A Review of Advanced Composite and Nanostructured Coatings by Solid-state Cold Spraying Process

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Abstract

Cold spraying (CS) has been widely explored over the last decade due to its low process temperature and limited thermal effect on spray materials. As a solid-state process, the inherent deficiencies of traditional thermal spraying such as oxidation, decomposition and grain growth are avoided. This article summarizes the research work on the fabrication of composites and nanostructured coatings by the promising CS process. After a brief introduction to CS and its deposition mechanisms, the preparation methods of spray powders are classified. Different methods are appropriate for particles of various properties, and the tendency is to design composite powders by combined methods in order to create coatings with specified properties. Then the co-deposition mechanism of composite particles as well as research findings on metal-metal, metal-ceramic and metal-intermetallic composite coatings are reviewed concerning the deposition characteristics, microstructure and its relation to properties. Moreover, CS has been used to deposit a variety of nanostructured materials, including metals, metal-ceramic composites, and even ceramics, retaining their nanocrystalline nature in the coating without grain growth or phase transformation. Finally, the potential applications of CS and issues to be addressed in coating deposition are discussed.

Keywords: Cold spraying; Composite powder; Process parameters; Composite coatings; Nanostructured coatings

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Cold spraying (CS) is a relatively new solid-state coating technique based on supersonic fluid dynamics and high-speed impact dynamics. The cold spray system basically consists of a compressed gas delivery system, a gas heater, a powder feeder, a supersonic de-Laval nozzle, a robot arm, and an operation system as schematized in Figure 1a. High-temperature compressed propulsive gas passes through a de-Laval nozzle, generating a supersonic flow inside and outside the nozzle. The sprayed powder particles commonly in a size range of 5-50 μm are then realized in front of the nozzle inlet and accelerated to a high velocity ranging usually from 300 to 1200 m/s by the supersonic jet and projected onto a substrate or a previously deposited coating in a nominally solid state, i.e. at a temperature well below the melting point of the powder. CS was originally developed in the mid-1980s at the Institute of Theoretical and Applied Mechanics of the Russian Academy of Science in Novosibirsk by Papyrin and his colleagues. They successfully deposited a wide range of pure metals, metal alloys, and composites onto a variety of substrate materials. A U.S. patent was issued in 1994, with a European one in 1995. Following these, CS has drawn worldwide attention, prompting numerous experimental and theoretical studies, especially in the last decade.
Thermal spraying (TS) was primarily used to produce coatings or thin films before the invention of CS. However, as a fusion-based technology TS coatings generally suffer from weak coating-substrate interfacial bonding, high porosity, high oxidation and possible negative impact on the underneath substrate.\textsuperscript{13} CS features higher particle velocity and lower processing temperature (see Figure 1b), producing a series of advantages compared to TS. For example, there are limited heat effects on substrates and spray powders. The oxidation, decomposition, phase transformation and grain growth of the spray materials or substrates can be avoided, allowing the deposition of phase transformation sensitive materials (e.g. nanostructured materials,\textsuperscript{12-14} amorphous materials,\textsuperscript{15-19} and WC-Co\textsuperscript{20-22}) and oxidation sensitive materials (e.g. Cu,\textsuperscript{23,24} Al,\textsuperscript{25,26} Ti\textsuperscript{1,12,13}). In addition, the resulting residual stresses are normally relatively low and mostly compressive compared to TS,\textsuperscript{31,32} which permits the deposition of thick coatings. Thus, considering its characteristics of high deposition efficiency (DE), high deposition rate, recyclable feedstock, together with no need for high temperature heat source, CS is an economical technique.\textsuperscript{33,35}

As for the bonding mechanisms of metallic particles in CS, much work has been done in the last decade. The widely accepted hypothesis on the bonding process is that the high velocity impact of particles induces intensive plastic deformation at the interface enabling a bond to be formed, as shown in Figure 2, i.e. metallurgical or metallic bonding.\textsuperscript{36-46} This holds true even for the cases where the substrates are ceramics or glasses,\textsuperscript{47,48} where the deformation will totally occur within the particles. The second issue is that how strong the metallurgical bonding is or how significant is the contribution of metallurgical bonding to the final adhesion or cohesion, as compared to the so-called mechanical interlocking effect in TSeD coatings.\textsuperscript{38,55} The third question concerns the possible localised interface melting and its effect on adhesion.\textsuperscript{56-61} The fourth issue is how submicron- or nano-sized ceramic particles are bonded in some circumstances.\textsuperscript{62,63} The literature contains brief reviews on these questions, e.g., by Hussain.\textsuperscript{37} Nevertheless, no matter which mechanism controls the bonding, there should be enough bonding strength to prevent the rebounding force, i.e., a critical velocity is needed to provide enough deformation and clean interfaces.\textsuperscript{34} Several important factors influence the critical velocity, i.e. materials properties,\textsuperscript{4,36,37} particle surface oxidation\textsuperscript{50,64-66} and particle/substrate temperature.\textsuperscript{39,64,67-73} The process parameters that influence these factors will affect the coating deposition.\textsuperscript{6,73-87}

Up to now, CS has been used to fabricate a variety of coatings, including mostly elemental metals and alloys, but also composite coatings, providing corrosion resistance,\textsuperscript{26,88-93} wear resistance\textsuperscript{21,94-96} and high temperature resistance,\textsuperscript{97-99} as well as functional coatings\textsuperscript{100-108} for industrial applications. The detailed microstructure evolution in CS coatings have been reviewed by some researchers, e.g. Lee and Kim\textsuperscript{109} and Borchers et al.\textsuperscript{24}
Apart from coating deposition applications, additive manufacturing with CS (also called Cold Gas Dynamic Manufacturing (CGDM)) has also been proposed based on its low processing temperature, high DE and controllable spray print. By this method, components can be fabricated with relatively complex shapes from dissimilar materials, while retaining the inherent materials properties, having great potential in rapid prototyping and component restoration, which may even overturn the traditional fabrication and restoration techniques. It is worth noting that the U.S. Department of Defense has approved a military standard (MIL-STD-3021) in 2008 on coating fabrication and repair of components, and that the U.S. Patent and Trademark Office has granted a number of patents, e.g. US20110129351A1 for the deposition of a protective strip onto the leading edge of a composite airfoil. Recently, CS has been added into the current additive manufacturing process families, as defined by the “Standard Terminology for Additive Manufacturing Technologies”, which is part of the ASTM F2792-12A standard series.

In the majority of industrial applications, coatings consisting of a single material may not fully meet difficult specifications such as high wear and corrosion resistance, excellent chemical stability, while composites, which combine the properties of different components, can be useful. In particular, compared to traditional composite fabrication technologies, such as powder metallurgy (PM), pressure infiltration, spark plasma sintering, in-situ reaction spraying and thermal spraying, friction stir processing, CS does not possess deleterious effects of interface reaction, oxidation, and under-utilization of the reinforcement phase. Therefore, CS shows great potential in the fabrication of composite coatings. Furthermore, many techniques have been explored to fabricate nanocrystalline materials, e.g. inert gas condensation, precipitation from solution, mechanical alloying, rapid solidification, and crystallization from amorphous phases. However, it is very difficult to produce large-area nanocrystalline metallic films or large volume bulk nano metallic materials used in structures. The key point lies in avoiding grain growth and oxidation in order to retain the nanostructure of metallic materials, and CS does show great potential because of its low processing temperature.

Since Shukla et al. first studied a CS nanostructured WC-10Co coating in the year 2000 and Ti-25 vol.% nano-hydroxyapatite (HA) composite coating in 2001, a number of articles on composite coatings, including metal-metal, metal-ceramic and metal-intermetallic composite coatings, as well as nanostructured coatings have been published. This paper mainly summarizes the important aspects related to the deposition characteristics of composite and nanostructured coatings by CS to enlighten its further applications.

2. Composite feedstock
Three methods can be used to deposit a composite coating. The first commonly used method is to prepare the
composite powders before spraying, the second one is to mix powders during spraying, e.g. using two or more powder feeders; the third one is to make the composites by post-spray treatment, e.g. heat treatment, laser surface remelting or friction stir processing, possibly with additives. This section focuses on the pre-prepared composite powders for CS.

It is a well-known fact that powder preparation is very important before spraying. Well-prepared powders contribute to the increase of deposition efficiency and favourable modification of coating microstructures. Besides, it is possible to develop high performance coatings through powder design. As per the CS process requirements on high deposition efficiency and stability of powder feeder, the size of powder is commonly in a size range of 5-50 μm, while the powder morphology prefers round-shaped particles.

Powder preparation for composite powders includes the selection of a matrix phase and a reinforcement phase, as well as the production methods. Generally speaking, mechanical blending, ball-milling, spray drying, agglomerating and sintering, coating or cladding are mainly employed to process composite powders. Different methods have their merits and downsides in terms of powder feeding, volume fraction and distribution of reinforcement particles, and interfacial bonding between the matrix and reinforcement in the coatings (see Table 1). The main considerations and challenges that need to be addressed in powder preparation are as follows.

2.1 Mechanical blending

Mechanical blending or mixing is a very simple process that has been widely used in previous studies due to its ease of operation, i.e., to put the powder mixture in a bottle and blend it manually or by a mixer. For instance, Wang et al. mechanically blended spherical Al (mean particle size of 10 μm) with Al₂O₃ (mean particle size of 20 μm) in a mixer to prepare Al-Al₂O₃ composite feedstock (Figure 3a). Yandouzi et al. mixed Al12Si (5-65 μm) and SiC (9-44 μm) powders with different ceramic contents (Figure 3b). Li et al. mechanically mixed gas atomized Al2319 powder (5-63 μm) with irregular TiN powder (10-45 μm) for CS, and Yu et al. also used this method to produce Al5056-SiC composite powder. Besides metal-ceramic mixtures, some researchers mixed two or more metals for some special applications, e.g. Al/Zn, Al/Cu, W/Cu, and Cu/Ni/Al.

Although it is relatively easy and very inexpensive, it cannot ensure adequate uniformity of the mixed powders. In addition, the differences in particle density, size or morphology between the mixed ingredients will result in various ranges of particle velocities, and thus various deposition efficiencies, which may lead to significant deviation of the coating composition from that of the starting powders. Furthermore, because the reinforcement is distributed at the interfaces of the deformed matrix particles in this method, the distribution of reinforcement seems relatively nonuniform, especially when the matrix particles are relatively large. Nevertheless, if the matrix and reinforcement...
particles are both fine, the distribution seems acceptable.

2.2 Ball-milling

The ball-milling method can avoid the shortcomings of mechanical blending as it is based on the cold-welding and crushing effects of the balls to refine the ingredient materials, producing finer and more homogeneous powders for mixtures. In this way, one can control the content, size and distribution of the two phases, and thus control the composition of the coatings. It is very important for use.

