A Review of the Mechanical and Tribological Behavior of Cold Spray Metal Matrix Composites

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Abstract Cold spray is an effective solid-state process for the fabrication of metal matrix composites where metallic, ceramic, or intermetallic reinforcements are embedded in a metallic matrix. Cold-sprayed metal matrix composites (CS MMCs) enable combining favorable properties of their constituent phases. Combinations of the ductility of metals with the high strength of ceramics or with the creep resistance of intermetallics are two typical examples. Here, we review recent advances in the understanding of the mechanical and tribological behavior of CS MMCs, with particular emphasis on the physical mechanisms and predictive understanding. We start the review with deposition mechanisms, defects, and microstructural features in CS MMCs. We continue the discussion with the mechanical behavior of CS MMCs, including elastic modulus, hardness, strength, ductility, as well as adhesive and cohesive failures. We also explore various aspects of the tribology of CS MMCs, from frictional response to abrasive and erosive wear. We discuss the effect of cold spray parameters and post-spray thermal and mechanical treatments on the microstructure and properties of CS MMCs. We connect experimental findings on the mechanics and tribology of CS MMCs with theoretical frameworks to the extent possible. Finally, we propose several critical unresolved issues in the field as future research directions.

Keywords cold spray · mechanical properties · metal matrix composites · tribological properties · review

Introduction

Cold spray is a solid-state process in which micrometer-sized particles (5–50 μm) are accelerated by a supersonic carrier gas in a de Laval nozzle to high velocities (300–1200 m/s) and impact a substrate material. If the impact velocity of the particles exceeds a threshold, referred to as critical velocity, the particles bond to the substrates in solid state without having to induce high homologous temperatures or melt either material. As a result, limitations associated with high temperatures such as phase transformation, tensile residual stresses, and significant distortion can be avoided, making cold spray a competitive deposition technology for different classes of materials. Ever since the first “cold” deposition of metallic particles onto metallic substrates was reported after Papyrin et al.’s classic two-phase flow experiments (Ref 1), cold spray has proven successful in the deposition of not only pure metals and engineering alloys, but also metallic glasses (Ref 2, 3), ceramics (Ref 4–7), high entropy alloys (Ref 8), and composites (Ref 9–11) onto a variety of substrates including metals, ceramics (Ref 12), polymers (Ref 13), and metalloids (Ref 14, 15). Several books (Ref 16–20), as well as thorough reviews (Ref 21–30), have covered different aspects of the remarkable progress in the field in the past decades, from processing science of cold spray to microstructural characteristics and properties of the coatings.

The focus of this review paper is on cold spray metal matrix composites. In many situations, single-phase coatings may not be able to meet multiple requirements imposed in practice. For example, while Al coatings can provide excellent sacrificial protection, they can be relatively easily scratched. Combining the properties of their constituents, metal matrix composites can offer a

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combination of properties that could be otherwise challenging to achieve or even mutually exclusive, from strength to toughness to high wear and corrosion resistance and high-temperature stability. From the processing perspective, cold spray offers a unique space compared to more traditional composite fabrication technologies. Unlike powder metallurgy processing, spark plasma spraying, pressure infiltration, and thermal spraying, there is considerably lower applied heat in cold spray to induce liquid phase formation and/or to activate sintering. As a result, one can not only avoid oxidation and deleterious matrix-reinforcement interfacial reactions, but also preserve the microstructure of feedstock materials.

To deposit metal matrix composite via cold spray, one can prepare a batch of composite powders before spraying, or co-deposit two separate batches of matrix and reinforcement powders. Different techniques, including mechanical blending (Ref 31, 32), ball milling (Ref 33), spray drying (Ref 34, 35), agglomeration and sintering (Ref 34, 36–42), and coating powder particles to form a core–shell arrangement (Ref 43) can be used to prepare powder feedstocks. Different methods provide various levels of control over composition, particle size, shape, and distribution of the two phases, but all together enable a vast design space for deposition of metal matrix composites. For a detailed discussion on the advantages of each of the above powder preparation techniques and a material-based classification of metal matrix composites, we refer the readers to a recent review paper on the topic (Ref 26).

The purpose of this paper is to present an overview of the mechanical and tribological properties of cold spray metal matrix composites with a particular emphasis on the underlying fundamentals and predictive frameworks where possible. This class of cold spray materials comprises a metallic matrix phase together with a reinforcement phase, which could be ceramic, metallic, or intermetallic. In this paper, we discuss the influence of the reinforcement phase on the deposition process, coating microstructures, and coating properties. We start the review with a discussion on bonding mechanisms. We highlight how the differences between deposition of a single-phase material and co-deposition of two phases can influence the deposition efficiency and porosity in cold spray metal matrix composites. We will then discuss elasticity, hardness, ultimate tensile strength, ductility, adhesive and cohesive failures, wear rate and mechanisms, as well as the frictional response of cold spray metal matrix composites. While reviewing the literature in these sections, we emphasize predictive understanding and compare experimental findings with the theoretical prediction of the properties as a function of reinforcement content when possible. We include discussions on how cold spray process parameters and post-spray thermal and mechanical treatments can be exploited to

design microstructure and improve properties of metal matrix composites. We end the review with a discussion on several important unresolved issues for the field and propose new avenues for further research and developments.

Bonding Mechanism

Impact-induced bonding in cold spraying of metallic materials can be broadly classified into metallurgical bonding and mechanical interlocking. For metallurgical bonding to occur, clean metallic contact at the atomic level is required. This condition can be met by the large interfacial strain during jetting—an intense outward ejection of material at the interface between particle and substrate. Whether triggered by adiabatic shear instability mechanism (Ref 44–47) or shock wave release mechanism (Ref 48–50), there exists a consensus that jetting can disrupt and displace the native oxide layer, create fresh metallic surfaces, and thus, significantly facilitates metallurgical bonding (Ref 46, 47, 51–59). Mechanical interlocking, on the other hand, occurs when impacting particles anchored or embedded into substrates (Ref 60–63). These conditions are most likely to prevail when particles are much harder and heavier than substrates. Mechanical interlocking can significantly contribute to bonding, in addition to chemical interaction, when different classes of materials are used as powder particles and substrates, e.g., ceramics particles on metallic substrates (Ref 64) or metallic particles on polymeric substrates (Ref 65). Interfacial gaps can be present in the case of mechanically interlocked interfaces, whereas the continuity of material has been confirmed for the metallurgically bonded cold spray interfaces. Impact-induced bonding has been studied empirically through post-spray microstructural characterizations (Ref 23, 27). Recently, in situ observations of a single-particle impacting onto a substrate (Ref 40, 49, 52, 66–68) have also provided a complementary approach to further understand impact bonding. However, there are many interesting material phenomena that are still challenging to study empirically at the length scales and timescales amenable to cold spray. Computational approaches, both atomistic and continuum, have contributed significantly to the current understanding of this multifaceted phenomena at different scales. Examples include resolving adiabatic softening (Ref 45–47), jetting (Ref 50) and pressure shock waves (Ref 48, 50, 69), native oxide fracture (Ref 70, 71), dislocation activities, and microstructural evolution (Ref 72, 73) with molecular dynamics and finite element simulations.

While bonding and material buildup in metal matrix composites are also achieved by the general mechanisms discussed above, there can exist an additional synergistic effect when two phases are co-deposited. Such effect is of

Fig. 1 Schematics showing (a) surface activation, (b) cushioning effect of the matrix, (c) tamping effect of ceramic reinforcement, and (d) erosion in CS MMCs

particular dominance when one phase is metal, and the other is ceramic (Ref 74). In this case, impact of ceramic particles provides the so-called “surface activation” effect through (i) increasing substrate roughness by creating impressions and craters and (ii) disrupting native oxide layers and exposing clean metallic surfaces with higher metallurgical activity to subsequent impacts (Ref 25, 31, 39, 75–78). A schematic illustration of surface activation with ceramic particle impacts can be seen in Fig. 1(a). Both mechanisms enhance bonding between metallic particles. Metallic particles, on the other hand, can effectively dissipate the impact energy of ceramic particles by accommodating a significant amount of plastic deformation, shown in Fig. 1(b). They can, therefore, act as cushions for hard and non-deforming ceramic particles and provide an embedment mechanism (Ref 74). As the coating builds up, the impact of ceramic particles also provides a tamping or peening effect, which can lead to defect closure as well as enhanced metallurgical bonding in metallic phases and metal/ceramic interfaces (Ref 31, 78–81) as illustrated in Fig. 1(c). As will be discussed in the next section, there exists an optimum balance in the co-deposition of ceramic and metallic particles. A very small volume fraction of reinforcements may not fully activate the above reciprocal synergy. In contrast, too large contents of ceramic reinforcement can give rise to erosion, adversely affecting material deposition (Ref 76). Erosion, in the latter case, is activated due to an increased probability of ceramic particles impacting on ceramic particles (Ref 82–86). A schematic depicting the fracture of ceramic

particles is shown in Fig. 1(d). In CS MMCs with metallic reinforcements, the surface activation, tamping, and cushion effects (Ref 87) may or may not be present depending on the difference in mechanical properties of the two phases. If the two phases have significantly different properties, such as hardness and density, one can expect a similar synergy. The deposition behavior of CS MMCs with intermetallic reinforcement is similar to the one with metallic reinforcements as intermetallic phases are often formed during post-deposition heat treatments (Ref 88–90). In these latter cases where metallic interfaces interact with each other, chemical–physical factors can play an important role in bonding.

Deposition Efficiency and Porosity

The amount of reinforcement can significantly change the deposition efficiency and the porosity in CS MMCs. The addition of reinforcement produces a tamping/peening (Ref 91) effect on the matrix and substrate and helps retaining soft matrix particles as well as closing existing interfacial gaps and pores. As a result, an increase in reinforcement content, particularly when relatively small amounts of reinforcement are added (Ref 92), can increase deposition efficiency of the soft phase and reduce porosity. In general, the overall deposition efficiency is measured by measuring the weight of the substrate before and after the spraying process and comparing it with the weight of the powder used. Phase-specific deposition efficiencies are measured

Fig. 2 Deposition efficiencies of the metal-ceramic powder mixture versus nominal reinforcement volume fraction of various material combinations indicating an optimum reinforcement volume fraction in the range of 20–40% (Ref 93, 103, 106, 107, 148, 174)

by obtaining the volume or weight fraction of a specific phase, usually through composite coating images analysis. We have gathered the reinforcement volume fractions in powder feedstock for a variety of CS MMCs from the literature and the corresponding deposition efficiencies of the cold spray process. Figure 2 shows how deposition efficiency varies as a function of the nominal reinforcement content. The trend suggests that there exists an optimum reinforcement volume fraction ($\sim 30\%$) to achieve the maximum overall deposition efficiency. The initial increase in the deposition efficiency with increasing reinforcement content is attributed to surface activation and micro-asperities caused by the impact of ceramic particles. The micro-asperities facilitate the bonding of subsequent incoming particles (Ref 36). At higher reinforcement content, however, the impact of ceramic particles onto already deposited ceramics particles becomes predominant, and as a result, the overall deposition efficiency decreases. In fact, Fig. 2 shows that the deposition efficiency can be zero with a ceramic powder feedstock. Figure 2 also shows that the increasing–decreasing trend is not necessarily the case when non-ceramic reinforcement is added to metallic particles. The addition of a slight amount of graphene nanoplates (GNPs), for example, results in a significant reduction of the deposition efficiency in IN718-GNP coatings. The decrease in the overall deposition efficiency of 316L composite coating with the addition of Cu as reinforcement can be attributed to the metallic reinforcement being softer than the metallic matrix.

Figure 3(a) shows a cross-sectional micrograph of Al CS coating onto an Al 7075 substrate where a large number of pores denoted with the arrows can be seen. Addition of 7 wt.% Al₂O₃ particles in the feedstock as reinforcement can

significantly reduce the porosity, as shown with Fig. 3(b). The same phenomena can be observed in pure Al CS coating where porosity in the single-phase coating (Fig. 3c) is significantly decreased by the addition of 20 vol.% B₄C reinforcing particles in the feedstock (Fig. 3d). It is also interesting to note that the addition of reinforcing particles that are nominally softer than the matrix material could reduce the porosity level in CS MMCs. This is shown in Fig. 3(e) and (f), where the addition of 5% Cu particles in the feedstock as reinforcement can effectively reduce the porosity level in 316L CS coating where the gaps between the harder, less deformed 316L matrix can be filled in by the softer, highly deformed Cu phase. The three examples also show that both metallic and ceramic reinforcement can reduce the level of porosity in CS MMCs. However, at higher concentrations of reinforcement, incoming reinforcing particles will have higher probabilities of colliding with pre-deposited hard particles, resulting in an increased amount of rebounding as well as fracture, thereby reducing deposition efficiency and increasing the amount of porosity and defects (Ref 83, 93).

