity was obtained from milled Al. However, the addition of Al_2O_3 to the Al powder during milling decreased the powder and coating nano indentation hardness. The possible explanation is that using non-optimised milling parameters results in cracked particles with insufficient Al_2O_3 embedding in Al. The coating produced from the milled Al_2O_3/Al mixture did not present a good quality either.

Nanostructured Fe/Al alloy powder was prepared by ball milling process and subsequently deposited using HPCS.[139] Lamellar microstructure was observed for milled Fe–40Al powder and it affected the microstructure of the as sprayed Fe(Al) coating. A post-CS heat treatment was performed to transform the Fe/Al alloy coating to intermetallic compound coating. The heat treatment temperature has a significant effect on the transformation of the intermetallic compound. The heat treatment at 500°C resulted in a complete transformation of Fe(Al) solid solution to FeAl intermetallic compound.

In Fig. 16 a selection of cross-section microstructures of nanocrystalline composite CS coatings are shown. The lamellar microstructure in the Fe/Al coating can be clearly seen.

Critical discussion

CS could be a promising technology for consolidation of nanostructured powders while retaining their microstructure. It can even further refine the grain size during impact. However, the coating porosity is higher than conventional material deposition. The reason why increased porosities are observed in nanostructured powder deposition has not been addressed yet. It may be attributed to the irregular shapes of the powders or the significant increase in their hardness values. Studies show that combination of conventional and nanostructured powders can result in a denser coating and improve the coating properties. Another way could be increasing deposition velocity. Since the particle hardness is higher, the powders need to obtain higher velocities to be able to adhere to the substrate. In this case optimisation of deposition parameters is the key to achieve better coating properties. In addition, deposition of nanostructured powders and producing the resultant coating involve both milling and coating processes. Optimisation of milling parameters can also be another way to achieve a denser coating. This is even more important in the case of composite powders because the

milling process may cause defects in the softer material and result in a coating with poor mechanical properties. The problem associated with relatively high coating porosity should be addressed to make CS a leading consolidation process for nanostructured powders.

Special substrates

Most studies and applications have dealt with fabrication of a coating layer on metal substrate. However, it has been shown that metals can also be deposited onto non-metallic substrates such as ceramics, glasses and polymers (we reviewed polymer substrates in the section on 'Polymers', and some studies on ceramic substrates fit in different sections which we will not revisit here again). The mechanisms of cold spraying metal particles on ceramics or glasses involve more factors such as chemical properties of the impact particles and substrates. Cold spraying on brittle substrates is challenging because the particle impact induces a certain degree of mechanical shock to the surface. Furthermore, there is a possibility of thermal shock in ceramics while using high temperature techniques. Although roughening of the substrate surface by grit blasting is common for improving the coating's adhesion to metals, it may not be appropriate for some brittle materials. In this section we will go through a few records available in the literature on non-metallic substrates.

First we review a study of depositing aluminium particles on soda lime glass using HPCS.[140] The interface between cold sprayed Al particles and a soda lime glass substrate was characterised by transmission electron microscopy (TEM). A low density interface layer of thickness up to 80 nm was found. The layer is composed of amorphous and nanocrystalline grains, and has a different chemical composition from Al and glass. The layer is resulted from the reaction of the sprayed Al with glass, which acts as a bonding layer between them.

HPCS was also used to deposit conductive aluminium coatings onto lead zirconate titanate (PZT) piezoceramics.[141] Processing parameters were optimised for better deposition. Substrate temperature during spraying was maintained at a low level by controlling the upstream, CS temperature and robot movement. Increasing the average particle velocity helped to reduce grain removal from the PZT surface due to the impact of Al particles. Surface domain reorientation was detected by XRD. The electrical resistance of the cold sprayed aluminium was $9 \cdot 9 \pm 0 \cdot 5 \ \mu\Omega$. The impedance characteristics of poled specimens were shown to be unchanged.

Conclusion

CS is a high deposition rate coating process that utilizes kinetic rather than thermal energy. The powder feedstock remains well below its melting point. Eliminating the deleterious effects of high temperature on coatings and substrates offers significant advantages and new possibilities, making CS promising for many industrial applications. The number of studies in this field is expanding rapidly. In this review, an attempt has been made to present the current state of research and development in this field with a material point of view.

In preparing our survey of the field, we have identified that experimental investigations form the major part of the body of knowledge in the field and less attention has been paid to the basic principles and computational modelling of CS. Experimental studies have been mainly focused on studying the microstructure of the coating and basic characteristics that increases the fundamental understanding of the process. However, the response of cold sprayed components to the conditions experienced in service such as fatigue/fretting fatigue, corrosion, wear, …, etc. is also an important avenue to be explored in order to transfer the technology to real in service products.