It has been reported that ball-milling parameters including milling speed, time and atmosphere have a significant influence on powder morphology and coating quality. Li et al. milled Al5356 and TiN powder in a planetary ball mill (Figure 4a). Zhang et al. applied this method to produce Ni-Al composite powder with the atom ratio of 1:1. Yandouzi et al. ball-milled Al-12Si and B,C mixture in a liquid nitrogen atmosphere (cryomilled) (Figure 4b). Besides, Wang et al., Kang et al. and Tria et al. also used the ball-milling method to produce Fe-Al, W-Cu and Ni-Ti composite powders, respectively. It is clear that all the ball-milled powders produce better mixtures and bonds, and thus a better coating. Li et al. deposited TiN reinforced Al5356 coatings with the feedstocks prepared with both ball-milling and mechanical-blending as shown in Figure 5. It was found that the ball-milled powder yields a denser and homogeneous coating with super fine TiN particles dispersed into the Al5356 matrix, leading to a higher microhardness due to the “constraint effect” of ceramic particulates on the deformation of the soft Al matrix.

Recently, Luo et al. reported a novel ball-milling based method for powder preparation. They ball-milled 20 vol.% Co powder and 80 vol.% WC-10Co powder to produce a core-shelled structured WC-Co powder as shown in Figure 6. The WC-10Co cores were covered with Co-rich WC-75Co shells of a thickness of 3-6 μm, in which the WC particle sizes are in a submicron range (Figure 6b). Therefore, the outer layer has higher deformability than the hard core, and the coating deposited by this kind of feedstock has improved fracture toughness compared to that by pure WC-10Co powder.

The ball-milling method is also an effective way to produce nanostructured feedstocks. In certain cases, the milling process is carried out in a liquid nitrogen atmosphere (called cryomilling) in order to lower the ductility of the metallic powders and to avoid the formation of small flakelets that are very difficult to feed. Li et al. milled Fe and Si powders in a planetary mill in ethanol for various times to produce nanocrystalline powders as shown in Figure 7a. The Si peaks almost disappeared after 32h, at the the same time the broadening of Fe (110) peak could be clearly observed. This fact suggests the formation of a nanocrystalline structure in the milled powder as evidenced by the TEM analysis (Figure 7b). Wang et al. milled Fe and Al powders in a high-energy
ball mill in an argon atmosphere to produce composite powders with a composition corresponding to Fe$_{60}$Al$_{40}$ (Figure 7c). Ajdelsztajn et al.	extsuperscript{144} cryomilled Al5083 powders with ball-to-powder weight ratio of 32:1 to prepare nanocrystalline powder (Figure 7d). Richer et al.,	extsuperscript{145} Ghelichi et al.	extsuperscript{146} and Zhang et al.	extsuperscript{147} prepared nanocrystalline Al-Mg alloy, Al7075, and Al2009 feedstocks, respectively.

Few papers have focused on the effect of the ball-milling parameters on the resultant powders and the CS coatings.	extsuperscript{142} Woo et al.	extsuperscript{148} used the high-energy ball-milling method to produce nano-diamond-reinforced aluminum matrix composites powders. They found that by altering the ball-to-powder ratio and milling time, the particle size and shape, Al crystal size and residual strain, the structural integrity and dispersion of nano-particle inclusions can be controlled as indicated in Figure 8, which is a crucial requirement for subsequent CS powder consolidation.

In summary, ball milling is a good way to control the composition of the composite powder as well as that of the composite coating. The differences caused by the different ingredients will be eliminated because they will flight as “one” single composite particle. However, the mill parameters should be carefully selected to produce composite particles: (1) with a near-spherical shape, and (2) appropriate size range, for easy powder feeding. Sometimes, screening of milled powders should be conducted. This method is also cost-effective to make nanostructured powders, but careful control of milling process is necessary to produce particles of acceptable shapes, e.g. in a liquid nitrogen atmosphere.

2.3 Spray drying

In spray drying, the ingredients are fully mixed with a liquid forming slurry, and then atomized and dried by hot gas, obtaining homogeneous composite powders with a near-spherical shape. Bakshi et al.	extsuperscript{149} applied this method to ensure a good dispersion of carbon nanotubes (CNTs) in a micron-sized gas-atomized Al-Si eutectic powder as shown in Figs. 9 (a, b). The spray-dried powders had a particle size of 57±21 μm, containing 5 wt.% CNTs. Kang et al.	extsuperscript{139} spray-dried Cu-W powder, which had already been ball-milled, to achieve better agglomerated W-Cu composite powder as shown in Figs. 9 (c, d), thus minimizing the effects of the large difference in density between Cu (8.96 g/cm$^3$) and W (19.3 g/cm$^3$), and ensuring homogeneous distribution of W in the CS W-Cu composite.

In addition, nano-particles normally need an agglomeration treatment before CS in order to form micron-sized particles, because it is very difficult to feed small particles, and they do not possess enough inertia to penetrate the bow shocks zone.	extsuperscript{21,150} This method has also been used to produce micron-sized particles for conventional powder feeders in thermal spraying. Hodder et al.	extsuperscript{151} agglomerated 20 nm Al$_2$O$_3$ powder to form porous particles
with a size range from 2 to 10 μm as shown in Figure 10a, then mechanically mixed them with pure Al at various weight ratios to form metal-ceramic composite feedstocks. Phani et al.\textsuperscript{152} agglomerated ball-milled nanocrystalline Cu-Al\textsubscript{2}O\textsubscript{3} powder to a size range of 22-45 μm for CS as shown in Figure 10b. Kim et al.\textsuperscript{153,154} used an agglomerated nano-WC-12%Co powder for CS as shown in Figure 10c. The powder after agglomeration is relatively spherical and compact, and the size of WC is in a range of 100-200 nm. Similarly, Yandouzi et al.\textsuperscript{155} also deposited nanocrystalline WC-15Co coatings with a feedstock prepared by spray drying, but the coating quality is less than that by the sintered WC-Co powders.

In summary, spray drying is easy to produce homogeneous composite powders with a near-spherical shape ready for feeding, especially with nano-particles. However, it is worth to note that the used organic solvents may influence the hardness and wear resistance of the resultant coatings.\textsuperscript{156}

2.4 Agglomerating and sintering

Powders made by spray drying usually have poor cohesion strength, requiring a post sintering treatment to avoid this defect. This method is mainly used in the fabrication of cermet powders for TS, e.g. WC-Co and Cr\textsubscript{3}C\textsubscript{2}-NiCr. The agglomerated and sintered powders usually present a spherical morphology with high volume fraction of micron-sized carbide particles embedded in the metallic Co binder (Figure 11a).\textsuperscript{155-157} For example, Wolfe et al.\textsuperscript{75} used a Cr\textsubscript{3}C\textsubscript{2}-25 wt.% NiCr powder prepared by agglomerating and sintering for CS as shown in Figure 11b.

The agglomerating and sintering method can also be used for nano-WC-Co powders. Li et al.\textsuperscript{158,159} agglomerated nano-sized WC with Co, which was then sintered. The powder produced had a size range from 5 to 44 μm, with the WC grain size in the range of 50-500 nm as shown in Figure 12.

In summary, besides the broader use in TS, agglomerating and sintering are very useful in making appropriate CS powders with spherical shapes and suitable size range. However, the production cost is a little high. In addition, this method has mainly been used in producing cermet powders. It would be very helpful if this method is used to produce other types of composite powders.

2.5 Coating or cladding

Apart from the above commonly used methods, coating (or cladding) is also an effective way to produce composite powders. Generally, one metal is coated on a hard phase. By regulating the thickness of the coated layer, one can obtain powders with various volume fractions of the hard phase, and thus depositing a coating with a high and controlled volume fraction of the hard phase. Li et al.\textsuperscript{160,161} employed a Ni-coated Al\textsubscript{2}O\textsubscript{3} powder produced by the hydrothermal hydrogen reduction method in order to increase the volume fraction of ceramic particles in the
deposited composite coating as shown in Figure 13a. The alumina particles are cladded with Ni particulates with a thickness of about 10-20 μm, thus the volume fraction of alumina in the coating can reach values as high as 29%.\(^{160}\) Feng et al.\(^{162}\) deposited Ni coating on B\(_4\)C particles by chemical vapor deposition (CVD) in order to prevent B\(_4\)C fragmentation and promote B\(_4\)C adhesion as shown in Figure 13b. Other combinations include Ni-coated diamond\(^{163}\) mixed with bronze and Ti-coated diamond mixed with Fe\(^{164}\), Cu-coated diamond mixed with Cu,\(^{165}\) to avoid the fracture of diamond particles and decrease the difference in mass between diamond and metallic particles at the same time. However, there may be a problem that the optimal thickness of the soft clad layer should be thick enough to successfully bond the hard phase but not too thick to lower the coating hardness.\(^{166}\)

This method was originally used for TS powders. If it is used for CS, certain adjusting of the process is necessary to yield a suitable coat to optimize the coating properties. In addition, it is difficult to generate very fine particles, which is expected for particle acceleration in CS. Again, the cost of this method is relatively high.

2.6 Other methods

It should be noted that the combination of different powder preparation methods might be useful in powder design, and thus coating design. Kim et al.\(^{167}\) produced TiB\(_2\)-43 vol.%Cu nano-powders containing TiB\(_2\) particles 50-100 nm in size as shown in Figure 14a, which was in-situ produced in a copper matrix using high-energy ball-milling of Ti, B and powders and self-propagating high-temperature synthesis. Yang et al.\(^{168}\) designed a bi-modal WC-12Co powder as shown in Figure 14b. The fabrication procedure uses at the beginning high-energy ball-milling of conventional WC-Co and nano WC particles, followed by sintering and crashing, then annealing at 1000°C in a hydrogen atmosphere to further modify the feedstock, producing a powder with both high hardness and high fracture toughness. Other methods, e.g. spray drying and simple mechanical blending,\(^{149}\) crushed grinding and sintering\(^{75}\), casting and crushing\(^{156}\), wet chemically synthesizing and agglomerating,\(^{169}\) all aim at acquiring a homogeneous feedstock and enhancing the deposition efficiency of the hard reinforcement phase. However, these combined methods will inevitably increase the cost.

In summary, a well-prepared powder would be beneficial to the tailoring of coating microstructure and properties. However, different methods have various pros and cons as summarized in Table 1. Even with combined methods, careful control of the powders is necessary.