Effect of Reinforcement Content on Deposition Efficiency and Porosity

In Al-based CS metal matrix composites (MMCs), it was found that the addition of relatively small amounts of a variety of reinforcing particles, e.g., Al₂O₃ (Ref 79, 91, 94–96), Al-Si (Ref 97), SiC (Ref 83), and TiN (Ref 98) resulted in a significant decrease in porosity of the composite coatings and at the same time increased the deposition efficiency (Ref 83, 93). Such an increase was attributed to the dramatic tamping effect of ceramic particles on the pre-deposited Al splats (Ref 79) signified by increased flattening ratios of the splats (Ref 97). However, with a further increase in the reinforcement content to 40 vol.% and higher in the feedstock, the porosity of Al 2024-Al₂O₃ coating increased (Ref 94). The deposition efficiency of Al 5056-SiC and Al-Al₂O₃ coating decreased (Ref 83, 93) with increasing reinforcement contents due to increased interactions between hard particles, which also created increased amounts of pores and cracks.

In Cu-based CS MMCs, effects of reinforcements such as Al₂O₃, SiC, and AlCuFeB quasicrystal were studied. An increase in the volume fraction of Al₂O₃ in the powder feedstock resulted in an increase in the deposition efficiency of coatings sprayed at 0.8 MPa (Ref 99) and 3 MPa (Ref 100), and a decrease in the porosity in both low- and high-pressure cold-sprayed coatings with working pressure from 0.6 to 4 MPa (Ref 96, 99). Composite CuSn8 coatings reinforced with AlCuFeB quasicrystal (QC) presented much denser microstructures than the pure CuSn8 coating due to the tamping effect from the QC reinforcement. The

Fig. 3 A reduction of porosity can be achieved with the addition of reinforcing particles in CS MMCs. Figures on the left have higher porosity. Selected pores are shown with arrows. In (a) and (b), the addition of Al_2O_3 particles in Al- Al_2O_3 composite coating significantly reduced porosity (Ref 82); In (c) and (d), it can be seen that

B_4C reinforcement reduced CS Al coating significantly as well (Ref 150); in (e) and (f), it can be seen that addition of 5% Cu particles in CS 316L coating resulted in a reduction of porosity from $3.2 \pm 1.1\%$ to $0.9 \pm 0.3\%$ (Ref 107). Images are reproduced with permissions from Springer and Elsevier

porosity level of the CuSn8-based composite coatings decreases from ~ 2.6 to below 0.25% with increasing the content of the QC phase from 19.5 to 57.6 vol.% in the feedstock (Ref 101). The deposition efficiency of the Cu-CNT-SiC composite coatings was shown to decrease from 20 to 12% when 5 vol.% of CNT was added to pure Cu. The deposition efficiency continued to decrease to 4% when 10 vol.% SiC was added but increased to 19% as SiC

content was increased from 10 to 20 vol.% in the feedstock (Ref 102).

An opposite trend, i.e., a decrease in deposition efficiency from 55 to 22% and a decrease in porosity from 3.8 to 1.1% with an increase in reinforcement content from 0 to 36.2 vol.% in the feedstock, has been reported in the case of Ni-based coatings reinforced with tungsten carbide (WC) particles in high-pressure cold spray at 4 MPa. That

was attributed to the impact-induced fragments of WC particles found in the coating, which was shown to prevent intimate contact between Ni particles (Ref 103, 104). However, a recent study with low-pressure cold spray showed reduced porosity with increased WC content in Ni-CrC coatings (Ref 105). Similar to Ni-WC in high-pressure cold spray, it was found that the deposition efficiency of the IN718-GNPs composite coatings decreased from 84 to 2% with the increase in the GNP content from none to 1%. The authors argued that the presence of the GNPs prevented the occurrence of adiabatic shear instability and particle bonding (Ref 106). The addition of BN particles to Ni, similar to WC, was shown to be effective in decreasing the porosity level (Ref 96).

In CS MMCs made of stainless steel, Cu, and Tribaloy powders, highly deformed Cu particles were shown to fill the gaps between the less deformed stainless steel and Tribaloy particles, resulting in lower porosities in the composite coatings compared to the single-phase stainless steel coating (Ref 107). The compositions of the deposits significantly differed from the initial mixtures, which could be explained by differences between deposition efficiencies of each phase. Cu had higher phase-specific deposition efficiency than stainless steel, resulting in an increased Cu content in the coating. However, the overall deposition efficiency of the coating decreased as higher amounts of Cu were added. The deposition efficiency of the Tribaloy particles was shown to depend on the particle type they impacted strongly. The probability of retaining Tribaloy particles on copper or steel particles was significantly higher than on Tribaloy particles (Ref 107).

In other material classes such as magnesium and cobalt, studies of porosity and deposition efficiency have been conducted too, but to a lesser extent compared to the typical matrix materials in CS MMCs (Ref 96, 108). In Mg-based coating (AZ91D reinforced with SiC), the reinforcement content in the coating was shown to increase up to 51 vol.% as the content in the feedstock powder was increased to 60 vol.% (Ref 108). The same increasing trend was found for the deposition efficiency, albeit only up to 30 vol.% SiC in the powder feedstock. Beyond 30 vol.% SiC, the deposition efficiency started to decrease as the probability of rebounding of incoming particles increased with the number of hard particles increasing in pre-deposited layers (Ref 108).

Effect of Heat Treatment on Porosity

Heat treatment (HT) can significantly change the coating microstructure by recovery, grain growth, recrystallization, and formation of intermetallic phases. It can be an effective method to improve bonding and decrease porosity (Ref 90). In B₄C-reinforced Al coatings deposited on 6061-T6

substrates and heat-treated under high-purity Ar environment for 4 h, HT at 400°C resulted in a decrease in porosity from 3.9% in the as-sprayed condition to 1.9% (Ref 109). Further increase in HT temperature to 500°C did not yield further decrease in porosity since inter-splat crevices and triple junctions/pores were either completely healed out or reduced in size (Ref 109). For Al₂O₃-reinforced A380 coating, on the other hand, a slight increase in porosity was reported after heat treatment (Ref 110). The increase in porosity was attributed to spheroidization and augmentation of the smaller pores and formation of relatively large pores during the heat treatment.

The in situ reaction of metallic phases during heat treatment is a processing strategy broadly adopted for the syntheses of metallic/intermetallic CS coatings, particularly for Ni-Al (Ref 87), Ti-Al (Ref 111), Fe-Al (Ref 90, 112), and Ni-Ti (Ref 89). In CS Ni-Ti composite coating, vacuum annealing at 700, 800, and 900°C for 2 h was used to produce a uniform distribution of intermetallic phases. However, coating porosity increased rapidly at elevated temperatures due to the Kirkendall effect (Ref 89). Formation of intermetallic phases was also reported in CS TiAl₃-Al coating, along with an increase in porosity, since the formation of TiAl₃ intermetallics was accompanied by volume expansion (Ref 111).

Effect of Processing Parameters on Deposition Efficiency and Porosity

In addition to powder feedstock-related parameters such as the reinforcement material, content, size, and morphology, cold spray processing parameters such as gas temperature, pressure, propelling gas type, standoff distance, as well as spraying nozzle type, material, and scan speed provides an additional space for the design of CS MMCs with desired performance. Higher propelling gas and preheating temperatures lead to increased deposition efficiencies and reduced porosities in CS MMCs by inducing thermal softening, particularly in metallic particles, and/or by enabling higher impact velocities (Ref 11, 113). What is more, higher gas temperatures were shown to improve the retention of the reinforcement in the coatings due to greater deformation of metallic particles and enhanced metallic bonding between the deformed splats (Ref 114).

It is well established that higher propelling gas pressure leads to elevated impact velocity and momentum of the particles (Ref 114). A series of studies on different material systems have found that increased propelling gas pressures lead to an increase in deposition efficiency, a decrease in porosity, more retention of reinforcing particles, and an increase in bonding strength. In particular, reinforcement retention can be improved due to increased particle momentum that helps embedment. In CS Ti/TiC coating,

deposition efficiency and homogeneity of the coating were found to increase with increasing deposition pressure from 3.5 to 4 MPa (Ref 115). In CS Maraging steel 300 (MS300) reinforced with WC, the retainability of WC particles increased from 78 to 85% with an increase in propelling gas pressure from 4 MPa to 5 MPa (Ref 116). Increasing impact velocity was also shown to lead to lower porosity levels in Al_2O_3 -reinforced Cu and Al MMCs (Ref 96, 117).

In summary, there exists a general trend that smaller amounts of reinforcement tend to increase the overall deposition efficiency of the powder blend, while larger amounts of reinforcement present a detrimental effect. Porosity and defects tend to decrease with the initial increase in the reinforcement content. However, at higher reinforcement contents, the benefit can be reduced due to fractured reinforcement particles resulted from impacts between the hard particles. Post-spray treatments such as heat treatment and friction stir processing can alter coating porosity and microstructure, often leading to a reduction in the number of defects, the formation of intermetallic compounds, and a more uniform microstructure through diffusion or mechanical blending.

Elastic Deformation

In general, cold spray coatings exhibit an anisotropic microstructure. The deposition process involves the high-speed impact of the particles onto a substrate or a pre-deposited layer, resulting in flattening of the particles, as well as compaction and tamping of the pre-deposited layer. As a result, the microstructure of CS coatings in the plane parallel to the substrate surface is different from that in the plane normal to it where higher densities of dislocations and grain boundaries are formed (Ref 118). In addition, due to influences of later arriving particles on the pre-deposited layers, differences in microstructure can occur at various depths. The degree to which such anisotropic microstructure could lead to elastic anisotropy has been the subject of a few studies (Ref 119–122). Resonant ultrasound spectroscopy (Ref 119) and depth-sensing indentation (Ref 120) measurements on Al, Cu, Ni, Ti, and Ta coatings have shown only a slight deviation from perfect elastic isotropy in contrast to thermal spray counterparts (Ref 121, 122). The same approximately isotropic behavior, albeit to a lesser degree compared to the single-phase counterpart, was reported for CS MMC coatings (Ref 118). This can be regarded as an advantage of cold spray MMC materials over fiber or laminate-reinforced composites that show strong anisotropic behavior.

Elastic deformation of CS MMC deposits occurs when the constituent phases are proportionally sharing the load, without plastic deformation or decohesion that can lead to

load transfer and permanent damage of the coating. The elastic modulus of composite coatings depends on the volume fraction of the reinforcing particles. There are a few theoretical frameworks developed to predict the elastic modulus of composites with the rule of mixture (ROM) being the simplest one. Using an iso-strain (Voigt) model that assumes that reinforcement and matrix were fibers aligned along the loading direction subject to the same strain, an upper bound estimate of the elastic modulus is given by Eq 1:

$$E_{\text{upper}} = (1 - V_P)E_M + V_P E_P \quad (\text{Eq 1})$$

where V_P is the volume fraction of the reinforcing particles, and E_P and E_M are elastic moduli of the particle and the matrix, respectively.

To account for the particulate-reinforced nature of CS MMCs, one of the most widely used models is the Hashin–Shtrikman (H–S) model (Ref 123). The H–S model (Eq 2–6) assumes an isotropic aggregate based on the variational principle of linear elasticity:

$$K_{\text{upper}} = K_P + (1 - V_P) \left[\frac{1}{K_M - K_P} + \frac{3V_P}{3K_P + 4G_P} \right]^{-1} \quad (\text{Eq 2})$$

$$K_{\text{lower}} = K_M + V_P \left[\frac{1}{K_P - K_M} + \frac{3(1 - V_P)}{3K_M + 4G_M} \right]^{-1} \quad (\text{Eq 3})$$

$$G_{\text{upper}} = G_P + (1 - V_P) \left[\frac{1}{G_M - G_P} + \frac{6V_P(K_P + 2G_P)}{5G_P(3K_P + 4G_P)} \right]^{-1} \quad (\text{Eq 4})$$

$$G_{\text{lower}} = G_M + V_P \left[\frac{1}{G_P - G_M} + \frac{6(1 - V_P)(K_M + 2G_M)}{5G_M(3K_M + 4G_M)} \right]^{-1} \quad (\text{Eq 5})$$

$$E = \frac{9K}{1 + \left(\frac{3K}{G} \right)} \quad (\text{Eq 6})$$

where K and G are the bulk and shear moduli of the composite. The subscripts “upper” and “lower” refer to the upper and lower bound estimates, and “M” and “P” refer to matrix and particle, respectively.