Lack of knowledge requires trial and errors in order to obtain a successful coating. As an example, numerous studies have been performed on MMC coatings and yet their detailed bonding mechanisms are still unclear. In addition, there are some other open questions regarding MMC coatings including but not limited to:

  (i) effect of the mass ratio of different components and consequently the different velocities on coating characteristics
 (ii) the relationship between the ratio of hard particles in starting powder and in the deposited coating, and the involved influential parameters
(iii) characterisation standards of composite coatings for comparison of the coating quality
(iv) how much we can increase the reinforcement particle content in the coating before invoking any drawbacks such as reductions in fracture strength or wear properties.

In the case of depositing nanostructured powders, both milling (to obtain nanostructured powders) and CS processes should be taken into account, while their respective effects should be distinguished. There are some open questions such as:

  (i) what is the reason for higher porosity when depositing nanostructured powders in comparison to depositing conventional powders? Is it related to the increased hardness of nanostructured powders that leads to a higher critical velocity, or the irregular shapes of the powders, or both?
 (ii) if it is related to the hardness increase, would an improved method for depositing hard particles such as VCS be beneficial to reduce porosity?
(iii) if it is related to the irregular shapes, could we solve the problem by improving the milling process?
(iv) what is the relation between the initial powder grain size and the coating grain size? Knowing this relationship better will help us avoid over milling powders and instead let the subsequent CS process further refine the grain size.

On the contrary to MMC and nanostructured powders, ceramic and polymer material systems have been introduced more recently in the field. Their bonding mechanisms are also still not very clear. It seems that CS in its current state cannot deposit the whole range of ceramics and polymers successfully. For ceramic deposition we need much higher velocities (in comparison to metals) and for polymers generally we need far lower velocity for deposition. VCS for ceramic deposition, placing a diffuser at nozzle exit or using a cylindrical nozzle for polymers are suggested modifications of CS process that need to be further studied.

As we discussed, future investigations associated with different material systems should have different focuses.

Table 1 Overview of material systems used in cold spray and their examined and/or potential applications

Coating	Substrate	Application
I. Metals		
Cu and its alloys	Varies	Anti-microbial characteristics, high Good electrical and thermal conductivities applications
Al and its alloys	Varies	Corrosion resistance, dimensional restoration and repair
Zn and its alloys	Varies	Catholic protection for ferrous alloy and aluminium alloy–corrosion resistance
Stainless steel	Mild steel	Dimensional restoration and repair, medical application
Titanium and Ti alloys	Varies	Dimensional restoration and repair, medical application
Nickel and its alloys	Varies	Dimensional restoration and repair
Ta	Al	Use of refractory materials is currently being developed for gun barrel coatings and liners
Al–5Fe–V–Si	6061-T6	High temperature resistance-Internal combustion engine
$Fe_{44}Co_6Cr_{15}Mo_{14}C_{15}B_6$	$AlMg_3$ alloy, Cu, Ti, SS316L high hardness spring steel	Feasibility study and investigating deformation behaviour of metallic glasses
CuNiTiZr	Cu Bulk metallic glass	General metallic glass application
Al–Co–Ce	AA 2024-T3	Corrosion protection
$Cu_{54}Zr_{22}Ti_{18}Ni_6$	Al 6061	Unsuccessful in corrosion improvement-better performance in wear comparing to pure Cu
II. Metal matrix composites		
Ti/Al	Al	Feasibility study for coatings or components
$TiAl_3$–Al	orthorhombic-Ti-22Al-26Nb	High temperature oxidation resistance
Al Al/Ni	Ni Al	Intermetallic compounds for possible structural applications
Co based refractory alloy + adding Ni	Steel	Applications that need refractory materials i.e. lighting, tools, lubricants, nuclear reaction control rods, …
SS316 + Co–Cr alloy	316L-mild steel	Improving strength and corrosion resistance for medical applications
$Nd_2Fe_{14}B$ + Al	Al 5083	Magnetic components for electronic application, electric motor, sensor, magnetic coupling and actuators
Al Al + $Mg_{17}Al_{12}$	Az91D Mg alloy	Corrosion protection
Al_2O_3 + 316 austenitic	AZ91Mg alloy	Corrosion improvement
Al Al + Al_2O_3	Mild steel and Al7075	Wear resistance application and sustaining corrosion behaviour
Cu–Al Al_2O_3–SiC (all combinations)	Al	Improve tribological properties
Al + Al_2O_3	Si and Al 6061	Improve tribological properties
Al + SiC, Al + Al_2O_3 composites as well as pure Al, SiC, and Al_2O_3	Si	Feasibility study of deposition on hard substrate
Al–Al_2O_3 Al6061–Al_2O_3	AZ91E-T6	Improving corrosion and wear resistance
Cu–Al_2O_3	Fe52 steel	Improve tribological properties
Al–Al_2O_3	AZ91D magnesium alloy	Wear and corrosion improvement
Al–Bronze–Al_2O_3	…	Improve tribological properties
Al–Al_2O_3–Zn Different weight percent	AA2024-T3	Corrosion protection
W/Cu	Mild steel	Heat sink application in electronic package
WC–Co	Stainless steel (SUS 304	Wear resistance application
WC–15Co WC–10Co–4Cr	Al	Wear resistant applications particularly heavy machinery sector
WC + 25Co	Al7075-T6 Carbon steel	Wear and corrosion resistance improvement
Cr_3C_2–NiCr Cr_3C_2–Ni	4140 alloy steel	Wear resistance application
SUS304/diamond binary composite	Al alloy	Studying coating builds up mechanism
Bronze/diamond	Al	Machining tough ceramics because diamond has excellent mechanical properties such as extremely high hardness, low frictional coefficient and high wear resistance
Cu/Cu_2O	…	Anti-fouling coating
Al/CuO	…	Thermit-Propellant application
B_4C/Ni	316L	Wear and corrosion protection-for geological sensors operating under severe service condition of deep drilling
Ti/HA	Ti and Al	Biomedical application