3. Co-deposition behavior and mechanism of metal-reinforcement consolidation

3.1 Experimental work

In the case of composite powders, their deposition behavior is different from that of the deposition of metals as the reinforcement particles hardly deform upon impacting. The soft metal phase deforms significantly, acting as matrix, while the hard phase (hard metal or ceramic) embeds in the matrix, acting as reinforcement. An interesting
experiment was performed by Shkodkin et al., where they sprayed pure Al on a steel substrate in one pass and simultaneously sprayed pure ceramic particles also in one pass but in a cross way with Al. It was found that a smooth thin Al layer was developed at the Al particle jet line, and steel erosion was found at the ceramic particle jet line, while the coating thickness increased linearly at their intersection position as shown in Figure 15a. This is the so-called “co-deposition”. They attributed this interesting fact to the ‘surface activation’ effect of ceramic particles, i.e., the erosion effect of hard ceramics results in an increased substrate roughness and a clean active surface, which promotes the deposition of Al particles as indicated in Figure 15b. Coatings can only be seen at the left side, which had been gritted beforehand. Lee et al. reported that it is easier to deposit a ceramic-soft metal (Al, Cu) mixture than pure Al or Cu metal or pure ceramic in low-pressure CS as shown in Figure 16. It should be pointed out that this is possibly true for low-pressure CS (with low DE), but not necessarily the case for high-pressure CS (with high DE). The thicknesses of pure Al and pure SiC coatings are about 30-40 μm and 4 μm, respectively, while that of composite coating can be as high as 80-100 μm under the same spray conditions. This fact is due to the addition of hard ceramic particles that produce many craters at the substrate surface before Al deposition. This is beneficial to Al adhesion, and the binder effect of soft metal in turn promotes the deposition of SiC, similar to the observation by Shkodkin et al. Grigoriev et al. and Sova et al. further pointed out that the addition of ceramics can lower the critical velocity for pure metals, and consequently “critical” temperature (the minimum gas stagnation temperature at which particles begin to adhere) necessary for spraying these metals, and the deposition efficiency also increases at the same time as indicated in Figure 17. A small fraction of ceramic powders (Al₂O₃, SiC) in the feedstock does produce a strong activation effect on the substrate surface and increases the deposition efficiency of the metal component in the mixture compared to spraying of pure metals. While a too large fraction of ceramic particles considerably hinders coating deposition because their erosion effect exceeds their activation effect.

For the activation mechanism of ceramics, Grigoriev et al. further identified two mechanisms: (1) ceramic particles increase the substrate roughness, and (2) clean the oxide films from the substrate surface increasing their chemical/metallurgical activity as shown in Figure 18. They also proposed (3) the possible interactive effect of metal and ceramic particles during flight under a very high powder flow rate, which cleans away oxide films on the surface of metal particles and increases chemical/metallurgical activity, though this is not supported by experimental evidence. The traditional grit blasting is efficient in removing oxide films, but the surface morphology produced is possibly not optimal as compared to the in-situ activation with ceramic particles. Other approaches such as combination of ablation and laser heating do provide optimum surface topography and
improve metallurgical activity, promoting intimate bonding between the coating and substrate.\textsuperscript{166,172}

The deposition process mainly consists of the impact between metal and ceramic particles, the deformation of metal particles and the tamping effect of ceramic particles,\textsuperscript{85,88,129,173,174} so the co-deposition behavior between metal and ceramic phases can increase coating deposition efficiency and bonding strength.\textsuperscript{91,129,175} However, the collision between ceramic particles at higher ceramic contents will become predominant and result in decreased deposition efficiency, since the deposition will still depend on the ductile metal due to the poor deformability of ceramic particles as shown in Figure 19.\textsuperscript{76,85,88,177-181} It is worth noting that the deposition efficiency increased in all cases with temperature, though the maximum deposition efficiency achieved was always for a ceramic content of about 30\% for each temperature.\textsuperscript{85} The mechanism responsible for this needs further exploration.

Additionally, it was found that the addition of hard phase (hard metal or ceramic) in the powder mixture can lower coating porosity and improve coating hardness due to their tamping effect during deposition as the extra kinetic energy of the hard phase promotes the deformation of the metal particles.\textsuperscript{137,182,184} The coating hardness increase is due to the increased strain hardening effect as well as the strengthening effect of ceramics. The microhardness of the as-sprayed TiN-reinforced composite coatings, as shown in Figure 20,\textsuperscript{185} decreases remarkably after heat-treatment at different temperatures for 2h due to recovery and/or recrystallization, but is still higher than that of pure Al coating. This fact clearly indicates that the uniformly dispersed hard particles significantly strengthen the matrix.

Moreover, the presence of hard phase allows the working gas to reach high temperatures without nozzle clogging or blocking, which in consequence improves the coating compactness as it increases particle deformation and bonding due to the thermal softening effect at elevated temperatures.\textsuperscript{182,183,186} The adhesion strength between the coating and the substrate as well as the cohesion strength of the coating itself can be increased to a certain degree as shown in Figure 21. The adhesion strength is mostly determined by the bond between metallic particles and substrate,\textsuperscript{88} while the cohesion strength depends on the scale of deformation as well as the intimate contact area of metallic particles in the coating.\textsuperscript{131} The mechanical interlocking between ceramics and deformed metallic particles or the substrate can also affect in a positive way the bonding strength (Figure 21(a)). However, an excessively increased number of ceramic particles can decrease the contact area between the deformed particles, and thus the cohesion strength will decrease at the same time as shown in Figure 21(b). The coating shear strength is affected in a similar way.\textsuperscript{129}

Recently, to identify the strengthening mechanisms of hard particles in CSed composites, Huang and Li\textsuperscript{187} designed an experimental method to qualitatively calculate the proportions of different strengthening effects on
the microhardness as shown in Figure 22. By comparing the microhardness of the as-sprayed and heat-treated TiNp/Al5356 coatings deposited with different TiN fractions (Figure 22a), two strengthening mechanisms of TiN particles in composite coatings were identified, i.e. the strain-hardening effect of TiN particles tamping on the Al5356 matrix and the dispersion strengthening effect of uniformly dispersed TiN particles (Figure 22b, also see Figure 20). The dispersion strengthening effect of TiN particles plays a greater role in microhardness increment than the strain-hardening effect of TiN tamping the Al5356 matrix. In addition, with the increase of TiN fraction in the coating, the microhardness increment induced by both effects rise. High resolution TEM analysis indicated that an intimate contact is formed at the TiNp/Al5356 interface. However, some cracks and pores around the TiN particle can be found at the interface, and the bonding is still relatively weak.\textsuperscript{187}

3.2 Simulation work

Bearing in mind the above findings, Assadi et al.\textsuperscript{188} and Yu et al.\textsuperscript{184} tried to understand some important aspects during the deposition of composite/inhomogernous particles by numerical simulations. Although it is just on the beginning, some results are interesting. Assadi et al.\textsuperscript{188} found that for a hard-core/soft-shell particle (i.e., a ceramic core coated by a metal layer), as shown in Figure 23, the shell thickness had some influence on particle deposition. The rupture of the shell and detachment of the hard core becomes evident when the shell thickness is decreased from 2 to 1 µm. By further decreasing the shell thickness to 0.5 µm, there is also a jump in the maximum stress level. Since the core does not deform plastically, the same amount of kinetic energy must be dissipated via plastic deformation of the shell, regardless of the shell thickness. This means that for a smaller shell thickness, the deformation work would be higher. A higher deformation could in turn result in rupture and detachment, especially for complex deformation patterns as brought about by inhomogeneous material properties.

Yu et al.\textsuperscript{184} also found the similar result, as shown in Figure 24. The plastic deformation of the Al5056 particles was increased due to the non-deformation of In718 particle. In other words, all the kinetic energy of the In718 particle is transferred as the additional deformation of the neighboring Al5056 particles. Thus, it is understandable that the addition of In718 improves the compactness of the Al5056 coating as the experiment shows.\textsuperscript{184}

To better understand the underlying mechanism, a better simulation model and smart procedure are necessary.

4. Composite coatings

Composite coatings produced by CS can be either of metal-metal, of metal-ceramic, or of metal-intermetallic type. The research findings on the composite coating microstructure and properties are accordingly summarized in term of
these three types, rather than the elemental materials.

4.1 Metal-metal composite coatings

The metal-metal composite coatings are mainly applied in the circumstances that normally need a high thermal conductivity, where corrosion resistance is required, or in sputtering targets. Examples follow:

1. Heat sinks in electronic packages require high conductivity and low coefficient of thermal expansion, making the W-Cu composite a good candidate.\(^\text{139}\)

2. The addition of Al in Zn coatings can increase greatly the coating lifetime when used as a sacrificial layer for protecting the substrate materials from corrosion.\(^\text{90,189}\)

3. A Ni-Cr composite can be used as oxidation resistant coating.\(^\text{99}\)

4. A Cu-In composite can be used as a sputtering target.\(^\text{190}\)

5. A Cu-Cr coating can be used as an electrical contact material for its excellent electrical conductivity, high breaking current capability, and high resistance to electric arc corrosion and surface fusion welding.\(^\text{191}\)

CS can deposit blended elemental metal powders with two or more components to produce metal-metal composite coatings with a dense structure, in a relatively easier and economic way compared to thermal spraying.\(^\text{139,192}\) Further to these, there is no reaction or phase transformation during the CS process, and the deposited materials can be easily machined to the expected shapes before forming intermetallic compounds via post-spray heat treatment, and preserving the functional integrity of each component.\(^\text{90,192}\) For example, during CS Al/Zn mixture, severely deformed Al particles act as a dense matrix phase, while the slightly deformed Zn particles are homogeneously distributed in the Al matrix.\(^\text{193}\) Other articles have focused on various combinations, e.g. Ti-Al,\(^\text{192}\) Fe-Al,\(^\text{197}\) W-Cu,\(^\text{139}\) Ni-Al,\(^\text{98,195,196}\) Cu-Cr,\(^\text{191}\) Al-Co-Ce,\(^\text{194}\) Ni-Ti,\(^\text{140}\) and even bronze-quasicrystal (AlCuFeB)\(^\text{197}\). Typical cross sections of metal-metal composite coatings are shown in Figure 25. It is clear that one material is embedded in or surrounded by the other one, forming a compact structure with limited porosity and uniformly distributed hard particles, indicating the dense feature of CS coatings.

Compared to traditional processing methods, metal-metal composite coatings made with CS may possess excellent corrosion and oxidation resistance because of the dense structure. For example, Bala et al.\(^\text{99}\) deposited Ni-20Cr and Ni-50Cr coatings on boiler steels with CS, where the coatings showed a dense microstructure with porosity less than 1.9%. The coatings also showed higher hardness than the substrate steel without discernible oxidation. High temperature oxidation tests at 900°C showed that Ni-20Cr and Ni-50Cr coatings reduced the weight gain of the steel by 84% and 93%, respectively. They also found that the Ni-20Cr coating had excellent hot corrosion resistance in a Na\(_2\)SO\(_4\)-60%V\(_2\)O\(_5\) environment at 900°C, reducing the weight gain of the steel by 87.2%.\(^\text{93}\) The
dense, strongly adhered coatings block the penetration of corrosive species towards the substrate, and lower the corrosion rate of substrate.\textsuperscript{198,199} Zhao et al.\textsuperscript{90} used induction or laser to remelt the surface of a CS Zn-Al-Si composite coating. A protecting surface layer with gradient Zn concentration was formed with a gradient electrochemical potential, providing more effective protection from corrosion than a pure coating. Li et al.\textsuperscript{189} reported that the self-corrosion rate of CS Zn-50Al coating is lower than that of a Zn coating, thus providing a better protection for steel.