Mura’s model (Ref 124), described with Eq 7–8, has also been proposed to estimate the elastic modulus of composite materials. In Mura’s model, reinforcement geometry is assumed to be spherical, and only a relatively small volume fraction (< 25%) of reinforcement is considered:

$$K = K_M \left[1 + \frac{V_P(K_M - K_R)}{K_M + \frac{1}{3}(K_R - K_M) \frac{1+v_M}{1-v_M}} \right]^{-1} \quad (\text{Eq 7})$$

$$G = G_M \left[1 + \frac{V_P(G_M - G_R)}{G_M + 2(G_R - G_M) \frac{4-5\nu_M}{15(1-\nu_M)}} \right]^{-1} \quad (\text{Eq 8})$$

where ν is the Poisson's Ratio, and K and G can then be used in Eq 6 to calculate the elastic modulus of the composite material. In order to address Mura's model's deficiency in calculating the elastic modulus of the material at higher volume fractions of reinforcement ($> 50\%$), the model proposed by Kroner (Ref 125) and Budiansky (Ref 126) yields to Eq 9–11 that when solved together, can be used to determine the elastic modulus:

$$K = K_M + \frac{V_P K (K_R - K_M)}{K + \frac{1}{3}(K_R - K) \frac{1+\nu}{1-\nu}} \quad (\text{Eq 9})$$

$$G = G_M + \frac{V_P G (G_R - G_M)}{G + 2(G_R - G) \frac{4-5\nu}{15(1-\nu)}} \quad (\text{Eq 10})$$

$$\nu = \frac{3K - 2G}{2(G + 3K)} \quad (\text{Eq 11})$$

Again, elastic modulus can be obtained using Eq 6 once Eq 9–11 are solved for K and G .

It is also worth noting that in addition to the theoretical models described above, finite element simulations can be used to predict the elastic modulus of the composite material (Ref 127) by a proper choice of representative volume elements. However, both theoretical and simulation models fail to account for defects such as pores, fractured particles, and poor bonding, as well as possible anisotropy within cold-sprayed MMCs.

To assess the applicability of these models, measured elastic moduli for Al-SiC cold-sprayed coatings were collected from the literature (Ref 128) and plotted as a function of the SiC content. Theoretical predictions described

above were superimposed on the same plot. Figure 4 shows that the elastic modulus of CS MMC increases with an increase in the reinforcement volume fraction, but the ROM significantly overestimates the increase in the case of Al-SiC MMCs. A similar increase in elastic modulus at higher volume fractions of reinforcement was also noticed in Al-Cu (Ref 129) composite coatings. We also note that the experimental measurements are below the lower bound to all theoretical predictions, including the lower bound of the H-S model. This can be attributed to the presence of poorly bounded interfaces and porosity that influenced the stiffness of the composite material.

In addition to the reinforcement content, particle size and shape can also affect elastic moduli of MMC coatings. Particle size and shape can influence the reinforcement content in the coating even when all other spraying conditions are the same (Ref 130). Concerning particle size, cold-sprayed Ni-Ni₃Al deposited with the Ni₃Al particle size less than 45 μm was found to show a 12% higher elastic modulus as compared to the same material deposited with Ni₃Al particles larger than 45 μm (Ref 131). A decrease in mechanical properties with an increase in particle size is attributed to lower impact velocities achieved during spraying of larger particles, which in turn results in weaker interlocking/bonding between deformed particles (Ref 131). However, in another study of a CS Ni-FeSiAl soft magnetic composite coating, a 10–15% increase in elastic modulus of the composite coating was obtained by increasing reinforcing particle size from $d_{0.5} = 40$ to 56 μm (Ref 132). The improvement was attributed to the enhanced peening effect of the rebounded large particles during deposition.

Regarding reinforcing particle shape, indentation measurements on A380/Al₂O₃ composite coating with different Al₂O₃ powder morphologies (Ref 133), showed the composite with irregular Al₂O₃ to have higher hardness/elastic modulus, compared to the composite with spherical Al₂O₃ reinforcements. The elastic modulus of the composite made with a mixture of spherical and irregular reinforcements was shown to lie between the two. The difference in elastic modulus due to reinforcement shapes was attributed to a higher amount of reinforcement content that was retained during the spraying process. The irregular-shaped reinforcing particles were found to impose higher constraints against the deformation of neighboring splats.

In conclusion, theoretical predictions can be used to estimate the elastic modulus of cold-sprayed MMCs. However, due to the shortcoming of not accounting for defects and porosities, predicted moduli are in general higher than the actual ones. Predictions do not account for anisotropy of CS MMC coatings which leads to a higher elastic modulus on the cross-sectional plane. Predictions

Fig. 4 Predicted and measured elastic moduli of Al-SiC CS composite coatings as a function of reinforcement volume fraction (Ref 128)

also do not account for particle size and shape which have case-specific effects on coating elastic properties.

Plastic Deformation

Indentation Hardness

It is well established that the hardness of cold spray coatings is generally higher than those of both powder feedstock materials and bulk counterparts (Ref 112, 134–136). This is rooted in the work hardening phenomenon as a result of severe plastic deformation of powder particles during deposition. The high-velocity impact of powder particles generates large plastic strains of the order of ~ 1 (up to 10) and strain rates up to 10^9 s^{-1} , particularly in the interfacial regions, in a short period (~ 10 to $\sim 100 \text{ ns}$) (Ref 47, 48). A large density of dislocations is generated to accommodate plasticity which can organize themselves into subgrains. The adiabatic nature of the rapid deformation causes local temperature rise, which in turn gives rise to dynamic recrystallization (Ref 137–141). If the plastic strain and temperature exceed critical values, the subgrains rotate and recrystallize into refined grains (Ref 142), which are harder than the original grains due to the Hall–Petch effect (Ref 143). A combination of dislocation-based activities (Ref 98, 102, 144) and grain refinement (Ref 114, 118, 144) is responsible for the higher hardness of cold spray coatings compared to the original powder feedstock. Repeated impacts of the reinforcing (usually harder) particles further promote plastic deformation of the matrix metallic material through the tamping effect and

provide extra work hardening. Figure 5(a) shows a transmission electron microscope (TEM) image of the interface between an Al particle and an Al_2O_3 particle in a cold spray composite (Ref 118). Nanocrystalline grains observed at the Al side near the interface indicate a significant level of plastic deformation in the metallic phase as a result of being impacted by the ceramic neighbor which does not show any evidence of plasticity. The resultant increase in dislocation density in the metallic phase and possible grain refinement such as shown in Fig. 5(b) can contribute to the overall hardening of the material.

In addition to grain-refinement-related strengthening mechanism, uniform distribution of the reinforcements in the coating constrains the deformation of the metallic particles and contributes to the hardening through a dispersion strengthening mechanism. Figure 5(b) shows an example of a uniform dispersion of BN particles in a NiCrAl alloy matrix processed via cold spray (Ref 145). The BN particles which are in intimate contact with the matrix do not deform when the material is loaded. BN particles provide hardening since a larger stress is necessary to expand a loop of dislocation between them. The sub-micron distance between BN particles, in this case, is beneficial as the flow stress is inversely related to the reinforcing particle distance. A comparison of the hardness of Al5356/TiN composites in the as-sprayed and heat-treated conditions suggests that the contribution of dispersion strengthening mechanism to the overall hardening is greater than that of tamping effect (Ref 146).

Hardness, along with other mechanical properties of MMCs such as strength and Young's modulus, can be, to the first order, predicted using ROM with two generalized

Fig. 5 TEM image of (a) metal-ceramic interface in Al- Al_2O_3 composite coating and (b) cross-section of BN-reinforced NiCrAl composite coating (Ref 118, 145). Images are reproduced with permission from Elsevier

assumptions of iso-strain and iso-stress conditions (Ref 147). Iso-strain (Voigt) model assumes that reinforcement and matrix are subjected to the same strain, and thus yield to an upper bound for hardness in Eq 12. Iso-stress (Reuss) model assumes that stress in the reinforcement is equal to the stress in the matrix and yields to a lower bound for hardness of the composite as shown with the inverse ROM in Eq 13:

$$H_{\text{upper}} = V_P H_P + V_M H_M \quad (\text{Eq 12})$$

$$H_{\text{lower}} = (V_P/H_P + V_M/H_M)^{-1} \quad (\text{Eq 13})$$

where V_P and V_M represent volume fractions of reinforcement and matrix, while H_P and H_M are hardnesses of the constituent phases, respectively. However, it is worth noting that the above equations only account for load sharing in fiber-reinforced composites arranged in axial or transverse loading directions and does not represent the particulate nature of reinforcements in CS MMCs. The effects of pores and defects on the load-bearing capacity of the MMC are not accounted for in Eq 12–13 either.

Figure 6 shows the lower bound and upper bound estimations of the hardness for Al–Al₂O₃ composite coatings, along with the experimental measurements from literature (Ref 93, 148). We highlight that the hardness of bulk pure Al (~ 15 HV) is lower than the hardness of pure Al coating (~ 40 HV), due to intensive work hardening during the spraying process. We have used the latter for the theoretical predictions. In Fig. 6, both theory and experiment show that the addition of reinforcement results in an increase in the hardness of CS MMCs. Reinforcement volume fractions in the coating are limited to ~ 45% in this case due to the relatively lower deposition efficiency of ceramic particles during the spraying process. We note that measured hardness values are all within the region defined

Fig. 6 Predicted and measured CS Al–Al₂O₃ composite coating hardness as a function of reinforcement volume fraction (Ref 38, 93, 148)

by the upper and lower bounds. The hardness values measured for Al coatings reinforced with angular Al₂O₃ reinforcement are closely following the trend predicted by the lower bound. The lower bound prediction, however, underestimates the hardness of the composite coating, as it does not take into account the work hardening of metallic phases during cold spray deposition. The hardness values for Al coatings reinforced with spherical Al₂O₃ are closer to the upper bound prediction. This is due to lower deposition efficiency in the latter case which led to a higher number of impacts and reboundings of ceramic particles and consequently a higher level of plastic deformation in the Al phase (Ref 93, 148). It is also interesting to note that the addition of nanoscale Al₂O₃ as reinforcement results in higher hardness of the composite coating as compared to the addition of microscale Al₂O₃. Al₂O₃ nanoparticles, initially in the form of agglomerated powder in the feedstock, were shown to get effectively dispersed in the matrix during deposition. It is their decreased interparticle distances, compared to the microscale counterpart, that provides the composite coating with higher hardness through the dispersion strengthening mechanism (Ref 38).

Effect of Reinforcement Content on Hardness of CS MMCs

In Al-based composite coatings, the aforementioned general trends have been widely reported with various types of ceramic reinforcements. Hardness of Al–Al₂O₃ composite coatings increased from ~ 45 HV to ~ 110 HV with increasing the Al₂O₃ content in the feedstock from 0 to 100 wt.% (Ref 93). However, the hardness of A380/Al₂O₃ coating first increased from 105 HV to ~ 140 HV as ceramic content increased from 0 to 30 wt.% and then decreased to ~ 125 HV with 40 wt.% reinforcement in the feedstock (Ref 95). The degree of fragmentation of the Al₂O₃ particles in the latter case increased with the increase in Al₂O₃ content and resulted in higher porosity and consequently lower hardness of the composites with high ceramic contents (Ref 95). A general increase in hardness with the addition of a variety of reinforcements including Al₂O₃ (Ref 91, 149), Al–Si (Ref 97), Cu (Ref 129), B₄C (Ref 130, 150), SiC (Ref 84, 128, 150, 151), TiN (Ref 98), and TiB₂ (Ref 114) particles has been reported with various Al-alloy compositions.

Similar trends have also been reported in Ni-based coatings. Effect of various types of reinforcement including Ni₃Al (Ref 88), WC (Ref 103, 104, 152), Co (Ref 152), and IN718 (Ref 153) has been studied. In all these cases, the addition of reinforcing particles led to an increase in the hardness of composite coatings. The largest gain in the hardness of Ni-based coatings was achieved with the addition of WC reinforcements. One special case was that

the microhardness of the graphene nanoplate (GNP)-reinforced IN718 composite coatings was measured to be $\sim 14\%$ lower than that of the pure IN718 coatings (Ref 106). The reduction in hardness was attributed to the poor bonding between GNP and IN718 particles.

In Cu-based coatings, it was reported that the addition of Al_2O_3 (Ref 99, 100, 154), carbon nanotubes (CNT) (Ref 102), SiC (Ref 102) (Ref 154), AlCuFeB quasicrystal (QC) (Ref 101), Cr (Ref 155), Ni (Ref 156, 157), Zn (Ref 157), and WC (Ref 158) reinforcing particles leads to an increase in hardness. However, Cu-MoS₂ (Ref 158, 159) composite coating presented a lower hardness than pure Cu coatings, due to MoS₂ being softer than Cu.

In Ti-based composite coatings, it was found that the hardness increased in Ti-13.8 vol.% TiC compared to pure Ti due to relatively uniform dispersion of the hard TiC particles (Ref 160). However, the addition of more TiC particles in Ti-33.4 vol.% TiC did not further improve the hardness due to decreased bonding between Ti particles as well as fragmented and cracked TiC particles (Ref 160). Hardness of the Ti6Al4V-23 vol.% TiC composite coating also increased to 273 ± 19 HV compared to the unreinforced Ti6Al4V coating with a hardness of 191 ± 12 HV (Ref 161).