Table 1 Continned

Coating	Substrate	Application
Multi wall carbon nanotube–reinforced Cu	Al	Heat sinks in the electronic device
III. Ceramics		
SiC	Inconel 625	Oxidation resistance at high temperature
WO$_3$	Si	Application as photoelectrodes
TiO$_2$	SS, Al, Cu, Ti	Promising photo catalyst, potential application to environment purification, solar cells, sterilisation, cancer therapy and anti-fogging films
Al$_2$O$_3$	Al$_2$O$_3$	Evaluating NPDS for ceramic on ceramic deposition
HA	Az51	Bio application-improving bio degradability
TiN	α-Al$_2$O$_3$	Machining tool protection, decoration and diffusion barriers due to its superior properties such as high hardness, good wear and corrosion resistance and unique electrical characteristics
Ti$_2$AlC	AA6060 1·0037 steel Cu SS304	Ceramic like behaviour and high hardness coating-feasibility study for later industrial application
IV. Polymers		
Cu, Al and Pb powder	on a range of substrates such as PC/ABS, polyamide-6, polypropylene, polystyrene and a glass-fiber composite	Feasibility study of spraying metal on polymer and composite for engineering application
Al Al/Cu	Carbon fiber reinforced polymer matrix composite-(PEEK540CA30)	Aerospace and military application because of low density and high specific strength and stiffness
Al	CFRP (carbon fiber reinforced plastic)	Aircraft fuselage-coating plastic with metal to avoid damaging from lightning strikes
HA	Polyetheretherketone (PEEK)	Bio medical application
Ti	PEEK	Bio medical application
Polyolef	Polyethylene Al	Feasibility study
Polyethylene	Al 7075-T6	Feasibility study
Cu	High density polyethylene (HDPE) and nylon	Anti-fouling
Cu	polyurethane, high density polyethylene, polypropylene, nylon 6, polytetrafluoroethylene and polycarbonate	Anti-fouling
Cu	Polyurethan	Anti-fouling
V. Nanocrystalline coatings		
Al 5083	…	Nanocrystalline powder deposition study
Al 6061 Al 5083	Al 6061	Meso scale machining
Al 2618+Sc	Al	Aerospace, aeronautic and automotive applications
Al 2009	Al alloy	General application–increasing hardness
MCrAlY	Al 6061	Improving oxidation behaviour for thermal barrier coating on hot components of gas turbine to improve performance and durability
Al/Al$_2$O$_3$	Mild steel	Automotive and aerospace industry–improving tribological properties
Cu/Al$_2$O$_3$	Cu	Spot and seam welding electrodes, electrical contacts, lead wires and conductors in high temperature application
Fe/Al	Stainless steel	Attractive materials for several industrial applications for medium to high temperature
CuNiFe	Ni alloy [nickel aluminium bronze alloy (C63000)]	Inert anodes for Al production in low electrolyte due to their ability to form a protective, adherent and electrochemically conducting NiFe$_2$O$_4$ rich scale on their surface during Al electrolysis
VI. Special substrates		
Al	Soda lime glass	Study and characterisation of interface between Al and glass
Al	Lead zirconate titanate	Diverse application that needs conversion of mechanical to electrical energy and vice versa

It is clear that CS process is a valid and versatile technique for obtaining multifunctional surfaces that can be used in many industrial fields. However, we want to emphasise that it is important to study in depth the fundamental mechanisms of coating formation in different material systems from MMCs to ceramics

and polymers. Future efforts will definitely help the technology to find new applications and at much reduced costs.

Finally the material systems that have been cold sprayed and their examined and/or potential applications are listed and summarised in Table 1 as reference.

Acknowledgements

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