The other properties, e.g. electricity, are also increased. Kang et al.\textsuperscript{139} deposited the W-Cu mixture on a carbon steel substrate with CS and plasma spraying. There was no oxidation of Cu in the CS coating, while that produced with plasma spraying had a high concentration of copper oxides. Wu et al.\textsuperscript{191} fabricated the Cu-15%Cr coating with porosity, hardness and electrical resistivity of 0.24±0.04%, 232±7 HV, and 71.5±0.7%IACS, respectively, which are superior to those of the composites prepared with explosive compaction and meet industrial standards. Rolland et al.\textsuperscript{101} deposited an Ag-30%Ni composite coating for electrical contacts, and durability testing in industrial facilities showed that the erosion of CS contacts is lower than conventional PM ones.

4.2 Metal-ceramic composite coating
4.2.1 General aspects

Particle reinforced metal matrix composites (PRMMCs) combine the properties of metals (high strength and toughness) with those of ceramics (excellent wear resistance, corrosion resistance and chemical stability), increasing the service life of components. The preparation of PRMMCs has become one of research hot topics. However, it is difficult to fabricate high-performance PRMMC by conventional means, especially those with high volume fraction of ceramics. CS showed great potential in producing MMC coatings with metal matrices, such as Al and its alloys,\textsuperscript{76,88,89,95,119,120,127,129,131,138,179,180,200} Ni and its alloys\textsuperscript{91,75,160-162,201} and Cu based composites,\textsuperscript{153,167,202} cermets,\textsuperscript{22,157,203} and other metal-ceramic coatings. The composite coatings are compact, have high microhardness and bonding strength, and are superior or comparable to traditional thermal sprayed (TSed) coatings.

Considering the high temperature in TS, it is not suitable for depositing metallic powders containing oxidization sensitive or phase transformation sensitive components. Here we take WC-Co for example. WC-Co coatings are widely used in wear resistant applications. The hard WC particles form the major wear resistant constituent, while the Co binder provides toughness.\textsuperscript{155} Thermal spraying of WC-Co coatings will inevitably generate the brittle η phase and causedecarburization of WC, which severely affect their hardness and wear
resistance. A simple comparison on the WC-Co coatings deposited by both CS and TS is made (Table 2), which is based on the work by Couto et al. The WC-xCo coatings fabricated by CS maintained the original phases of the particles, while the counterparts by high velocity oxy-fuel spraying (HVOF) or high velocity air-fuel spraying (HVAF) experienced decarbonization and formed hard brittle W2C, Co6W8C and Co3W3C phases, which cause the coatings to possess a higher hardness but lower toughness. However, the CS coatings showed lower deposition efficiency and adhesion strength. The wear rate is in the same magnitude but the volume loss is much lower than that by HVOF or HVAF, which suggests an increased wear resistance. Moreover, the corrosion resistance of coatings by CS is increased by 8-37% than that by HVOF or HVAF due to its dense microstructure. Thus, apart from the low deposition efficiency, the coating properties by CS seem better than those by HVOF or HVAF.

4.2.2 Microstructure and mechanical properties

Typical cross-sections of a few CS metal-ceramic composite coatings are shown in Figure 26. All the coatings present a dense microstructure. The soft metals deform severely acting as matrix, while the ceramic particles remain undeformed acting as reinforcement. As shown in Figure 26d, an intimate interface was formed between Al and Al2O3, and severe plastic deformation of Al led to grain refinement, while no trace of deformation was observed at the Al2O3 side. Normally, the tamping effect of hard ceramics promotes the deformation of metal phase and enhances the coating density and hardness.

Tables 3 and 4 summarize corrosion and wear behaviors of CS composite coatings. From Table 3, it can be concluded that the addition of ceramics has no negative effect on the coating corrosion behavior, e.g. the corrosion resistance of Al-Al2O3 coatings is comparable to that of pure Al coating or bulk Al alloys, and is independent of the ceramic content. For CS coatings, two factors will influence their corrosion behavior, the coating porosity and residual stresses. The reported increased corrosion resistance of the composite coating is due to the increased coating compactness. The addition of hard ceramics allows using a higher gas preheating temperature with no clogging, which increases the softening effect as well as the tamping effect of ceramics to produce compact structures. Moreover, post spray heat treatment (PSHT) can also increase corrosion resistance by relieving residual stresses, the elimination of defects through recovery and recrystallization, and the reduction of voids by rearranging grains. The wear performance of these composites, as indicated in Table 4, is improved with the addition of ceramic particles. The increased coating hardness as well as the effect of third-body abrasion by ceramic particles may decrease the coefficient of friction (COF) significantly and reduce the wear rate by an order of magnitude, as shown in Figure
The decreased COF is because that the ceramic particles in the worn track change the wear mode from adhesion to abrasion. The separated ceramic particles mix with the soft surface forming a strain-hardened layer, which protects the underlying coating and leads to the decreased wear rate. Nevertheless, there are exceptions, for example, Triantou et al. reported that for CS Cu-Al$_2$O$_3$, the COF increased with increasing the content of Al$_2$O$_3$. However, the wear rate decreased because the plastically deformed Cu and its oxides formed a protective layer. Thus, the effect of ceramics on COF and wear rate is material dependent. Typical wear surfaces of pure coating and composite coating are shown in Figure 28. The narrower worn track on the composite coating than the corresponding pure coating indicated that the addition of hard ceramics increases the wear resistance significantly. Furthermore, Li et al. and Xiao et al. found that the wear mechanism of coatings depends on ambient temperature. Sevillano et al. found that the CS Ni-Al$_2$O$_3$ coating exhibits good oxidation resistance even at 520°C, and Heimann et al. reported a similar finding for Al-Al$_2$O$_3$ composite.

The feedstocks for metal-ceramic composite coatings are mostly prepared with mechanical blending. Figure 29 summarizes the contents of ceramics in the mechanically blended feedstocks and their volume fractions in the final coatings. The slopes of three dotted lines in Figure 29 are 1, 0.7 and 0.3, which correspond to the percentages of ceramics in the coating to that in the feedstock are 100%, 70% and 30%, respectively. We gave these values based on the observation that the content of SiC in the deposit is mainly 70-90% of that in the feedstock, while the value for Al$_2$O$_3$ is 30-70% with most contents of about 50%, giving a relative deposition efficiency of SiC higher than Al$_2$O$_3$, except for the case of Al-12Si-SiC coating. It is also clear that the content of ceramics in the composite is generally lower than that in the feedstock because of their relatively different deposition efficiencies. However, at a low concentration, the fraction of ceramics in the coating may be higher than that in the feedstock due to the relatively high deposition efficiency of the reinforcement phase. It should be noted that the Al-TiN coating has the highest deposition efficiency with the comparable TiN retaining in the coating (even more in other powder blends). These facts are possibly because (1) the different densities of TiN, Al$_2$O$_3$ and SiC of 5.2g/cm$^3$, 3.9g/cm$^3$ and 3.2g/cm$^3$, respectively, compared to the density of Al alloys, (2) the different relative deposition efficiencies of various materials in CS. Experiments clearly show that the fraction of ceramics can be controlled by adjusting feedstocks.

Figure 30 summarizes the findings for microhardness of composite coatings with the change of ceramic particles in the coatings. The coating hardness is higher than the corresponding pure Al or Al alloys, and it increases with SiC or Al$_2$O$_3$, which is due to the severe plastic deformation of the Al matrix and the tamping effect of hard ceramics. Uniformly dispersed ceramic particles also contribute to the increase of the coating hardness.
hardness by restricting the deformation of soft Al matrix.\textsuperscript{218} It is worth noting that Al alloys based composite coatings show higher hardness than pure Al based coatings, because Al alloys is harder than pure Al. Moreover, there is a strong dependency of hardness of Al alloys based coatings on ceramic content. The hardness of coatings reinforced by SiC is remarkably higher than that by Al\textsubscript{2}O\textsubscript{3}. In addition to matrix phase effects, the higher deposition efficiency of SiC compared to Al\textsubscript{2}O\textsubscript{3} (Figure 31), together with the fact that Al-SiC coatings show a more compact structure compared to Al-Al\textsubscript{2}O\textsubscript{3} coatings, may also account for the higher hardness.

Therefore, with these trends in mind, one can control the coating hardness and tribological properties by altering the type and content of ceramics in the feedstock.

Furthermore, it has been reported that the grain size in the Al matrix decreases with increasing SiC content, and smaller size SiC particulates improve refinement. In addition to this effect, aging response is sensitive to the reinforcement size.\textsuperscript{219} Changing the reinforcement content in the metal matrix in a controlled manner, CS can accurately produce predictable changes in thermal properties like conduction and expansion.\textsuperscript{220}

4.2.3 Effect of post spray heat treatment

Researchers have also studied other aspects of the metal-ceramic composite coatings. It has been found that PSHT can enhance the adhesion and compactness of the coating,\textsuperscript{185} but has little effect on size, morphology and distribution of ceramic particles.\textsuperscript{221} Zhou et al.\textsuperscript{212} found that PSHT can significantly improve corrosion and mechanical properties of CS HA-Ti coatings due to the annihilation of defects, porosity reduction and residual stress relief during PSHT. Watanabe et al.\textsuperscript{222} carried out four-point bending tests on WC-Co/Al multilayer composite coating, and found that the ductile metal phase is very effective in enhancing the toughness and damage tolerance of sprayed cermet coatings. Wang et al.\textsuperscript{211} used electron backscattered diffraction (EBSD) to characterize the CS Al-Al\textsubscript{2}O\textsubscript{3} coating, to find anisotropic nano-mechanical properties due to the higher density of dislocations and grain boundaries on the cross plane formed during coating deposition. Heimann et al.\textsuperscript{217} reported that the Al-Al\textsubscript{2}O\textsubscript{3} coating states low thermal conductivity, low solar absorptance, comparatively high infrared emittance and oxidation stability, which can protect space-bound structures against deleterious effects of the space environment.