In Fe-based composite coatings, addition of 20 wt.% Ni-coated SiC particles resulted in a 17.8% increase in the microhardness of 316L CS MMCs compared to the unreinforced coating (Ref 162). In CS MMCs deposited with mixtures of stainless steel 316L, 10 wt.% copper, and Tribaloy T-700 powders, increasing Tribaloy particles content to 10, 30, and 60 wt.% resulted in increase of the coating hardness by 8, 24, and 28% compared to the 316L-10%Cu coatings. The addition of the copper particles to the powder feedstock, on the other hand, resulted in a lower hardness of the CS composite due to copper being the softest of the three phases (Ref 107).

The hardness gain in other types of composite coating based on magnesium and ceramic matrices has been studied as well. In SiC-reinforced AZ91D coating (Ref 108), the microhardness of the composite coating increased from 150 to ~ 200 HV_{0.3} as the volume fraction of SiC increased from 19 to 51%. In Al_2O_3 -CNT composite coatings, well-dispersed 2 wt.% CNTs within the Al_2O_3 matrix led to a significant fourfold increase in hardness of the composite coating compared to pure Al_2O_3 . Further increase in CNT to 4 wt.% did not result in significant improvement. The improvement in hardness in Al_2O_3 -CNT composite coating is due to a load sharing phenomenon that is activated by the CNTs bridging the crack surfaces (Ref 163).

We have gathered indentation hardness and reinforcement volume fraction measurements for different CS MMCs from the literature and populate them in the plot

shown in Fig. 7. We highlight that the reinforcement volume fraction in this plot is measured from CS coatings, not from powder feedstocks. Al-based, Cu-based and Ni-based CS MMCs are the widely studied material systems compared to Mg-, Ti-, and Fe-based systems. We note an overall increasing trend in the hardness of CS MMCs with an increase in the reinforcement volume fraction. To the first order, the trend can be approximated as a linear increase, but with different rates depending on the material system and possibly spraying conditions. Among the widely studied material systems, Ni-based composite coatings present significantly higher hardness values compared to Cu- and Al-based MMCs. Covering a wider range of hardness and reinforcement volume fraction, Ni-based coatings also offer more flexibility in terms of CS MMC design for a desired hardness. Cu-based coatings offer an intermediate hardness level but with the reinforcement volume fractions mainly limited to the lower end. While the hardness of Al-based CS MMCs is lower than the Cu-counterparts at similar reinforcement contents, their ability to accommodate higher reinforcement volume fractions can be exploited to achieve comparable hardness values to the Cu-based MMCs. The few data points for other material systems indicate that the hardness of Mg-based coatings is close to that of Al-based ones, while the hardness of Fe-based and Ti-based coatings is more similar to that of Ni-based coatings. We also note that Cu-reinforced SS 316L coating is an exception to the general trend of Fig. 7. The decrease in hardness with an increase in the volume fraction of Cu in this latter case is attributed to the reinforcement being softer than the matrix.

Effect of Particle Size and Morphology on Hardness of CS MMCs

In addition to the volume fraction of reinforcing particles, it has been shown that particle size and morphology can also influence the hardness. Microhardness tests on A380/ Al_2O_3 composite coating showed that the coating with irregular Al_2O_3 has a higher hardness (~ 145 HV_{0.3}), compared to the hardness of the composite reinforced with spherical Al_2O_3 (~ 127 HV_{0.3}). However, both composite coatings have higher hardness than pure A380 coating (~ 119 HV_{0.3}), which lacks the tamping effect from ceramic particles (Ref 133). The composite made with a mixture of spherical and irregular reinforcements was shown to have intermediate hardness of ~ 137 HV_{0.3}. The reason that irregular Al_2O_3 particles resulted in significantly higher hardness than the spherical counterpart is due to a large amount of retained irregular Al_2O_3 particles in the coating. WC powders with plasma spheroidized cast and agglomerated and sintered morphologies were used to produce Ni-WC MMCs (Ref 37). Higher hardness in Ni-

Fig. 7 Hardness of CS MMCs versus reinforcement volume fraction in the coatings classified based on the matrix material. Generally, an increase in hardness can be seen with an increase in reinforcement

content (Ref 36, 37, 42, 83, 98, 100, 101, 106–108, 148, 152, 154, 174, 213–216)

cast WC was found compared to Ni-aggregate WC coatings. This was attributed to significantly lower mean free paths between WC particles in Ni-cast WC. As in Ni-cast WC, ultrafine ($< 1 \mu\text{m}$) WC fragments caused by severe fragmentation upon impact were dispersed in the coating (Ref 37). Besides, the hardness of the cast WC particles is also higher than that of aggregate WC, contributing to the overall higher hardness. From the above-mentioned examples, it is important to realize that details of manufacturing processes can influence various material properties. As a result, for CS MMCs reinforced with irregular particles, one needs to consider additional aspects that can influence mechanical performances of the coating.

In terms of particle size, in CS Ni-FeSiAl soft magnetic composite coating, higher deformation of FeSiAl particles and higher microhardness (10–15%) of the composite were obtained by powders with a larger size ($d_{0.5} = 56 \mu\text{m}$ compared to $40 \mu\text{m}$) due to the enhanced peening effect of the rebounded large particles (Ref 132). In another study, however, $\sim 2.5\%$ higher hardness for the coatings deposited with Ni_3Al particles smaller than $45 \mu\text{m}$ was obtained as compared to the coating sprayed with particles larger than $45 \mu\text{m}$ (Ref 131). The decrease in hardness with an increase in particle size was attributed to lower velocity during spraying of the larger particles, resulting in a weaker mechanical interlocking between deformed particles. It was also reported that microhardness values were independent of the Al_2O_3 particle size in $\text{Cu-Al}_2\text{O}_3$ composite coating (Ref 100).

Fig. 8 Heat treatments lead to reduced hardness in Al-TiN MMC coating (Ref 146). The comparison shows that in this case, the hardness gain by dispersion strengthening is greater than that by work hardening. Image is reproduced with permission from Elsevier

Effect of Post-spray Heat and Mechanical Treatments on Hardness of CS MMCs

While the gain in hardness due to work hardening can be completely relieved by heat treatment, the gain in hardness due to dispersion strengthening is maintained in CS MMCs. This has been confirmed by comparing the microhardness of the TiN-reinforced Al5356 coating before and after heat treatment at various temperatures with the hardness of the unreinforced coating in Fig. 8 (Ref 146). It is interesting to note the contribution of dispersion

strengthening to the overall hardening of CS MMC, in this case, is larger than the contribution of work hardening.

Several studies reported a decrease in the hardness of CS MMC coatings after heat treatment due to the removal of the cold work effect and grain growth (Ref 39, 109, 128, 164). Grain growth occurs due to the existence of a thermodynamic driving force to reduce the internal energy of the material, which can be achieved by reducing the total area of grain boundary while heat treatment is applied. However, due to a reduction of grain boundary in the coating, the effect of Hall–Petch strengthening is reduced (Ref 143). In B_4C/Al coatings heat-treated at 200, 300, 400 and 500°C under high-purity Ar environment for 4 h, increase in HT temperature up to 500°C resulted in a continuous decrease in coating hardness from 58 ± 2.8 in the as-sprayed condition to 35 ± 1.3 $HV_{0.2}$ (Ref 109). The same trend was found in the 20 vol.% cBN–NiCrAl coatings where the hardness decreased from $\sim 1063 \pm 67$ HV in the as-sprayed condition to 997 ± 43 HV after heat treatment at 750°C for 5 h (Ref 164). In heterogeneously structured WC–10Co coatings, no significant change in the hardness of WC reinforcing particles was noticed after annealing at 900°C for 5 h. However, a slight decrease in the overall hardness of the coating was observed and attributed to recovery, recrystallization, and grain growth of the Co phase (Ref 43). Heat treatment of Al–SiC CS MMCs in vacuum and air at 400°C for 4 h resulted in a 20 to 50% decrease in hardness, respectively (Ref 128). Heat treatment in air leads to oxidation at the inter-splat boundary region which may have hindered the complete bonding of the splats.

An increase in hardness after heat treatment at moderate temperatures can also be achieved as a result of enhanced inter-splat bonding and metallurgical bonding, e.g., formations of intermetallics, in CS MMC coatings (Ref 90, 111). However, in most cases, it was shown that excessive annealing temperatures result in a decline in hardness due to grain growth and removal of the cold work effect (Ref 90, 116). In CS $TiAl_3$ –Al composite coatings, while the average microhardness of the Al and Ti phases was 69 and 154 HV in the as-sprayed condition, respectively, the in situ reaction of Al and Ti during heat treatment led to a significant increase in the hardness to 525 HV in the intermetallic phase (Ref 111). The as-sprayed FeAl/ Al_2O_3 coating exhibited a hardness of about 600 $HV_{0.1}$, which slightly increased after annealing between 300 and 500°C for 5 h (Ref 90). The microhardness, however, decreased with annealing temperature further increasing beyond 500°C where phase transformation and recrystallization were activated. The microhardness of the deposit annealed at a temperature of 1100°C was only two-third of the microhardness in the as-sprayed condition (Ref 90). Increased microhardness is also achieved after the solution

and age hardening treatments in CS WC–MS300 coating (Ref 116). However, samples with higher treatment temperatures achieved lower hardness due to coarsened grain size offsetting precipitation hardening (Ref 116). The microhardness of oxidized CS Ni– Al_2O_3 coatings after vacuum heat treatment at a range of temperatures (650–850°C) was found to be comparable to the as-received condition (Ref 165). In this case, the oxidation process relaxed compressive stresses, and the formation of NiO in the coating counteracted the reduction in hardness.

In contrast to the initial increase in hardness followed by a later decline with increasing annealing temperature discussed above, heat-treated Ag/SnO₂ CS MMCs showed an opposite trend. The hardness decreased from 112 ± 3 HV in the as-sprayed condition to 76 ± 2 HV after annealing at 600°C, followed by an increase to 110 ± 3 HV after annealing at 850°C. In this case, the initial decline in the hardness was attributed to the release of residual stresses and recrystallization of silver particles as well as the transverse cracks in the coating–substrate interface. The increase in hardness at higher annealing temperature, on the other hand, was attributed to residual stress relaxation and simultaneously densification of the coating (Ref 166).

A common post-spray mechanical treatment for cold spray coating is friction stir processing (FSP) (Ref 167–170). During FSP, the frictional heat causes the materials to soften without melting and thus accommodate a high level of plastic deformation and mixing (Ref 169, 170). FSP of CS AA2024/ Al_2O_3 was shown to break the Al_2O_3 reinforcing particles into smaller particles and improve reinforcement dispersion in the AA2024 matrix (Ref 171). As the severity of the FSP process increases with increasing tool rotation speed, from Fig. 9(a), (b), (c) and (d), it is noticed that the Al_2O_3 fragments get finer and their distance decreases. Meanwhile, the dissolution of the Guinier–Preston Bagaryatskii (GPB) zone and the formation and coarsening of the high-temperature metastable $S(S')$ phase were shown to occur during FSP. FSP was shown to transform a two-phase microstructure in CS Ni–Ti composite coating in the as-sprayed condition (see the SEM micrograph and the corresponding EDS maps in Fig. 9e and f) into severely deformed and alloyed microstructure, shown in the SEM/EDS images in Fig. 9(g) and (h) (Ref 89). Ni–Ti intermetallic compounds were found in the alloyed layer, on the top surface. Cross-sectional observation of the coating after FSP (Fig. 9i) shows that a deformed layer, shown with the black arrow, exists beneath the alloyed top surface. While the alloyed layer on the top is homogenous, the deformed layer is characterized by heavily elongated particles along the rotation direction of the tool (Ref 89).

As a post-spray treatment to CS MMCs, FSP can lead to a significant increase in coating hardness due to

Fig. 9 AA2024/Al₂O₃ CS MMC in as-sprayed condition (a) and friction stir-processed (b-d). Friction stir tool rotation speed was increased from (b) to (d) where changes in the particle refinement degree, particle dispersion as well as interparticle spacing can be observed (Ref 209). SEM micrograph (e) and EDS maps (f) show the surface of as-sprayed Ni-Ti coating, where large Ni and Ti particles are present. After FSP, an alloyed layer of Ni-Ti, along with elemental mixture, and intermetallic formation occurred as shown in the SEM micrograph (g) and EDS map (h). A cross-sectional micrograph of the FSPed coating (i) shows an alloyed layer on the top and a deformed layer on the bottom. The former is characterized by the homogeneous layer on the top, while the latter presents heavily elongated particles along the rotation direction of the tool, as marked by the arrow (Ref 89). Images are reproduced with permission from Elsevier

microstructural and morphological refinement as well as improved mixing and bonding. After FSP, the hardness of AA2024/Al₂O₃ MMCs increases from ~ 125 to 145 HV due to the refinement of Al₂O₃ particles (Ref 171). The microhardness of the FSPed Ni-Ti coating significantly increased to 1003 ± 65 HV, about 4.5 times compared to the as-sprayed coating. For WC-CoCr MMC, post-spray FSP has resulted in a $\sim 120\%$ increase in the average hardness compared to the as-deposited coating. This increase is attributed to the WC particle refinement and the reduction in the reinforcing interparticle distance (Ref 172).