4.3 Metal-intermetallic composite coatings

4.3.1 Formation by post spray heat treatment of cold-sprayed metal-metal composites

Intermetallics possess the advantages of high melting point, high creep strength, low density, high oxidation resistance and corrosion resistance, which allow them to be used as high-temperature structural materials in aerospace industry. However, the intrinsic brittleness of intermetallics at room temperature makes it very
difficult to directly deposit intermetallic particles.\textsuperscript{223} The studies are mainly about producing intermetallic reinforced MMCs with PSHT of as-cold-sprayed metal-metal composite coatings.\textsuperscript{51,97,98,192,195,196,224-226}

Typical metal-intermetallic composite coatings prepared by CS and PSHT are summarized in Table 5. The work mainly covers Ni-Al, Ti-Al and Fe-Al intermetallics. In almost every case, feedstocks were prepared with ball-milling and the as-sprayed coatings were annealed in an inert atmosphere (Ar or N\(_2\)) at various times and temperatures. The following has been found:

(1) The intermetallics formed in the annealed Ni-Al coating are mainly Al\(_2\)Ni and Al\(_2\)Ni\(_2\). The quantity of Al\(_2\)Ni\(_2\) increases with temperature so as the hardness of the coating, which proves that intermetallics have a significant effect on coating hardness.\textsuperscript{98,195,196} In addition, pores were found in the annealed coating due to the Kirkendall effect.\textsuperscript{196} Zhang et al.\textsuperscript{137} also reported the Al\(_2\)Ni\(_2\) phase in the ball-milled NiAl coating annealed at a low temperature, however, at a temperature higher than 850°C (above the melting point of Al), the whole coating completely transformed to NiAl. The melting of Al will greatly facilitate the reaction diffusion of Ni atoms into Al, besides the conventional solid-state atomic diffusion. Moreover, Podrabinnik et al.\textsuperscript{227} observed AlNi and Al\(_2\)Ni\(_2\) intermetallics in laser annealed CS Al/Al\(_2\)O\(_3\)-Ni composite coating. The phase transformation from a Ni-Al composite to NiAl intermetallic can also result in closing non-bonded gaps in the coating at higher temperatures,\textsuperscript{228} but with the formation of pores by the Kirkendall effect.

(2) In the case of Ti-Al composite coatings, there is no significant reaction during the CS process.\textsuperscript{229} PSHT also leads to the formation of intermetallic phases. By changing the heat-treatment condition, the desirable intermetallic phases can be formed, however, coating porosity also increases rapidly with time at elevated temperatures due to the Kirkendall effect.\textsuperscript{192} Kong et al.\textsuperscript{226} deposited the premixed Ti-Al powder with the molar ratio of 1:3, to produce a coating with a dense structure and a porosity of 0.17%. After heat treatment at 650°C for 5h, there was phase transformation to form TiAl\(_3\) and an interlayer of (Ti, Nb)Al\(_3\) around 10 \(\mu\)m was formed at the coating-substrate interface, and the porosity was increased to 14.69% due to the Kirkendall effect. Similarly, according to Ti-Al phase diagram, the contact melting of Al at 650°C will also facilitate the reaction diffusion of Ti atoms. Oxidation tests did indicate a good high-temperature oxidation resistance of the coating. Cizek et al.\textsuperscript{230} also confirmed the Kirkendall effect and the oxidation resistance of the TiAl\(_3\) coating. They further pointed out that the optimal PSHT temperature is 500-580°C, where intermetallic phase formation is induced while Kirkendall pores are almost avoided at a relatively low temperature. Wang et al.\textsuperscript{231} fabricated a TiAl\(_3\) bond coat by CS together with PSHT for yttria partially stabilized zirconia (YSZ) thermal barrier coatings (TBC). A pure Al coating with a thickness about 40-60 \(\mu\)m was deposited on a \(\gamma\)-TiAl alloy, then heat
treated at 700 °C for 12h in Ar, obtaining a dense TiAl₃ coating with a thickness about 60-100 μm, thicker than as-sprayed Al coating, which is also facilitated by the melting and reaction diffusion. The surface of the formed TiAl₃ bond coat permitted the deposition of a YSZ top coat, and subsequent high temperature oxidation test showed that this coating system improves the oxidation resistance of TiAl substrate.

(3) Wang et al.²³² deposited Fe-Al composite coatings and XRD results showed that with increasing annealing temperature, the content of the intermetallic compound increases (Figure 32a). The differential scanning calorimetry (DSC) analysis showed that Fe₃Al₅ was the first intermetallic phase formed upon heating at 625°C. The deposit transformed to mainly FeAl phase with a trace of remaining Fe phase as the temperature reached 900°C, as indicated by XRD in Figure 32b. Note that the melting of Al under this condition greatly facilitates the reaction diffusion of Fe atoms. It was found that the formation of Fe₃Al₅ intermetallic compound could take place even at 450°C, far below the Fe-Al eutectic temperature (640°C), due to metastable interfaces that are produced by intensive deformation of deposited particles during CS.²³² They also reported the phase transformations in nanostructured Fe-Al²³³ and Fe(Al)-Al₂O₃ coatings.¹² The metastable nanostructured Fe(Al) solid solution is retained in the coating without phase transformation. However, apart from FeAl, there is no trace of other intermetallics formed during PSHT. An annealing temperature of around 600°C is adequate to complete the intermetallic transformation, and strong interface diffusion can take place when the temperature reaches 950°C because of the melting, which further improves the adhesive strength of the coating.¹² Jan et al.²³³ reported similar intermetallic phase change as Wang et al.⁹⁷, and they found that coating porosity increased with PSHT temperature, and these pores can be filled with molten metal to form a metallic-intermetallic composite.

(4) Therefore, the fabrication of metal-intermetallics composites through the CS + PSHT method should be carefully operated at a temperature range where expected intermetallics could form and it has less Kirkendall effect.

Besides, researchers have also identified intermetallics in the heat-treated Al-Cu,⁵¹ Ni-Ti,²²⁴ Ni-Sn,²³⁴ Al-Sn,²³⁵ Al-Mg²²⁶ and Ni/Al-Al₂O₃²²⁸ composite coatings. Figure 33 shows coatings that have undergone intermetallic formation after heat-treatment, with a reaction layer, and even multi-layers, at the interface of the components. It should be noted that an intermetallic phase transformation also takes place at the interface between the coating and the substrate as indicated in Figs. 33. Therefore, by controlling the annealing time and temperature, one may get pure intermetallic coatings provided the possible useful melting of one metal.

4.3.2 Directly cold-sprayed metal-intermetallic composites

There are a very limited number of studies directly cold-sprayed metal-intermetallic blend powders. With this method, one can clearly know the obtained intermetallic, while with the CS+PSHT method one can not
absolutely ensure the expected intermetallics.

Cinca et al.\textsuperscript{223} deposited Fe40Al intermetallics onto 304 stainless steel and Ti substrates. It was found that coating thickness decreases with the increase of spraying distance. Dense coatings were obtained on stainless steel while coatings on Ti substrate contained cracks, which may be due to the larger difference in the thermal expansion coefficients between the Ti substrate and iron aluminide. Chandanayaka et al.\textsuperscript{237,238} sprayed Ni-Ni\textsubscript{3}Al blends with two kinds of Ni\textsubscript{3}Al sizes. The smaller sized Ni\textsubscript{3}Al results in a stronger interlocking and the slightly increased mechanical properties due to its higher particle velocity than coarse one. Bu et al.\textsuperscript{230} reported that the Al-Mg\textsubscript{11}Al\textsubscript{12} composite coating has a comparable anti-corrosion performance to pure Al bulk material, and the corrosion current density is reduced by more than one order of magnitude for the Mg substrate. Cherigui et al.\textsuperscript{239} found that the CS FeSiBNbCu-Al coatings have a soft magnetic character (Hc<1000A/m), and the FeSiBNbCu-25 wt.% Al powder mixture is ideal to produce a homogenous coating with suitable magnetic properties. Steenkiste et al.\textsuperscript{240} applied CS to deposit composite coatings of Terfenol-D ((Tb\textsubscript{0.3}Dy\textsubscript{0.7})Fe\textsubscript{1.9}) and SmFe\textsubscript{2} in a ductile matrix of Al, Cu, Fe or Mo to avoid constituent reaction. An induced magnetic coercivity was measured for the composite coatings with Mo and Fe, and the addition of Mo yielded the largest value (Hci=3.7kOe).

However, in this method the bonding between metal matrix and intermetallic seems not good as that formed with the CS+PSHT, which possibly limits its applications.

5. Nanostructured coatings

It is well known that nano-materials have many advantages over conventional materials such as high mechanical strength, excellent thermal and electrical properties, and superior optical and magnetic performance. But it is difficult to produce bulk nano-materials, and especially nano metallic materials, to use as structural materials. As mentioned above, CS shows great potential in fabricating nanostructured coatings or bulk components due to its low processing temperature, which enables the deposition of nanostructured materials without noticeable oxidation or grain growth.

5.1 Nanostructured metallic coatings

The research on this kind of coatings is mainly focused on Al or Al alloys, and the powder preparation method is ball milling (mostly cryomilling) or agglomerating commercial nano-powders to form micro-powders. A nanostructured Al coating was firstly reported by Mondoux et al.\textsuperscript{241} in 2004. Using conventional and agglomerated nanostructured powders as feedstocks to deposit coatings, it was found that the microstructure of the powder was retained in the coating with hardness twice that of conventional coatings, which is attributed to
the smaller grain size (Hall-Petch effect). Following that, nanocrystalline Cu\textsuperscript{242} and Ni\textsuperscript{243} coatings by CS cryomilled powders were successfully produced as shown in Figure 34. The nanocrystalline coatings generally present a dense, crack-free microstructure, and have a higher hardness than coarse-grained coatings. The low porosity, absence of cracks, indistinguishable particle interfaces, and absence of spallation and delamination indicated that the CS nanostructured coatings may demonstrate good cohesion and adhesion.\textsuperscript{244} Ajdelsztajn et al.\textsuperscript{144} cryomilled Al5083 powder and acquired particles with nano grain size (20-30 nm). The deposited coating had a grain size distribution of the same order of magnitude as the cryomilled Al5083 powder, while its hardness (261±8 HV\textsubscript{0.3}) was higher than any other values reported for Al5083 consolidated with other techniques. Rokni et al.\textsuperscript{245} used the high-energy milled nanocrystalline Al5083 alloy powder (grain size: 40-50 nm) as feedstock, and found that the resultant coating retained the nanocrystalline structure of the powder in the range of 50-100 nm. Elongated grains were also observed due to high velocity impact as shown in Figure 34b. Ajdelsztajn et al.\textsuperscript{144} also found elongated grains in the coatings deposited by cryomilled Al5083 powders, which proves that the deposition of nanocrystalline metallic particles are still based on their plastic deformation.

In contrast, Ghelichi et al.\textsuperscript{146} deposited both micro and nanocrystalline Al7075 powders on Al5052 substrate, and found that the cryomilled powder yields a porous coating structure, while the coating with a micron-sized powder shows almost no pores as shown in Figure 35. This is possibly due to the poor deformability of the prepared nano-sized powder and the unsuitable process parameters that were drawn from micro-particles experiments. A similar phenomenon was also observed for CS cryomilled Al2618.\textsuperscript{246} It should be pointed out that although the nanostructures of feedstocks are totally retained in the resultant coatings and the hardness is greatly increased, the cohesion of the nanostructured coatings is still not clear because of less data on it.

5.2 Nanostructured metal-metal composite coatings
In addition to elemental powders, nanostructured metal-metal composite coatings are also studied. Bacciochini et al.\textsuperscript{247} produced gasless reactive energetic materials with CS high-energy ball-milled Ni-Al powder (atom ratio of 1:1). The coating showed a dense microstructure with a porosity of about 1%. Pitchuka et al.\textsuperscript{18} studied the dry sliding wear behavior of Al amorphous/nanocrystalline alloy powder (Al-4.4Y-4.3Ni-0.9Co-0.35Sc (at.%)). It was found that the as-sprayed coatings exhibit higher steady state coefficient of friction (COF) of 0.55 compared to that of 0.38 for heat-treated coatings. Wear volume loss in the as-sprayed condition is 68% higher than that of heat-treated coatings, which is attributed to the micro-abrasion and delamination of the weak splats. However, micro-scratch tests showed that the as-sprayed coatings have a
lower COF than that of heat-treated coatings, because these have a denser microstructure with embedded intermetallic phases, which results in higher scratch wear resistance. The scratch induced deformation mechanism changes from the shear-band dominated brittle mode in the as-sprayed coatings to the plowing type in the heat-treated coatings. Zhang et al.\textsuperscript{147} applied a mixture of 30 wt.% as-atomized and 70 wt.% as-cryomilled Al2009 powders as feedstock to produce a coating without obvious pores and denser than that produced with pure nanocrystalline powder as shown in Figure 36. The extensively deformed as-atomized particles act as a binder in the coating to link the nanocrystalline particles, tamp the cracks and fill in pores between layers and particles, forming a dense coating.\textsuperscript{147} This is similar to the co-deposition mechanism of the metal-hard phase composite coatings described above.

Besides nanostructured Al or Al alloy based composite coatings, researchers have also investigated other nanostructured coatings with CS. Li et al.\textsuperscript{142} ball-milled Fe and Si powders to produce nanocrystallites. As shown in Figure 37a, the grain size of the feedstock decreases with milling time and there is no grain growth during the CS process. Observations under TEM showed that the grains had a size of several tens of nanometers (Figure 37b). It should be noted that although grain size slightly decreases with increasing milling time, the coating hardness is little affected,\textsuperscript{142} possibly because the hardness of the milled powders has been saturated during ball-milling, so no further significant increase will yield for coatings. Wang et al.\textsuperscript{143} deposited ball-milled nanostructured Fe-Al alloy powder on stainless steel substrate. The metastable Fe(Al) alloy powders exhibit a lamellar structure (Figure 38a) and the lamellae are continuously refined with increasing ball-milling time. XRD results and TEM micrographs indicated that the phase structure of the as-sprayed coating was just a Fe-based solid solution, which transformed into the FeAl intermetallic phase during heat-treatment at 500°C for 25h, similar to that indicated in Figure 31. The grain size was in the range of 10-50 nm (Figure 38b), thus nanostructured FeAl intermetallic compound coatings were achieved. Kumar et al.\textsuperscript{249} deposited a 250 μm thick nano Ni-20Cr coating on SA 516 boil steel with the ball-milled feedstock. High temperature oxidation tests at 900°C for 50 cycles showed that the coating reduced the weight gain of the base metal by 94% because Ni and Cr react preferentially with oxygen, forming NiO and Cr2O3, respectively. Compared with micro-sized CS Ni-20Cr coating, the weight gain of specimen is reduced by 64%, and by 71% when the substrate was SA213-T22 steel,\textsuperscript{250} proving the high oxidation resistance of the nano Ni-20Cr coating.

In summary, by ball-milling of metal ingredients, nanostructured metal-metal composite coatings could be obtained with fine or metastable structures. The resultant coatings have higher hardness, but with a questionable cohesion, though some other properties are also superior.
5.3 Nanostructured metal-ceramic composite coatings

Similar to common metal-ceramic composites, CS also showed potential in the fabrication of nanostructured metal-ceramic coatings. One typical example is nanostructured WC-Co coatings. Though the CS of micro-sized WC-Co coatings showed poor deposition efficiency than that by HVOF,244 the use of nanostructured feedstock significantly improves the deposition efficiency and density of CS coatings. This is possibly because the critical velocity is lowered and there is a higher surface area for contact between the binder phase and hard ceramic particles for effective deposition of nanostructured particles. Researchers21,154,155,158,169,251 found that a dense WC-Co coating can be deposited with CS without phase transformation or decarburization, with the nanostructures retained in the deposits. Shukla et al.20 initially reported on a nanostructured WC-10Co coating without decarburization in 2000. Later in 2002, Lima et al.21 prepared nanostructured WC-12Co coatings with agglomerated and sintered particles as shown in Figure 39. Though the coating thickness is only 10 μm, it shows a dense microstructure without pores, cracks or phase transformation. Li et al.158 and Kim et al.154,155 produced high quality nanostructured WC-Co coatings with low porosity and hardness comparable to the bulk. Li et al.158 also found that heat-treatment has little effect on coating hardness but can improve the coating bonding strength. Besides, Li et al.158 observed a broader WC peak in the XRD pattern of coating compared to the original powder, due to the grain refinement caused by high velocity impacts as shown in Figure 40. A similar phenomenon was also found in nanostructured WC-17Co coating.169

Figure 41 compares cermet coatings deposited with agglomerated nanostructured WC-12Co feedstocks of various porosities.169 From the obvious change of coating thickness, it is interestingly found that deposition efficiency increases with particle porosity. This is possibly because the non-uniform deformation leads to the increased density at the lower part (impact zone) of the particle while retaining the porous structure at the upper part (far away from the impact zone) (Figure 41b). The particle retains the pseudo-deformability when the following particles impact on it, permitting thick nanocrystalline WC-12Co coatings to be fabricated. Research by Lioma et al.252 WC-12Co-xNi also indicated that the porous structure favors particle deposition. However, Yandouzi et al.156 deposited both nano-sized and microcrystalline WC-Co coatings, and the nanostructured coating showed higher porosity and the lower hardness due to lack of plastic deformation, as in nanocrystalline Al coatings.246 These results mean that tailoring particle porosity seems a possible approach to acquire dense WC-Co coating with high deposition efficiency.

As reported by Yang et al.168, the coating toughness decreases with the increase of coating hardness. It is therefore a serious challenge to achieve strengthening and toughening at the same time. In order to overcome
this problem, possible solutions include alloy phase toughening through plastic deformation, deviating the cracking path by reinforcement particles and increasing the interface bonding strength between the matrix phase and the ceramic particle. Yang et al.\textsuperscript{168,253} designed a bi-modal WC-12Co powder that possesses both high hardness and high toughness, as indicated by the square symbol in Figure 42a. The reinforcement phase is both micro-WC and nano-WC particles dispersed in the Co binder phase (Figure 14b). Fracture toughness can reach up to 18.9 ± 4.0 MPa·m\textsuperscript{1/2} after annealing at 1000°C for 6h in a hydrogen atmosphere, which is comparable to the conventional WC-12Co bulk. This is due to the larger area of the bi-modal-sized fracture surface and the crack bridging caused by the micro-sized strengthening WC particles as indicated in Figure 42b. Crack bridging increases fracture toughness as it increases the fracture surface area and the energy consumption during cracking. The zigzag feature is encountered at both the micro WC particles and the nano WC particles, producing high fracture toughness. Meanwhile, the bi-modal WC-Co possesses a hardness as high as 1683 ± 176 HV, which is similar to nano WC-12Co having a mean free path of the Co binder phase of 36 nm. PSHT further increases the coating toughness and doubles the wear resistance of the CS WC-(Nano WC-Co) coating.\textsuperscript{253}

It should be pointed out that although the grain size dose not get into nano-scale, the coating properties could be improved by powder design. Luo et al. [130] developed a core-shelled structured WC-Co powder as mentioned above (Figure 19), and the deposited coating is shown in Figure 43. The coating has a porosity of 0.7% and the hardness of this WC-10Co core is 1493±76.7 HV\textsubscript{0.1}. The total WC content in the core-shell structured WC-Co coating was calculated to be 57.6 vol.%. After annealing at 900°C for 2h, fracture toughness was increased by 70.6% (from 21.2±3.8 MPa m\textsuperscript{1/2} to 35.7±5.2 MPa m\textsuperscript{1/2}) due to the improved deformability of the Co-rich WC-Co binder matrix as well as the enhanced bonding between WC-10Co cores and Co-rich WC-Co binder, where cracks were only observed in the WC-10Co cores of relatively low deformability.

Another interesting reinforcement can be obtained by carbon nanotubes (CNTs). The CNTs possess excellent strength, elastic modulus and stiffness, high thermal and electric conductivity while having low thermal expansion. All these make them a promising candidate for reinforcements to synthesize light weight, high strength structural MMCs.\textsuperscript{100,254} Low process temperature can avoid the unwanted reaction between the metal and CNTs.\textsuperscript{255} CNTs distribute homogeneously in the CS coatings\textsuperscript{100,254,255} as indicated in Figure 44a. The porosities of Al-0.5 wt.% CNTs and Al-1 wt.% CNTs coatings are (1.6±0.5) % and (2.3±0.9) %, respectively. Nanoindentation of the composite yields a range of elastic modulus values between 40 and 120 GPa, whereas some regions had elastic modulus as high as 229 GPa for Al-0.5 wt.% CNTs, and 191 GPa for Al-1 wt.% CNTs coating. This is attributed to the reinforcement effect of CNTs and the local concentration of CNTs.\textsuperscript{149} Chen et
al.\textsuperscript{254} reported that the CNTs retain their graphitic structure in Al-CNTs coatings as shown in Figure 44b, and nano scratch measurements showed that the addition of CNTs into Al matrix contributes to the increase in elastic modulus, hardness, yield strength, shear strength and nano scale wear resistance. The wear resistance is increased by 40\% with the addition of 1.0 wt.\% CNTs, while the COF remains unchanged. The higher hardness can be attributed to the fact that the MWCNTs inhibit plastic deformation that results in dislocation accumulation and intersection.\textsuperscript{255}

For the CS Cu-CNTs coating,\textsuperscript{100} the CNTs dispersed uniformly in the Cu matrix, maintaining their tube structure as shown in Figure 44c. The composite coating had a higher thermal diffusivity than pure Cu coating, due to the dispersion of MWCNTs within the clean and closed CNT/Cu interfaces, which is the effect of high compressive stress during CS.\textsuperscript{100} Pialago et al.\textsuperscript{256} deposited Cu-CNTs composite coating with CNTs contents of up to 15 vol.\%. It was found that the particle size and deposition efficiency decreased with increasing CNTs content. The inner coating showed a lamellar structure while the surface layer showed a rough morphology containing 1.0-2.5 vol.\% micropores as shown in Figure 44d. They\textsuperscript{256,257} applied the Cu-CNTs composite coatings for boiling heat transfer, and found that the coating decreased the superheat and increased the maximum heat transfer coefficient by 1.21-1.74 times than that of the plain Cu plate. Besides, the addition of ceramics (SiC, AlN, and BN) in Cu-CNTs further increases boiling heat transfer, and a combination of (5 vol.\% CNT + 95 vol.\% Cu) + 20 vol.\% AlN yields the highest enhancement ratio of 2.57.\textsuperscript{258}