Effect of Processing Parameters on Hardness of CS MMCs

In general, higher deposition/preheating temperatures result in lower hardness for the CS MMC coatings. The microhardness of Al5056-SiC composite coatings was shown to slightly decrease with the gas temperature increasing from 400 to 600°C (Ref 83). The trend was found to be persistent in a wide range of reinforcement content from 0 to 60 vol.%. As particle preheating temperature increased from 25 to 500°C, the microhardness of Ni-FeSiAl composite coating decreased from ~ 330 to ~ 240 HV_{0.3} due to thermal softening (Ref 173). Thermal softening in this case reduced the hardness of the matrix more significantly than the hardness of the reinforcement. As a result, flattening of reinforcing particles was reduced.

Higher propelling gas pressure, unlike temperature, usually leads to increased hardness in CS MMCs due to a stronger work hardening effect during the deposition process. As an example, about a twofold increase in particle velocity resulted in about the same twofold increase in the microhardness of NiCrAl-BN and Ti-TiAl₃ CS MMCs (Ref 174, 175). In addition, the effect of higher momentum on the hardness of the MMC coatings can be high enough to compensate for the lower hardness of the initial powder feedstock, as exemplified by a comparison of B₄C and WC as reinforcement added to Ni coatings. While B₄C reinforcing particles are much harder than WC, Ni-WC coating showed similar hardness to Ni-B₄C coating due to higher momentum and tamping effect of WC particles (Ref 174).

In summary, hardness, as a widely studied material property, can be predicted with the rule of mixtures to a relatively better accuracy when compared with elastic modulus with the same framework. An increase in reinforcement content generally leads to an overall increase in coating hardness as long as the reinforcement is harder than the matrix. Particle size and shape can have dual effects on coating hardness and should be studied on a case by case basis. Heat treatment, while relaxing the intense cold work effect, preserves the dispersion strengthening in CS MMCs

and can lead to the formation of intermetallic compounds with certain material systems. As a result, it is often found that heat treatment can slightly decrease or even increase coating hardness. However, treatment conditions such as temperature and time should be carefully studied on a case by case basis to achieve optimal results for a particular coating. Post-spray mechanical treatment such as friction stir processing can significantly increase coating hardness by refining the reinforcing particles and matrix grain size as well as enhancing the dispersion strengthening effect.

Yield Strength, Tensile Strength, and Ductility

In addition to being a potent coating technology, cold spray can be used for near-net-shape and additive manufacturing (Ref 109, 154, 176, 177). Cold spray demonstrates a lower tendency of delamination compared to thermal counterparts, and as a result, can be used to manufacture bulk materials and components. The demand in free-standing CS materials motivates understanding and measuring mechanical properties such as yield strength, ultimate tensile strength (UTS), and ductility at the macroscales.

A recent study (Ref 105) on CS WC-reinforced Ni composite coatings has proposed a unified scaling law between the tensile strength and the characteristics of cold-sprayed composite materials:

$$\text{UTS} \propto \frac{\psi}{\sqrt{\phi} \times \sqrt{\lambda} \times \theta} \quad (\text{Eq 14})$$

where UTS represents the ultimate tensile strength of the MMC coating, ψ represents the total interfacial area between the metallic matrix and ceramic reinforcements, λ represents the mean free path between the reinforcing particles, ϕ represents the average particle size, and θ represents the porosity of the coating (Ref 105). From the proposed model, the tensile strength of the coating will increase as the reinforcement content increases due to larger interfacial areas available to transfer and share the load. Larger reinforcement contents will also lead to a reduced mean free path between the particles and thus present greater constraints on the plastic deformation of the coating. An increase in the average size of reinforcing particles, however, will result in a decrease in tensile strengths, as larger particles result in larger mean free paths, adversely affecting the load-bearing capacity of the MMC (Ref 105, 178). Besides, increasing porosity will result in an inversely proportional reduction of the tensile strength. These effects are interconnected since changing reinforcement content can change all four variables in the equation. The scaling described above can be observed in Fig. 10, where the scaling between UTS and ψ , ϕ , λ , and θ are shown for Ni-WC composite coatings in (a)-(d), respectively (Ref 105).

Fig. 10 Effect of (a) total interfacial area between the metallic matrix and ceramic reinforcements, ψ , (b) mean free path between the reinforcing particles, λ , (c) the average particle size, ϕ , and

(d) porosity, θ , on ultimate tensile strength of Ni-WC composite coatings (Ref 105). Images are reproduced with permission from Elsevier

There is a relatively limited amount of studies that investigated the effect of reinforcement content on the tensile properties of free-standing CS MMCs. Consistent with the indentation hardness results, the addition of reinforcing particles improves the UTS of free-standing MS300/WC (Ref 116), A380/Si (Ref 179), Al-B₄C (Ref 176, 180) composites compared to unreinforced ones. However, the effect of the amount of reinforcement on the ductility of CS MMCs is more limited with the brittleness in the as-sprayed condition; all the above-mentioned coatings have shown ductility in the range of 0–1% without post-spray treatments (Ref 116, 176, 179, 180). Brittle nature of CS MMCs is due to a large amount of inter-splat defects and intensive cold working effect (Ref 109). Pores, defects, and interfaces with a lack of metallurgical bonding are favorable locations for crack initiation. Heat treatments

such as annealing and solution aging, and mechanical treatments such as hot rolling, or a combination of the two will be required to promote metallurgical bonding and to enhance the ductility of CS MMCs.

Although limited, there are some reports on the effect of reinforcement content on the strength and ductility of various CS MMC coatings. In Al₂O₃-reinforced Al CS MMC, the UTS of the coating increased from 61 to 88 and 98 MPa as the reinforcement content increased from 0 to 25 and 50 vol.%. (Ref 79). The addition of SiC also led to a higher strength in Al coating, with the UTS increasing from 40 to ~ 60 and 95 MPa with an increase in SiC content from 0 to 23 and 47 vol.% (Ref 128). Such increase in strength can be due to the tamping and depression strengthening effects (Ref 79, 100). Ductility, however, decreased from 0.5% in the pure material to ~ 0.2% in the

composite reinforced with 23 and 47 vol.% of SiC (Ref 128). In Cu-metallic glass (MG) CS MMCs, the strength increased 14% and the ductility was also improved from 3.0% (pure Cu) to 6.6% by the addition of 4 wt.% MG particles. Ductility, however, remained relatively low compared to heat-treated samples ($\sim 20\%$) due to the cold work effect (Ref 181).

In terms of the effect of powder morphology, it was found that in Al_2O_3 -reinforced A380 coating (Ref 110), the addition of 20 vol.% spherical and irregular ceramic particles in the feedstock resulted in a 70% and 40% increase in the UTS respectively. Ductility improved from $\sim 3\%$ in the as-sprayed condition to 4% and 4.5% for irregular and spherical reinforcements, respectively. The enhanced performance found with the spherical particles is due to a stronger tamping effect resulted from spherical particles' tendency to rebound when they impact upon the substrate to a depth that is not significantly greater than their radius. In contrast, irregular particles were easier to embed and had a smaller probability to rebound during the deposition process, producing a less compact deposit.

Heat treatment can have profound impacts on the tensile properties of CS MMCs. It can lead to a significant increase in ductility by improving inter-splat bonding as well as the recovery and recrystallization in the cold worked regions. However, the typical strength-ductility tradeoff is observed in this class of materials. A comparison of engineering stress-strain curves in Fig. 11 shows that the strength and ductility of CS MMCs can be adjusted by applications of heat treatment. While the Cu-MG coating showed relatively lower ductility in the as-sprayed condition (Ref 181), an increase in ductility of the composite coating was obtained by increasing temperatures up to 300°C in a 1-h annealing treatment. Elongation was improved from 6.6% in the as-sprayed conditions to 26.1%, in exchange for the

reduction of tensile strength from 366 ± 10 MPa to 290 ± 10 MPa. The significant increase in ductility was attributed to the recrystallization of the Cu matrix, which reduced the density of dislocations and the work hardening effect produced during the cold spray process. In Al_2O_3 -reinforced A380 coating (Ref 110), post-spray heat treatment at 350°C for 4 h was shown to fuse splat boundaries and increase ductility by a factor of two compared to the as-sprayed condition. In $\text{B}_4\text{C}/\text{Al}$ composite coating, as-sprayed and heat-treated coating at 200°C showed entirely brittle behavior due to large amounts of inter-splat defects and intensive cold working effect (Ref 109). An increase in both ductility and strength was achieved with increasing annealing temperature to 500°C . The tensile strength reached 60 MPa compared to 38 MPa in the as-sprayed condition and the ductility increased from 0.3 to 1.4% (Ref 109). In solution-aged CS WC-reinforced MS 300 coating, the tensile strength of the coating processed with two different sets of processing parameters significantly increased from 147 MPa/308 MPa in the as-sprayed condition to 744 MPa/821 MPa, and the ductility improved from 0.6%/0.96% to 2.53%/3.06% with solution treatment at $800/1000^\circ\text{C}$ for 1 h and aging at 480°C for 6 h (Ref 116).

Hot rolling, as a post-spray treatment to cold spray, was shown to increase both strength and ductility of Si-reinforced A380 composite coatings (Ref 179). A thickness reduction of 40% at 500°C led to a significant increase in UTS, from 100 ± 13.4 MPa in the as-sprayed condition to 420 ± 2.1 MPa after hot rolling. This was accompanied by a concurrent increase in ductility from none to $5 \pm 2.3\%$ elongation. The improvement in strength and ductility was found to be due to various forms of strengthening from grain boundary to solid solution to precipitation strengthening to dispersion as well as enhanced inter-splat bonding (Ref 179). Hot rolling was also found to be more effective than annealing at 300°C for 10 h which resulted in a moderate increase in strength to 186 ± 17 MPa and ductility to $0.93 \pm 0.05\%$.

Similar hot rolling with various thickness reductions (20%, 40%, and 60%) was performed on CS $\text{Al}-\text{B}_4\text{C}$ composite coating as part of a thermomechanical treatment with consecutive heating and rolling steps (Ref 180). The resultant UTS and elongation were found to increase with higher levels of thickness reduction. The strength and ductility of the as-sprayed coatings (~ 37 MPa and $\sim 0.3\%$ elongation) significantly increased after 60% thickness reduction to 131 MPa and $\sim 5.2\%$ elongation. Fracture surface analysis of the as-sprayed coatings showed debonding of mechanically interlocked Al splats at $\text{B}_4\text{C}/\text{Al}$ interfaces. Al splat boundaries were partially healed out after 20% thickness reduction, while the bonding between B_4C and Al was found to be still too weak to transmit the load. In the case of 40% and 60% thickness reductions, on

Fig. 11 Heat treatments lead to enhanced ductility in CS Cu-MG MMCs (Ref 181). Image is reproduced with permission from Elsevier

the other hand, uniform dimple morphologies were found on the fracture surface indicating the homogeneity of the microstructure composed of uniformly distributed refined Al grains and B_4C particles (Ref 180). A one-step 30% thickness reduction at 500°C and a hybrid hot compression and hot rolling with a total thickness reduction of 70% were both found to be effective with a concurrent increase in strength and ductility. In contrast to an isothermal heat treatment at 500°C for 4 h, the hybrid treatment resulted in about threefold higher strength and fourfold higher elongation (Ref 176).

The tensile properties of CS AA2024/ Al_2O_3 MMCs are significantly enhanced after FSP, showing a 20% concurrent increase in both UTS and ductility. The improved interparticle bonding decreased reinforcing particle spacing, and their refinement was the main strengthening mechanism, while removal of weak interfaces was the origin of the improved tensile ductility (Ref 171).

From the various studies above, it can be seen that interparticle bonding quality is an important factor affecting the tensile strength of CS MMCs. To provide a better prediction of the tensile strength, numerical studies on the load-bearing behavior of CS MMCs are required. Although not specifically modeling CS MMCs, several finite element simulations on the particulate-reinforced materials (Ref 182–187) in general show that interfacial bonding strength and interfacial fracture energy dictate the overall strength of particulate-reinforced MMCs. Also, the morphology and volume fraction of the reinforcements can influence the overall stress–strain response (Ref 187). Due to the differences between CS MMCs and other types of particulate-reinforced materials, additional studies using finite element methods on the CS MMCs, in particular, are required to provide a more comprehensive understanding of the load-bearing behavior of CS MMCs.

In summary, while the tensile strength of CS MMCs is higher than the unreinforced counterparts, their ductility can be relatively low in the as-sprayed condition due to a large number of defects and lack of metallurgical bonding. Heat treatment can lead to a significant increase in the ductility, albeit with a typical compromise in the tensile strength. A concurrent increase in ductility and strength can be achieved by applying thermo-mechanical treatments such as hot rolling and friction stir post-processing. In general, higher reinforcement contents lead to a higher tensile strength. Spherical reinforcing particles have been shown to result in higher tensile strength and ductility of the composite compared to irregular reinforcements.