In literature there are certain works on other metal-ceramic nanostructured composite coatings. Cavaliere et al.\textsuperscript{259} found that addition of ceramics (Al\textsubscript{2}O\textsubscript{3}, SiC, BN) into metal matrix (Al, Ni, Cu) has strong effect on grain refinement, coating porosity and adhesion strength as shown in Figure 45. The presence of reinforcement phase affects the adiabatic shear instability governed recrystallization, as well as local plastic deformation, which accounts for the decrease in grain size and coating porosity. However, coating adhesion is decreased with increasing ceramics.\textsuperscript{259} Poirier et al.\textsuperscript{136} added 5 vol.\% nano-sized Al\textsubscript{2}O\textsubscript{3} in an Al matrix, which lowers the powder and coating nano-hardness because the poor milling parameters were selected, leading to cracked particles with insufficient Al\textsubscript{2}O\textsubscript{3} embedding in Al. Hodder et al. [140] deposited commercially pure Al mixed with either 10 μm or agglomerated 20 nm Al\textsubscript{2}O\textsubscript{3} in weight fractions of 25 to 95 wt.\%, with the highest ceramic contents in the coating being 48 wt.\% and 38 wt.\%, respectively. However, the maximum microhardness of the latter was higher than that of the former due to the increased spreading of the nano particles in the coating, which increases load-bearing capability of the reinforcement particles. Yandouzi et al.\textsuperscript{260} fabricated the nanocrystalline Al5356-20 wt.%B\textsubscript{4}C coating with pulsed cold spraying (PCS), and the coating showed a low
porosity with B\textsubscript{4}C uniformly distributed in the nanostructured Al\textsubscript{5356} matrix, which greatly improves the coating dry sliding wear resistance. Nanostructured Fe-Cu-Al\textsubscript{2}O\textsubscript{3} exhibited lower COF and wear rate than their constituting elements and/or to benchmark materials due to the appropriate balance of soft and hard phases, and to the nanostructuring of the matrix. High amounts of grain boundaries hinders the formation and motion of dislocations, thus, the deformation of nanostructured materials is restrained.\textsuperscript{261} Luo et al.\textsuperscript{14} fabricated a cubic BN particle-reinforced NiCrAl nano-composite coating by CS. A Ni-based amorphous layer with a thickness ranging from 3 to 8 nm was located at the cBN/NiCrAl interface and was surrounded with crystalline Ni-based alloy. These Ni-based alloy crystals exhibited a preferred orientation with the \{111\} plane frequently parallel to the interfaces of cBN/NiCrAl as shown in Figure 46. They also reported that the as-sprayed 20 vol.% cBN/NiCrAl nano-composite coating yields a hardness of 1063 HV\textsubscript{0.3}. Both hardness and wear resistance are comparable to that of the high velocity oxygen fuel (HVOF)-sprayed WC-12Co coating. After heat-treated at 750°C for 5h, the coating wear resistance is increased by 33% due to the enhanced particle bonding.\textsuperscript{13} In addition, Phani et al.\textsuperscript{153} studied the effect of high temperature heat-treatment on porosity, thermal conductivity and grain size of Cu-Al\textsubscript{2}O\textsubscript{3} nano-composite coating. It was found that heat-treatment has little effect on porosity. In the meantime, conductivity rises a little with the increase of temperature. The grain growth was restrained due to the presence of Al\textsubscript{2}O\textsubscript{3} even when heat-treated at 950°C, which is close to the melting point of copper owing to the presence of fine Al\textsubscript{2}O\textsubscript{3}.

In summary, the nanostructured metal-ceramic coatings are one of the most promising composites because of their excellent properties. The careful tailoring of powder and processing parameters will make these kinds of coatings very attractive in applications. However, again, the cohesion, ductility and toughness of the composite are the crux. PSHT can help improve them with the retaining of their nanostructures.

5.4 Nanostructured ceramic coatings

It is interesting that CS can also be used to deposit nanocrystalline ceramic coatings, although initially it appears impossible as CS requires plastic deformation to work. The key requirement for deposition is a vacuum chamber and a specially designed nozzle, and it is therefore named as vacuum cold spraying (VCS). It was initially developed by Akedo and his coworkers\textsuperscript{263} and initially termed as aerosol deposition (AD), in which nano-particles are sprayed in a vacuum chamber using a propellant gas flow of helium or air. Although the velocity reached is lower than that of usual CS, this process reduces significantly the bow shock effect, making it possible to deposit very small particles. It has been used to fabricate lead-zirconate-titanate (PZT), α-Al\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, YSZ, AlN, MgB\textsubscript{2}, and other nanocrystalline ceramic films of high transparency, high hardness, and
high-breakdown voltage at room temperature. Hanft et al. detailedly summarized the materials that could be deposited by AD and applications.

As indicated in Figure 47, dense $\alpha$-Al$_2$O$_3$ coating with a thickness of about 3 μm was deposited on a SiO$_2$ substrate. XRD results confirmed that there is no phase transformation during deposition. The broadening of the spectral peaks indicates the reduction of grain size. Figure 47c indicated randomly oriented polycrystalline nanostructure with crystal grains smaller than 20 nm in length. It is worth pointing out that the ceramic particles seem to have experienced some extent of plastic deformation. The fracture and the multiple impacts of fine particles during deposition induce the generation of active surfaces of particles, allowing the bonding of particles and forming a dense ceramic layer. Cao et al. identified that lattice collapse and damage, internal dislocation, brittle fracture, and inelastic crack nucleation near dislocations are the main factors responsible for particle deformation at high impact velocities. Thus, as Park et al. elaborated, plasticization and fragmentation are the main deposition mechanisms of VCS.

Because of the very low process temperature and the ability to deposit thin ceramic films on various substrates, even curved surfaces, VCS has been applied in the fabrication of electro-ceramic for piezoelectric devices and electro-optic materials for optical devices. In the case of PZT, for example, in order to eliminate structure defects and the reduction of the crystallite size during deposition, PSHT is necessary to improve the ferroelectric properties. As shown in Figure 48, the PSHT temperature for the coating deposited by AD is lower compared with traditional methods. After annealing at 600°C, the dielectric constant and the piezoelectric constant of layers were comparable to the values of conventional thin-film formation methods.

Following Akedo et al., researchers have investigated other nanostructured ceramic coatings by VCS, such as HA, TiO$_2$, TiN. The photocatalytic efficiency of CS nanostructured anatase (TiO$_2$) coating is comparable to the one obtained by competitive technologies like dip-coating P25® photocatalysts. The solar cells assembled by VCS nanocrystalline TiO$_2$ powders yielded a short-circuit current density of 7.3 mA/cm$^2$ and an energy conversion efficiency of 2.4%, which are comparable to those by other methods such as mechanical compression and hydrothermal crystallization. After post-sintering at 450°C for 30mins, these values increased to 14.0 mA/cm$^2$ and 4.9%, respectively, due to the improvement of intimate contacts between nano-TiO$_2$ particles in the coating. In addition, applying nano-TiO$_2$ as a blocking layer on fluorine-doped tin oxide glass can increase the open-circuit voltage and short-circuit current density due to the blocking of electron leakage from the fluorine-doped tin oxide surface to the electrolyte, hence, the photon-to-current conversion efficiency was increased from 3.3% to 5.6%. Moreover, Yang et al. found that the short-circuit photocurrent...
density of the cell increases with accelerating gas flow due to the improved coating compactness. The VCS TiN coating exhibits a low hardness of 279-490 HV with a porosity ranging from 58.3 to 67.6% and the pore size mainly ranging from 2 to 8 nm, which results in a relatively good fracture toughness of about 3.12 MPa·m^{1/2}. It was also found that the sheet resistance and electrical resistivity of the TiN coatings decrease in a dramatic way with increasing coating thickness because of the higher tamping effect, which results in fewer defects, and in turn decreases the electron transfer resistance. The minimum sheet resistance (127 Ω) is lower than that of the TiN film deposited by CVD (186.7 Ω), and a minimum electrical resistivity of 3×10^{-3} Ω·m is achieved.²⁷³,²⁷⁴

5.5 Nanostructured ceramic composite coatings

A few researchers have also investigated nanostructured ceramic composite coatings by VCS, such as hydroxyapatite (HA)-graphene nanosheet (GN),¹⁰⁵,¹⁰⁶ SiC-TiN²⁷⁶ and graphene-TiO₂²⁷⁷ composite coatings. Cross sections of the nanostructured ceramic composite coatings are shown in Figure 49. The coatings also present a relatively dense structure with the presence of micro-cracks and micropores. Liu et al.¹⁰⁵,¹⁰⁶ found that nanocrystalline GN homogeneously embedded in the HA matrix and certain nano HA particles experienced plastic deformation (Figure 62b), which is similar to the phenomenon reported by Akedo et al.²⁶³ and Cao et al.²⁶⁶,²⁶⁷. The HA-GN composite coating markedly enhanced the attachment and proliferation of the osteoblast cells, which has great potential in bio-application.¹⁰⁵

Kim et al.²⁷⁷ found that the optimal concentration of 0.3 wt.% graphene in TiO₂ feedstock increased the energy conversion efficiency from 3.14% of pure TiO₂ to 5.02%. Further, the electrical resistivity of nanocrystalline SiC-TiN composite coating decreases with increasing TiN content, from the order of 10^{14} Ω·m of the undoped-SiC to the minimum 1.82 Ω·m with 50 mol% TiN in the coating,²⁷⁶ which is contributed to the electron-transporting of the conductive TiN phase.

By forming a composite film, properties can be adjusted, for instance, electrical parameters like conductivity or permittivity, as well as mechanical characteristics like hardness, porosity, or adhesion to the substrate. Depending on the mixing ratio and relative particle sizes of the powders, one can obtain either a dispersion of one phase in a continuous matrix of the other, or two interpenetrating continuous phases.²⁶⁴,²⁷⁸

6. Potential applications of composite or nanostructured coatings

Based on the above results, CS is expected to be applied to most fields where thermal spraying has been already used because CS can produce metallic or composite coatings with properties superior or comparable to thermal sprayed ones. Its applications can be summarized as follows.

6.1 Protective coatings
The basic use of CS is to fabricate coatings providing resistance to corrosion environment, elevated temperatures and wear.

(1) **Corrosion resistant coatings.** It is well known that TS coatings with post-sealing treatment seem to provide good protection for the substrates by dual functions, i.e. physical isolation and electrochemical protection acting as a sacrificial anode to the substrate. However, the excessive heat input to the substrates may lead to distortion and more residual stresses. Therefore, CS emerges as a better choice to protect the substrate. For components which work in corrosive environments such as sea water or acid atmosphere, anti-corrosion coatings are necessary. CS can be used to fabricate anti-corrosion coatings, such as Zn, Al, Ni and their alloys based composite coatings such as Al-Al₂O₃, Ni-Al₂O₃, Al-Zn and Al-Si-Zn, without the oxidation of the metallic powders. Cu-Al-bronze composite coatings can enhance the corrosion and cavitation resistance of ship propellers in marine environments. In contrast to the relatively porous and oxidized thermal sprayed protective coatings, such as Zn, Al and their alloys, CS coatings have higher resistance to corrosive media and longer service life. The key problem for these CS protective coatings is to develop industrial equipment and techniques to economically and easily deposit coatings on large and complex surfaces.