Fig. 12 SEM micrographs and EDS mapping of failed coating–substrate interfaces after adhesion tests. Here the coating is Al– Al_2O_3 of varying Al_2O_3 contents and the substrate is Mg. Effect of increasing reinforcing content from 0 to 25, 50, and 75 vol.% in powder feedstock is shown in the SEM micrographs (a–d) and corresponding EDS maps (e–h) (Ref 31). Images are reproduced with permission from Elsevier

Failures

Understating adhesive and cohesive failures of CS MMCs is of particular importance due to the widespread application of such materials as protective, structural, and functional coatings. The addition of reinforcing particles has shown both positive (Ref 31, 93) and negative (Ref 84) effects on the coating's adhesion to the substrate. A relatively small amount of reinforcing particles can produce a strong activation effect on the substrate surface and thus improve adhesion strength of CS MMC by (1) roughening of the substrate surface and (2) cleaning the oxide film off the substrate surface (Ref 25). Both effects facilitate the formation of metallurgical bonds between the substrate and the matrix. It is also suggested that the removal of oxide film from metallic particles can happen by the impact of ceramic particles during the spraying process, increasing chemical/metallurgical activity and as a result the strength of the coating (Ref 25).

The effects of reinforcing particles on matrix and substrate can be seen in the SEM micrographs and energy-dispersive x-ray spectroscopy (EDS) maps shown in Fig. 12, where the surfaces of the Mg substrate underneath an Al– Al_2O_3 coating was characterized after adhesive failure. Figure 12(a) shows the failed interface for the case of unreinforced coating. Figure 12(b), (c) and (d), on the other hand, shows the failed interfaces for MMCs reinforced with 25, 50, and 75 vol.% Al_2O_3 , respectively. The corresponding EDS maps are shown in Fig. 12(e), (f) and (h) where green areas show the Al residue on the Mg substrate (red) after the adhesive failure. It can be seen that the addition of Al_2O_3 reinforcement significantly improved Al adhesion onto the Mg surface and changed the failure mode from adhesive to cohesive, demonstrated by the increase in aluminum adhering to the magnesium substrate. The enhanced adhesion is attributed to the above-mentioned roughening effect as well as the removal of oxides from the surface. Bonding strength increased from ~ 15 MPa at no reinforcement to ~ 45 MPa at 50 vol.% Al_2O_3 with the failure mode being adhesive. However, the bonding strength decreased to ~ 30 MPa with an increase in the Al_2O_3 content to 75 vol.% where the failure mode was changed to cohesive (Ref 31).

In AZ91D–SiC composite coating, 15 vol.% addition of SiC particles resulted in an increase in the adhesion

strength from ~ 12 MPa in the unreinforced condition to ~ 22 MPa (Ref 108). The improvement was attributed to the tamping effect of the SiC particles on the first layer coating. In Al-Al₂O₃ composite coating on Al 6061 substrate, adhesion strength increased with the addition of 70 wt.% of ceramic particles to the feedstock powder, reaching the adhesion strength of the glue used to conduct the test (70 MPa) (Ref 93). The significant increase in the adhesion from the coating devoid of reinforcement at below 20 MPa was due to the roughening effect of ceramic particles and micro-asperities promoting mechanical interlocking at the coating–substrate interface. Oxide removal is also potentially increasing the adhesion strength by promoting metallurgical bonding between the particles and the substrate. The effect of oxide removal was studied by depositing a single layer of coating with different feedstock powders and observing an increase in oxides on the surface after 72 h. Also, the effect of asperity was decoupled from oxide removal by calculating the single-layer deposition efficiency (Ref 93).

It is worth noting that at a relatively higher amount of reinforcement, reduction of adhesion strength can happen due to reduced effective contact area between the metal matrix and the substrate surface. What is more, higher contents of defects and pores, usually found at larger volume fractions of reinforcement, negatively affect the adhesion strength. In Al 2024-Al₂O₃ composite coatings on AA 2024-T3 substrate, for example, while the addition of 20 wt.% Al₂O₃ particles resulted in an increase of adhesion strength from 20 MPa to 50.68 MPa, further increase in Al₂O₃ from 20 to 60% did not result in a significant further increase in adhesion strength (Ref 94). The initial increase was attributed to the indented substrate surface by reinforcing particles which enhanced mechanical interlocking. Coating adhesion strength also decreased slightly with increasing the amount of SiC reinforcements from 0 to 15 vol.% in Al-12Si coating on the 6061-T6 substrate (Ref 84). The presence of SiC particles at the substrate–coating interface by large amounts was shown to reduce the number of anchoring sites between the coating and the substrate. For Co-WC coating on Al substrate, increase in Co content from 12 to 17 wt.% resulted in a higher adhesion strength of 26 ± 10 MPa compared to 19 ± 1 MPa (Ref 113).

In addition to improvement in strength in the normal direction, the addition of particle reinforcement restricts deformation within the MMCs and thereby can influence the shear strength of the CS coating as well. In CS Al composite coating onto Mg substrate, a 25 vol.% addition of Al₂O₃ particle reinforcement improved adhesion strength in shear mode by 50% compared to pure Al coating (Ref 91). The shear strength of B₄C-reinforced Al-12Si coating deposited with cryomilled powder feedstock

onto Al 6061 substrates showed a higher value of 22.6 ± 5.6 MPa compared to 17.6 ± 3.8 MPa obtained without reinforcement. However, the coating produced with powders that were simply mechanically mixed had a shear strength of 16.1 ± 2.2 MPa, lower than that without reinforcement (Ref 130). It was attributed to the fact that in cryomilled feedstock, ceramic particles are mostly sub-micron in size and are trapped inside the matrix particles. This prevents direct contact between reinforcing particles and the substrate and reduces the extent of impingement on the effective bonding area between the substrate and matrix.

While the tamping effect by a relatively small number of reinforcing particles can improve cohesion strength, larger amounts of ceramic particles can prevent intimate contact of metallic particles. Consequently, the effective load transfer between metallic particles is reduced, resulting in a lower cohesion strength (Ref 151). The cohesion strength of the CuSn₅-Al₂O₃ coatings was shown to increase from 11.2 to 32.5 MPa with an increase in Al₂O₃ content from 0 to 30 wt.% in the feedstock (Ref 99). The addition of SiC particles in the 316L matrix resulted in an increase in the cohesion strength from 48 ± 7 MPa to 53 ± 9 MPa (Ref 162). In Al5056/SiC coating, the cohesion strength of the coating increased from 107.1 to 146.9 MPa with an increase in the SiC content from 0 to 26.4 vol.% (Ref 151). Further increase in the reinforcement content to 41.4 vol.%, however, resulted in a decrease in the cohesion strength to 112.7 MPa.

Figure 13 shows a fracture surface analysis of Al5056-SiC CS MMC failed in cohesion tests (Ref 151). Here the reinforcement content increases from top to bottom. Each row shows micrographs of the same fractured surface but at different magnifications. The first observation is that SiC particles significantly improve the deformation of Al5056 particles. While in the coating with no reinforcement, Al5056 particles are mainly spherical (shown by the green arrow in Fig. 13b), they are more flattened and transformed into oblate shapes when SiC reinforcing particles are present (shown by the yellow arrow in Fig. 13d). The second observation is that cracks between poorly bonded splats present in the coating with no reinforcement, shown by the red arrow in Fig. 13(b), are no longer present when ceramic reinforcement is added. Third, evidences of dimples and ductile fracture start to appear in the case of the coating reinforced with 21.1 vol.% SiC (see the white arrow in Fig. 13b). These effects together contributed to the cohesion strength's increase from 107 MPa for pure coating to 129 MPa for the coating reinforced with 21.1 vol.% SiC. Dimples in the fracture surfaces are more evident when the reinforcement content is increased to 26.4 vol.% (see white arrows in Fig. 13f), and the cohesion strength reached a peak of 147 MPa. Fourth, by further increasing the SiC content in the range of 33.6–41.4 vol.%, it was found that

Fig. 13 Effect of increasing reinforcement content in Al-5056-SiC CS MMC on fracture behavior (Ref 151). Images are reproduced with permission from Elsevier

the reinforcing particles reduced the effective contact area between the Al5056 particles (see enclosed particles in Fig. 13h and j). The number of cracks was also found to increase in these latter cases. As a result, the cohesion strength decreased to 122 MPa and 113 MPa at 33.6 to 41.4 vol.% SiC compared to the peak value of 147 MPa (Ref 151).

Cohesive failure can also occur under shear condition, and in addition to the amount of particle reinforcement, particle morphology also influences the cohesive shear strength of CS MMC coatings. Al-Al₂O₃ composite coatings with angular and spherical Al₂O₃ particles exhibited similar compressive stress-strain behaviors during pressure torsion test (Ref 9). However, a lower torque was needed to maintain shearing of the composite coating reinforced with angular particles as compared to the one with spherical particles, suggesting a lower shear strength in the former case. Stress concentrations at the sharp corners of the angular particles were found to promote the formation of microcrack in the matrix.

Fracture mechanisms can also change with the application of post-spray heat treatments. An example is given by the tensile tests conducted on 23 vol.% B₄C-reinforced Al CS MMCs after heat treating the specimens at 200, 300, 400 & 500°C under high-purity Ar environment for 4 h (Ref 109). Ultimate tensile strength was 38 MPa in the as-sprayed condition, which improved to 44, 56, 58, and 60 MPa after the above-mentioned heat treatments, respectively. Final fracture of the as-sprayed and heat-treated specimens occurred in the coating. The fracture analysis of the as-sprayed coating shown in Fig. 14(a) and (b) revealed a large number of inter-splat crevices and weakly bonded splat boundaries which acted as crack initiation sites. After heat treatment at 200°C, while some of the splats were found to be partially bonded, the same crack initiation mechanism as in the as-sprayed condition was found to be active due to the presence of significant amount of poorly bonded areas (Fig. 14 c and d). More evidence of dimple-like features and ductile fracture were found for the samples heat-treated at 300°C as a result of stronger metallurgical bonding. However, inter-splat crevices/pores were still present, acting as crack initiation sites for premature fracture (Fig. 14 e and f). A complete departure from brittle fracture was found for the samples heat-treated at 400°C and 500°C. In these latter cases, the entire fracture surfaces were characterized with ductile features signified by clear evidences of microvoid formation and coalescence (Fig. 14g, h, i and j). The observations of fracture mechanisms are in line with the increase in ductility from 0 in the as-sprayed and 200°C-treated conditions to 0.7%, 1.1%, and 1.4% when treated at 300, 400 & 500°C (Ref 109).

Figure 15 shows the fracture surfaces in the as-sprayed 7075Al reinforced with 4.2 vol.% nano-TiB₂ composite materials deposited with different processing conditions after cohesive failure (Ref 114). In this study, the carrier gas was systematically changed from air to nitrogen and helium, along with changes in gas temperature, pressure, and nozzle type. The corresponding fracture surfaces are shown in Fig. 15(a), (b) and (c), with the corresponding higher magnification images shown in Fig. 15(d),(e) and (f), respectively. Changes in processing conditions resulted in different levels of deformation during deposition. In Fig. 15(a), the fracture surface demonstrates a typical cleavage feature. Some dimples are found in the interparticle boundaries, where greater plastic deformation and recovery occurred. In Fig. 15(b), where nitrogen was used as the carrier gas, fracture took place along the splats interface rather than through them. Almost no dimples are observed on the fracture surface, displaying a brittle rupture. The fracture surface in Fig. 15(c), where helium was used as carrier gas, displays a curly structure with some fracture occurring through the deformed splats. Intra-splat fracture, observed in the latter case, confirms the stronger metallic bonding at the severely deformed interfacial regions due to the occurrence of material jetting and adiabatic shear instability. The change in failure mechanism is in line with the change in the degree of plastic deformation from Fig. 15(a), (b) and (c). It is also in line with the tensile strength values which changed from ~ 325 MPa to 280 and 350 MPa and elongation which changed from 1.2 to 0.6% and 1.2% for the microstructures shown in Fig. 15(a), (b) and (c), respectively. In the closer views of the micrographs in Fig. 15(d) and (e), some interior defects and pores within the deposits can be observed which can in turn accelerate the failure during tensile tests and lower the strength and elongation (Ref 114). However, even for the helium sample (see Fig. 15c and f), the fracture morphologies and elongation of the composite displayed a brittle feature, which indicates limited metallurgical bonding at the deformed splats.

Compared to adhesive and cohesive failures, fracture toughness and fatigue behavior of CS MMCs are less studied (Ref 41, 43, 134, 188, 189). In an indentation approach to study the fracture of cubic BN-reinforced in NiCrAl coating, it was found that the crack propagates preferentially along the interface between the matrix and the large BN particles (Ref 134). As a result, fracture toughness of the coating was reported to decrease with increasing BN reinforcement content. The same trend was also reported for the increase of nano-WC-17Co powder from 10 to 50 wt.% in the nano-/micropowder blend to produce WC-17Co CS MMC (Ref 188). While the fatigue behavior of free-standing CS MMCs has not been studied to the best of our knowledge, improved fatigue

Fig. 14 Change of fracture surface with heat treatment. From top to bottom is the as-sprayed (a, b) 200°C-treated (c, d), 300°C-treated (e, f), 400°C-treated (g, h), and 500°C-treated (i, j) conditions (Ref 109). Images are reproduced with permission from Elsevier

Fig. 15 Effect of processing conditions on fractured surfaces. The carrier gas use in cold spray is, from left to right, (a, d) air, (b, e) nitrogen, and (c, f) helium. (d, e, f) are higher magnifications of (a, b, c), respectively. (Ref 114). Images are reproduced with permission from Elsevier

characteristics of an additively manufactured 15Cr-5Ni stainless steel substrate were reported after being coated with CS Cr_3C_2 -Ni MMC coating (Ref 41). The improvement in fatigue crack growth rate, particularly in the Paris region (region II), was attributed due to a toughening mechanism provided by the reinforcing particles ahead of the crack tip.

In summary, coating/substrate adhesion strength is improved with increasing reinforcement content due to enhanced tamping effects, and such increase can lead to a change in failure mode from adhesive to cohesive. However, too much reinforcement can reduce the effective metallurgical bonding areas and results in reduced adhesion strength. A similar effect is also present for cohesion strength of the coating. Particle morphology can affect the coating cohesive strength. Coatings reinforced with spherical particles presented higher shear strength due to fewer stress concentrators compared to angular particles with sharp corners. Heat treatment can significantly improve bonding within the coating and as a result change the fracture mechanism of CS MMC coatings. With the limited reports available in the literature, fracture and fatigue of CS MMCs are areas that require future studies.

Tribology of Metal Matrix Composites

Wear Mechanisms

Wear is the process of material removal from surfaces that are in relative motion and is typically classified into low, mild, and severe regimes (Ref 190). In the low wear

regime, material removal is governed by localized surface deformation and plowing mechanisms at the asperity level without significant formation of debris particles (Ref 190). The primary mechanism in the mild wear regime, where the contact is still at the asperity level, is surface microcracking. The localized fracture in this regime leads to the formation of powder-like debris with sizes on the same order of magnitude as of the contacting junctions (Ref 190). In the severe wear regime, on the other hand, large subsurface crack and macroscopic fracture occur eventually leading to the formation of flake-like debris with length scales corresponding to the apparent contact area (Ref 190).

It has been shown that plasticity and plowing in the matrix (see the Ni matrix in Fig. 16(a) and the Al matrix in Fig. 16c and d) and fracture in the reinforcement (see cracked WC particles in Fig. 16g) are among the important processes governing the wear behavior in MMC CS coatings, particularly those with ceramic reinforcements. As important is the behavior of metallic/ceramic interfaces (Ref 103, 151, 157, 162). If the interfacial bonding is strong, then reinforcing particles can significantly contribute to the load-bearing capacity of the composite and reduce the wear rate (Ref 104, 177, 191). Imperfect interfacial bonding, on the other hand, can lead to debonding (see the pulled-out WC particle in Fig. 16(b) and Al_2O_3 particle in Fig. 16d), fracture, and fragmentation of reinforcing particles which can, in turn, result in severe wear through a variety of mechanisms (Ref 104, 192). First, fractured particles lose their ability to carry the applied load. As a result, the amount of shear strains in the matrix material increases significantly leading to localization of

Fig. 16 (a) and (b) show a typical particle pull-out in worn CS Ni-WC MMC coatings (Ref 104). (c) and (d) show the damage to the Al matrix in the form of scoring and plowing where carbide reinforcement was exposed (Ref 192). (e), (f), and (g) are cross-sectional images of worn surface in WC*Co-Ni coating. In (e), a tribofilm was found on the surface of the coating. The tribofilm resulted from the detached plastic wear debris smearing onto the worn surface, having low toughness, and a tendency to crack. The cracks below the surface

are within the Ni matrix and were initiated due to low-cycle surface fatigue, which was suggested to be the main material removal mechanism. (f) shows a coating with higher WC content than that in (e), but the wear behavior is similar to (e). (g) shows the coating with even higher reinforcement content and a different surface morphology where there is no tribofilm but a rough surface and cracked WC reinforcement can be found on the surface (Ref 152). Images are reproduced with permission from Elsevier

deformation and delamination of the subsurface layers. Second, fractured or debonded reinforcing particles can promote the rate of delamination by creating additional crack growth paths through particle–matrix decohesion. Third, fractured particles and pulled-out particles can provide additional material removal mechanisms through third-body abrasion.

Plasticity in a typical sliding wear experiment can also modify the microstructure of metal matrix materials. For coarse-grained metals, there is often a refinement to near-surface nanocrystalline structures, while grain growth can take place for an initially refined metallic microstructure (Ref 193). Both phenomena change the local mechanical properties in the so-called mechanically modified layer (MML). In addition to modified layers near the surface, adhesion between the coating and counterbody can initiate material transfer and removal leading to the formation of transfer film and wear debris (Ref 20).

Wear is a dynamic process where mechanisms can evolve as the microstructure of the coating changes during sliding. Using in situ tribometry, flows of third bodies (tribofilm, transfer film, and wear debris) were directly

observed during sliding wear of CS Ti and Ti-TiC composite coatings and correlated with observed trends in friction and wear mechanism (Ref 160). The results revealed that the adhesion of Ti to the counterface was initiated during the initial stage of pure Ti coating sliding. At later cycles, the main wear mechanisms changed to cracking of transfer films and generation of oxidized debris that led to further wear by abrasive particles. Locally developed mechanically modified layers through compaction of oxidized debris on wear track were not found to be protective. Incorporation of TiC into Ti coating was found to significantly modify the friction behavior, due to a dual effect of TiC particles. First, transfer and adhesion of Ti to the counterface, in this case, was found to be due to the dislodging of TiC fragments leading to an initial rise in the CoF. Second, through third body flows (e.g., material transfer, detachment, and debris recirculation), the TiC-containing coatings eventually formed compact, lubricating tribofilms that led to a stable, reduced friction at higher cycles (Ref 160).

In addition to being a dynamic process, wear and material removal mechanisms can vary significantly

depending on material type, reinforcement content in the CS MMCs, as well as testing conditions. In WC-Co-Ni composite coating, material removal of the coatings with lower ceramic content was shown to be dominated by the low-cycle surface fatigue caused by the load beyond the yield strength of the Ni phase (see the subsurface cracks in Fig. 16e and f) (Ref 152). Also, on the worn surfaces of the coatings with lower ceramic content, tribofilm was generated due to the detached plastic wear debris smearing onto the wear track (Fig. 16e and f). The tribofilm was shown to play a beneficial role in improving the coating wear resistance, preventing further wearing of the coating by the counterpart. No tribofilm, however, was generated on the surface of the coating with the highest ceramic content of ~ 62 vol.% (see Fig. 16g). The coating in the latter case was characterized by embossed WC reinforcements on the worn surface that effectively prevented the wear of the Ni matrix phase (Fig. 16g) (Ref 152). A comparison of solid-particle erosion in Ni and Ni-10.5 vol.% WC coatings revealed similar erosive wear resistance at a 30° incident angle but a lower erosion rate for the composite coating at a normal incidence angle (Ref 104). Cutting and plowing were the main wear mechanisms at a 30° angle, whereas Ni deformation localization and lip formation and WC fracture were observed at the normal impact angle. Embedment of the Al_2O_3 (counterbody) into the coating and subsequent formation of MML was found to be the reason for the high erosion resistance of both coatings at 90° . The presence of the WC particles in the composite coating, however, prevented the embedment of the Al_2O_3 particles and the MML formation, which contributed to the lower erosion resistance at a normal incident angle. At 30° , WC particles were able to protect Ni from erosion at some regions of the surface, as can be seen from the intact WC particle in Fig. 16(a). However, the content of WC was found to be too low for significant improvement (Ref 104).

The underlying principles of friction and wear modification involve reduction in contact area and reduction in interfacial shear strength between the coating and counterbody (Ref 194). One can achieve both in CS MMC coatings by incorporating reinforcing phases that can take form as a hard reinforcement, a solid lubricant, or both. Cu-MoS₂ and Cu-MoS₂-WC composite coatings and their sliding wear experiments are a good example to discuss the aforementioned general approaches in wear reduction (Ref 158). MoS₂ is a typical solid lubricant (Ref 194), while WC is a hard reinforcement. A comparison of the wear track morphology in Cu-MoS₂ and Cu-MoS₂-WC showed a large scale of detachment in the former but a smooth track with only small detachments in the latter (Ref 158). The difference was attributed to the slightly higher hardness of Cu-MoS₂-WC coating that reduced contact area as well as the presence of WC particles that limited deformation by

accumulating and storing dislocation during shearing (Ref 195). MoS₂ redistribution exhibited a similar manner on the wear tracks for both coatings. However, more MoS₂-containing debris attached to the Cu-MoS₂-WC counterface was found, forming a transfer film that separates the initial sliding contact, and therefore reduced the friction. The subsurface microstructure of the wear tracks revealed a contrast between two coatings and the influence of the WC particles (Ref 158). Major microstructural change, such as the formation of ultrafine grains, only occurred around WC particles showing the load-bearing capability of the reinforcing particles. In the Cu-MoS₂ coating, on the other hand, an ultrafine-grained region was only found on the top of the wear track. Ultrafine grain formation on the surface was observed to be minor in the case of unreinforced coating even after a longer sliding. For the Cu-MoS₂ coating, on the other hand, severe plastic deformation and microstructural refinement occurred more extensively due to a higher likelihood of crack nucleation and propagation around work hardened UFGs, leading to a thick, unstable tribolayer. This produced a more active material transfer in the contact and contributed to cracking, detachment, and eventually high wear rate (Ref 158).

The fretting wear behavior of the same materials was studied under gross slip regime, with a focus on the influence of WC particles on third body rheology and wear resistance at different stages of the test (Ref 196). During running-in, even though the participation of WC particles and fragments in the contact could not prevent drastic detachment induced by the presence of MoS₂, they promoted a more rapid formation of wear debris bed. The main velocity accommodation mechanisms took place through elastic and plastic deformation, as well as normal breaking within the first bodies. During early steady-state, WC fragments in the contact caused more material loss. However, during the following test, the presence of WC particles constrained velocity accommodation on the top of the wear scar. Such constraints contributed to the formation of continuous tribologically transformed structure (TTS) layers and transfer films in the contact. The presence of these structures resulted in a more stable and lower volume of third body flows, leading to significantly improved wear resistance of Cu-MoS₂-WC with a wear rate of $\sim 80 \times 10^{-6} \text{ mm}^3/\text{Nm}$, much lower than that of Cu-MoS₂ at $\sim 210 \times 10^{-6} \text{ mm}^3/\text{Nm}$. The presence of WC fragments inside the TTS and transfer films was discussed to be the key to maintain the stable and low source wear flows through microwedging and pinning. In contrast, at the Cu-MoS₂ contact, the velocity was accommodated across a large volume of third bodies and first body (i.e., a thick transition layer). The presence of MoS₂ led to frequent detachment from the TTS layer and transfer film,

which caused consistently high third body flows, resulting in a high wear rate (Ref 196).

In summary, plasticity and plowing in the matrix and fracture in the reinforcement are the main wear mechanisms in CS MMCs. In addition, weak matrix/reinforcement interfacial bonding can lead to particle pull-outs. Wear is a dynamic process as the surface constantly evolves during the process through material removal and formation of tribolayers. Wear mechanisms and processes can significantly vary from one material system to another, as well as under different conditions, requiring case-by-case studies. Wear mechanisms can be modified to achieve lower wear loss through the addition of hard reinforcement that distributes the load and/or incorporation of solid lubricants to reduce the shear force.

Wear Rate/Volume

While in general, the addition of reinforcements reduces the wear rate in CS MMC coatings, higher reinforcement content does not necessarily lead to a greater wear resistance. The improvement in wear behavior of CS MMC coatings compared to that of single-phase metallic counterparts originates from the fact that hard reinforcing particles, besides resisting the wear, can help distribute the compressive and shear stresses throughout the material (Ref 93). For compositions with lower reinforcement content, this stress distribution does not occur efficiently as the particles are too spread throughout the coating (Ref 93). At low concentrations of reinforcement, the ductile matrix phase endures excessive deformation. The excessive plastic flow of the matrix can plow the reinforcing particles as the wear tip slides through the coating, resulting in the reinforcement not contributing to the wear resistance of the coating (Ref 93). This mechanism, however, changes at higher ceramic contents, as the compressive and shear stresses are distributed from the matrix to the reinforcing particles better. The metallic phase does not suffer as much deformation, letting the reinforcement act as a wear-resistant material, as deformation on the surface will be limited (Ref 93). As the amount of ceramic content further increases, deterioration of bonding can occur which adversely impacts wear resistance of the coating (Ref 101).