(2) **High-temperature oxidation resistant coatings.** This kind of coatings is widely used in high-temperature parts, such as aero engines, turbines and boilers. For examples, Ni-Cr oxidation resistant coatings for boilers, Cu-Cr-Nb deposits for high thermal and electrical conductivities at elevated temperatures in rocket engines, intermetallics including Al-Ni, Fe-Al, nanostructured NiCrAlY alloy and CoNiCrAlY bond coat for thermal barrier coatings.

(3) **Wear resistant coatings.** To increase the wear resistance of industrial components, wear-resistant coatings can be deposited by CS, such as cermet coatings, ceramic reinforced MMC coatings and anti-friction alloy coatings (Al-Si alloy, bronzes, WC-Co and stellite coatings). In addition, abradable sealing coatings are designed to preferentially abrade when contact is made with a mating part. A patent on CS nickel-graphite abradable coating has been granted, and it is promising to expand to coatings with other materials such as Al-12Si alloy, Al-bronze, Ni-Cr-Al alloys and their composites with polymer or graphite additions.

6.2 **Functional coatings**

CS has also been applied to non-traditional fields, e.g. energy, photovoltaic, electronics, medical, catalytic. One such is the fabrication of nanostructured functional coatings. For examples, CS TiO₂ films on glasses with mesoporous microstructure can be used in applications of photocatalytic degradation and
dye-sensitized solar cells.\cite{269,270} TiO$_2$ and TiO$_2$-Zn coatings can also be used as catalytic coatings.\cite{102,103} Moreover, nanostructured TiO$_2$ may also be used as bioactive coatings.\cite{109,293,294} Ag-SnO$_2$ and Ag-Ni coatings can be used as industrial electrical contacts for contactors and circuit breakers.\cite{101,104} Cu-CNTs composite coatings are used for boiling heat transfer.\cite{100,256-258} FeSiBNbCu-Al coatings are used as soft magnetic materials.\cite{239,240} HA-GN and HA-Ti composite coatings are deposited on titanium substrates as load-bearing implant materials for biomedical applications.\cite{105-107,212,295} Furthermore, cold sprayed coatings, particularly Cu or Ag coatings, have showed excellent electrical conductivity which is comparable to their bulk state.\cite{296-298} In some cases, CS may gradually replace expensive and not flexible techniques such as physical vapor deposition (PVD) and silver frit screen printing.\cite{299}

6.3 Near-net forming or additive manufacturing

As a spray forming process similar to thermal spraying, CS can also be used to directly fabricate components because of its high deposition rate and ability to combine many dissimilar materials to produce a single component without obvious melting or oxidation of the feedstock,\cite{112} which is similar to near-net shape manufacturing technology. As such it is possible to construct components with freeform surfaces, internal channels and embedded devices.\cite{111} Recently, General Electric Co. (GE) reported that a new additive manufacturing technology, named Cold Spray 3D Printing, was developed aiming at building a part or adding material to repair an existing part. Although it is not new in the thermal spray community, it is a novel application of CS. CS components can be easily machined to a final shape. CS has been demonstrated to manufacture large parts, sputtering targets or large rotating targets (e.g. Zn-Al and Zn-Sn), and fin arrays,\cite{190,300} as shown in Figure 50.

6.4 Component repair

When compared to forming a part, CS seems more suitable for the quick repair by spraying powders onto damaged parts, such as turbine blades, aircraft skin, helicopter mast support, gearbox, panel fastener hole, pistons, cylinders, valves rings, bearing components, sputtering targets and pump elements,\cite{305-307} and most of them can be fulfilled with composites. As a result, the life of a component is extended, and this is especially important for expensive parts. In addition, with portable CS equipment, on-site repairing can be attempted without having to remove damaged parts out of the machine. For examples, CS has been used to repair military hardware such as the engine block,\cite{308} the flight control module of the gear box.\cite{309} Lots of patents on restoration with CS have been granted and it is also worth noting that the Air Force Research Laboratory of the US and the United Technologies are improving CS to repair major components of the UH-60 Black Hawk helicopters.\cite{310}
Besides, CS can also be used to restore corroded areas of the Steyr engine with the Cu-Zn-Al₂O₃ composite coating, and for repairs on corrosion sensitive materials such as magnesium and aluminum alloy components (Figure 51), worn surface of aluminum mold, degraded areas of titanium alloy turbine components and martensitic stainless steel components, in-situ repairing of the eroded bellows by using the Ni/Al₂O₃ coating. Furthermore, it has been found that a CS patch can enhance the damage tolerance of structural components and restrain crack growth, thus showing great potential in restoring the airworthiness and functionality of aging aircraft structures. Therefore, CS composites can have a wide use in repair and improvement of metal structures.

7. Summary and outlook

Based on the literature review and above discussion, it is clear that CS is a promising technique to fabricate advanced metallic, composite and nanostructured coatings, as well as near-net-shape components and repairs. It is gradually moving out of lab research to industrial applications because of the deeper understanding of the process, the advancement of technology, and the upgrading of spray equipment. The following concluding remarks could be made.

7.1 Importance of powder preparation

Powder preparation prior to spraying takes an important role in deposition of composites. The methods currently applied mainly include mechanical blending, ball-milling, spray drying, agglomerating and sintering, coating or cladding. Each method has its advantages and disadvantages. Mechanical blending is an easy and simple way to mix the powders, and the resultant coatings show all-right properties but the distribution of hard phase is difficult to control. Ball-milling is proved to be a good way to prepare well-dispersed composite and nanostructured powders, and the obtained coatings usually have good properties, but the flowability of the milled powders is poor, even for cryomilling, not well suitable for spraying. A following powder treatment may be needed to help powder feeding. In addition, the powders are ready to be polluted by the mill jar and balls, or by oxidation when exposed to air. Another good method is the coating or cladding process, which will yield a controllable volume fraction of hard phase. However, it is difficult to get a thick coated metal layer or small sizes of powders. As for spray drying or agglomerating and sintering, they are employed for some special materials, e.g. cermets. Spray drying can also be used to treat the milled fine powders. In order to increase the deposition efficiency of hard reinforcement particles and precisely control of its content and distribution in the deposits, as well as to prepare nanostructured powders, these methods should be carefully selected. With properly prepared feedstocks, one can produce coatings according to specification. The tendency is to design
composite powders by a combination of methods to produce coatings with desired properties for complicated working conditions. The main problems to be solved are as follows.

(1) to find economic and efficient methods for micro- or nano-sized powder preparation.

(2) ball-milling parameters take important roles in the quality of prepared powders, how do they influence the coating quality?

7.2 Co-deposition of composite powders

The bonding mechanisms of the composite particles lie largely on the co-deposition mechanism of metal and hard phases besides the conventional metal-metal bonding mechanisms. The severely deformed soft metal phase acts as a binder, while the hard phase embedded in the matrix acts as reinforcement. Further to that, the hard particles have an “activation” effect on the substrate or previously deposited metals, cleaning oxide films on particles and/or substrate surfaces and increasing their activity for metallurgical bonding at the same time. Another factor may be the “tamping effect” of hard phase. However, the collision between ceramic particles will take the leadership when its content is relatively high, and its erosion effect will lower the deposition efficiency.

7.3 Optimization of composite coatings

CS is a relatively easy and cost-effective technique to deposit composite coatings with comparable or improved properties than as compared other methods. Presence of ceramic particles in feedstock enhances the coating by creation of a composite structure, densifies the coating, increases the coating adhesion, and improves the process stability. The tamping effect of hard phase contributes to the increase of coating compactness and adhesion. The addition of ceramics generally has no negative effect on coating corrosion behavior, but can greatly increase coating hardness, possibly lower COF and enhance coating wear resistance if the hard phase content is appropriate. However, when the content of hard phase is too high, the deposition efficiency will significantly decrease by its erosion effect, and thus the coating adhesion is degraded. Generally speaking, the content of hard phase in the coating increases with the increase of that in the feedstock until a maximum value, and then decreases. Consequently, the coating hardness also increases with the content of hard phase. While for coating adhesion, it presents a tendency similar to deposition efficiency as increasing the hard phase content. By controlling the composition of the original feedstock, it is possible to deposit coatings with specified properties. Preliminary studies have also shown that CS together with PSHT is a promising technique to fabricate metal-intermetallic coatings or even pure intermetallics coatings. Careful selection of heat treatment temperature (e.g. 500-580 °C for Ti/Al deposit) could avoid the obvious pores formed by the Kirkendall effect. There are still some important issues to be solved for CS composites.
(1) the most important thing is how to optimize the size, concentration, and distribution of ceramic phase in metal-ceramic composite coatings to tailor composite properties;

(2) effect of process parameters as well as PSHT on composite coating microstructure and properties;

(3) how to control the degree of phase transformation in forming the intermetallics during PSHT to obtain the desired phase?

7.4 Optimization of nanostructured coatings

As for nanocrystalline materials, CS is also a promising coating technique for its low process temperature. The characteristics of nanocrystalline feedstock can be retained in the deposits, producing coatings with good properties such as high hardness, excellent wear resistance, high electrical and thermal conductivity, high dielectric constant and piezoelectric constant, which are difficult to acquire through other conventional methods. When spraying with nanostructured Al alloy powders, the coating usually presents a relatively high porosity compared to the micron-sized powders, possibly because the spray parameters are not well in the deposition window to make the particles deform extensively. As for WC-Co, the deposition efficiency of nano powders is higher than that of micron-sized powders, and a good toughness of nanostructured coating could be obtained by designing the feedstock powders. During annealing of the nano-particles reinforced composite coatings, the grain growth is restrained due to the presence of nano-ceramic-particles, for example, nano Al₂O₃ in the Cu-Al₂O₃ coating will keep the small grain size even heat-treated at 950°C. The current challenge to deposit nanocrystalline materials lies in the control of nanostructures in the coating via powder preparation and processing parameters. Some important issues to be solved are:

(1) as mentioned above, the preparation of appropriate powder is necessary.

(2) to optimize the process parameters including nozzle design for nanostructured coatings to ensure compact coating.

(3) how to ensure the deposition of thick, uniform and large-area coatings through process optimization.

(4) lack of data on the properties of nanostructured coatings, e.g. adhesion/cohesion.

7.5 Expanding the applications

In order to expand the applications of CS, some general aspects should also be considered.

(1) refer to thermal spraying, establishment of standards to quantitatively characterize the coatings microstructure and properties will be very helpful.

(2) the performance of coatings in service, e.g. corrosion, fatigue and wear, when exposed to industrial environments, is also an important aspect to be explored.
(3) how to improve the toughness of as-sprayed coatings, which is important in order to use in spray forming and restoration?

(4) develop high-performance portable CS equipment to extend range of open applications.

(5) develop laser assisted CS (or hybrid CS), where the necessary thermal energy is provide to soften the high strength materials, e.g. superalloys, intermetallics.

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