In Al-based CS MMCs, reduction of wear rate compared to pure Al coating was achieved with the addition of B₄C (Ref 130, 150), SiC (Ref 128, 150, 151), and Al₂O₃ (Ref 86, 93, 95, 118, 148, 149). While in general an improved wear resistance is expected with increasing ceramic content in Al-based coatings (Ref 118, 151), no significant dependence of wear rate on the reinforcement volume fraction (Ref 150) as well as its increase (Ref 93) at higher reinforcement contents was also reported. Increasing Al₂O₃ volume fraction in CS MMC was shown to gradually

change the wear mechanism from adhesive to abrasive (Ref 149). This change in the mechanism is accompanied by an increased but more stable friction coefficient (Ref 149). Once the mechanism of wear becomes fully abrasive, the reinforcement was shown to significantly contribute to wear resistance and reduce the wear rate by several orders of magnitude (Ref 149). For 6061 alloy-based composite coatings, transition in wear mechanism occurs with a much lower Al₂O₃ content when compared with that in pure Al-based coatings, due to the higher strength of the matrix that prevented pull-out of Al₂O₃ particles (Ref 149). In Al-AlSi composite coatings, the wear mechanism was found to be debonding between dissimilar splats of Al and AlSi (Ref 97). As a result, the composite coating showed a higher wear volume compared to pure Al coating despite being harder. A comparison of two carbide reinforcements, namely, B₄C and SiC, added to Al 7075 CS showed a better wear performance for the former case (Ref 150) where the load distribution between the matrix and the reinforcement was found to be more efficient. For a constant volume fraction of ceramic particles, the number of ceramic particles dramatically increases by introducing smaller and lighter (low density) particles. B₄C particles used in this study had four times smaller average particle size ($d_{0.5} = 7 \mu\text{m}$) as compared to that of SiC particles ($d_{0.5} = 28 \mu\text{m}$). Therefore, for similar amounts of ceramic particles in the composite coatings, higher contribution of B₄C particles to wear resistance can be explained by the presence of more B₄C particles which provides better load distribution between the reinforcing particles and the Al 7075 matrix (Ref 150).

In Cu-based CS MMCs, the addition of Al₂O₃ (Ref 99, 100, 154), AlCuFeB quasicrystal (QC) (Ref 101), metallic glass (MG) (Ref 181), Zn (Ref 157), diamond (Ref 197) and W (Ref 198) particles were all effective and resulted in lower wear rates than pure Cu coating. However, additional improvement in wear resistance with increasing reinforcing particles was not significant (Ref 99, 100, 198), with higher reinforcement content resulting in higher wear rate in some cases (Ref 100, 101). The addition of Ni particles as reinforcement to Cu-Al₂O₃ coatings did not result in significant improvement of the wear behavior since no change in wear mechanism took place (Ref 157). However, the addition of Zn in Cu-Al₂O₃ resulted in the wear mechanism to change from adhesive to a combination of adhesive and abrasive (Ref 157). The improved wear resistance at lower particle concentration range (below 7.5 vol.%) in QC-reinforced Cu coatings is mainly attributed to the reinforcing effect of the particles, which was shown to reduce plowing on the coating and also reduce the depth of the frictional layer (Ref 101). However, a higher concentration (11.5 and 20.5 vol.%) of the reinforcing phase adversely aggravated the wear

resistance of coatings due to debonded ceramic particles causing severe abrasion (Ref 101).

In Ni-based CS MMCs, the effect of WC, IN718, and graphene nanotube as reinforcement on wear performance was studied (Ref 103, 106, 153). The addition of WC resulted in a decrease in wear rate by a factor of seven in sliding wear tests, due to the formation of a stable and cohesive mechanical mixed layer (MML) on top of the wear track (Ref 103). The MML was formed due to the fine fragmented WC particles being redistributed on the surface during sliding. Fine-fragmented WC particles not only facilitated the fast development of the MML, but also improved its stability. In addition, they increased the hardness of the MML, which contributed to the superior wear resistance of the composite coating (Ref 103). Cavitation erosion test showed that Ni-IN718 composite coating is significantly more wear resistant than pure Ni coating in terms of both mass loss and the level of degradation (Ref 153). A 20% volume fraction of the IN718 particles resulted in an overall mass loss reduction by 80% compared to pure Ni coating (Ref 153). This can be attributed to different material removal mechanisms with the existence of IN718 particles impeding crater formations and detachment of the Ni matrix (Ref 153). Besides, the wear rate of graphene nanoplate-reinforced IN718 composite coating on IN718 substrates was found to be around half of the substrate and 29% lower than pure IN718 coatings (Ref 106). GNPs reduce wear rate by working as a solid lubricant which greatly decreases the abrasion of the matrix. Following the initial dislodge, GNPs also distribute along the sliding direction and stack on the wear track surface to form a protective layer between the abrasive tip and the sample to prevent further wear. Also, GNPs process a flake-like structure, and surface fragments of GNPs adjacent to the IN718 matrix provide an additional sliding effect (Ref 106). A comparison of WC, TiC, and B₄C as reinforcement to Ni-based MMC coatings showed that the lowest wear rate in similar testing conditions was achieved by WC (Ref 174). The highest wear resistance of the WC-Ni MMC coatings was shown to be attributed to the high fracture toughness of the WC particles, and the higher level of Ni matrix work hardening by WC particles achieved during deposition (Ref 174).

In other types of CS MMCs, the decrease in wear rate can also be observed when reinforcement is added. Higher contents of the reinforcement in WC-12Co coatings were shown to result in a 33% reduction in wear rate as compared to WC-17Co (Ref 113). An 80% reduction in wear rate of Ti6Al4V CS coating was achieved by the addition of 23 vol.% of TiC (Ref 161). Abrasive grooves along the sliding direction were observed in Ti6Al4V coatings, whereas tribolayers were found on the wear tracks of the composite coating. Reinforced TiC ceramic particles

favor the formation of tribolayers that was shown to resist localized deformation and result in low wear (Ref 161). In Ti-TiC composite coatings, higher TiC content led to a proportional reduction of wear rate (Ref 160). In Al₂O₃-CNT composite coating, a 2 wt.% CNT addition led to the nanoparticle acting as self-lubricant and providing improved wear resistance compared to monolithic Al₂O₃ coating. However, at 4 wt.% of CNTs, deterioration of wear properties was noticed in the nanocomposite which was associated with the presence of voids and cracks in the latter case acting as a source of delamination (Ref 163).

Similar to mechanical properties such as hardness and elastic modulus, the wear rate can also be quantitatively predicted as a function of reinforcement content. Two basic models predicting the lower bound (Eq 15) (Ref 199) and upper bound (Eq 16) (Ref 200) to specific wear rate have been developed based on an inverse and a linear rule of mixture, respectively:

$$\frac{1}{W_{\text{lower}}} = \frac{V_M}{W_M} + \frac{V_P}{W_P} \quad (\text{Eq 15})$$

$$W_{\text{upper}} = V_M W_M + V_P W_P \quad (\text{Eq 16})$$

where V_P and V_M are volume fraction of the reinforcement and the matrix, and W_P and W_M are specific wear rates of the two phases. W_{lower} and W_{upper} are the lower bound and upper bound to specific wear rates, respectively. For these models to be applicable, the two constituent phases are assumed to wear as bulk materials, not considering important factors such as interfacial bonding, relative sizes of the reinforcement and matrix, as well as fracture toughness of the phases, all of which may significantly influence abrasion behavior of the composite (Ref 201). While Eq 15 and 16 were expected to provide upper and lower limits of abrasive wear rate of a composite, there are instances where experimental results are not confined within these over-simplified bounds due to negative reinforcement effect (Ref 201). To address the shortcomings of these models, an improved physical model was proposed, where primary wear mechanisms, specifically, plowing, cracking at the matrix/reinforcement interface or in the reinforcement, and particle removal, were considered (Ref 201). These effects are all gathered in one additional parameter C in Eq 17:

$$\frac{1}{W} = \frac{V_M}{W_M} + C \frac{V_P}{W_P} \quad V_P \leq 0.5 \quad (\text{Eq 17})$$

In this improved model, C is the contribution coefficient of the reinforcement in which the relative contribution of cracking at the interface and cracking of the reinforcement was considered. Interfacial fracture toughness as well as the relative size of the wear-induced crack to the size of the reinforcement affects the magnitude of C , which varies

from 0 to 1 (Ref 201). $C = 1$ represents the case where there is no particle removal either because the interfacial fracture toughness is relatively high or because the penetration of the counterpart is small relative to the particle size. In this case, the model reproduces the lower bound to a specific wear rate (best performance) shown in Eq 15. As C approaches 0, particle removal dominates the response of MMC such that the predicted wear rates increase to a higher value than the monolithic matrix, a regime that is not predicted by the basic linear rule of mixture.

Figure 17 shows the experimental measurements of specific wear rate as a function of reinforcement volume fraction for Al- Al_2O_3 composite coatings. We have also superimposed the theoretical predictions of the specific wear rate on the same plot. The theoretical predictions are based on the specific wear rate of the matrix, $W_M = 4.4 \text{ mm}^3/\text{Nm}$ from experimental measurements of wear rate of the pure Al coating (Ref 93, 148), and an order of magnitude estimate for the specific wear rate of Al_2O_3 to be $\sim 10^{-5} \text{ mm}^3/\text{Nm}$ (Ref 202). It can be suggested from the plot that relatively lower levels of Al_2O_3 reinforcement contributed little to improve the wear resistance of the coating due to large losses that happen when particle removal is experienced. However, at higher reinforcement contents, the effect of particle removal is reduced with an increased bonding strength between matrix and particle which in turn increases interfacial fracture toughness. An increase in fracture toughness is reflected by the fact that the specific wear rates at higher reinforcement volume fractions can be fitted by a larger C ($C = 0.002$) value compared to those at lower volume fractions ($C = 10^{-5}$). We note that these C values are significantly smaller when compared to corresponding values for non-CS composites (Ref 201) which we attribute to the presence of defects and

Fig. 17 Theoretical and experimental wear rates of CS Al- Al_2O_3 composite coating as a function of reinforcement volume fraction (Ref 93)

imperfect bonded areas in cold spray deposits. The significant deviation of the experimental measurements from the lower bound prediction suggests that there is still room to improve wear behavior of Al- Al_2O_3 composite coatings.

Figure 18 shows a compilation of specific wear rate and reinforcement volume fraction measurements for the material systems whose tribological behavior is widely studied in the literature, namely, Al-, Cu-, and Ni-based CS MMCs. It should be noted the counterpart materials, sliding speeds, as well as applied loads, are not the same for all these measurements. Therefore, instead of cross-comparing different material systems, we focus on the trend observed in a single material system with the same experimental conditions, i.e., the data points denoted with the same color in Fig. 18. We note that the reduction of wear rate by orders of magnitude can be achieved with an increasing amount of ceramic content in Al-based CS MMCs, shown by circles of different colors. However, in Ni- and Cu-based coatings, shown by squares and triangles of various colors, respectively, improvement in wear resistance is less significant, and in some cases nonexistent with the addition of reinforcing particles to the coating. The success of the reinforcement strategy to improve the tribological performance of Al-based compared to Cu- and Ni-based coatings can be attributed to enhanced bonding resulting in a more significant load-bearing contribution of the ceramic reinforcement in the former case.

In addition to relating specific wear rate to the reinforcement content, one can also relate the specific wear rate to the hardness of CS MMCs in order to inform material design decisions. The Archard wear equation (Eq 18) states that the volume of material worn, V , is inversely proportional to hardness, H , for a given wear test conditions:

Fig. 18 Specific wear rate versus reinforcement volume fraction in CS MMC coatings (Ref 37, 100, 101, 106, 148, 152, 158, 174)

$$V = \frac{KLF}{H} \quad (\text{Eq 18})$$

where K is the wear coefficient, F is the normal load, L is the sliding distance. The equation can be reorganized to:

$$\text{Specific wear rate} = \frac{V}{FL} = \frac{K}{H} \quad (\text{Eq 19})$$

where it can be seen that there exists an inverse relationship between specific wear rate and the hardness with the wear coefficient as the numerator. We have collocated the specific wear rates of two types of Al-Al₂O₃ MMC coatings (reinforced with spherical and irregular particles) and plotted them as a function of the coating hardness in Fig. 19. We have also used the Archard scaling to fit the two sets of data points with the two lines in the log–log plot of Fig. 19. It can be observed that the wear rate of the Al coating reinforced with the spherical Al₂O₃ reasonably follows the Archard scaling. This is on the other hand only true up to a certain reinforcement volume fraction for the Al coatings reinforced with angular Al₂O₃; a significant deviation from the Archard scaling can be observed for the reinforcement volume fraction in the range of 20–50 vol.%. The deviation coincides with the sharp reduction in specific wear rate which was attributed to the gradual change of wear mechanism from adhesive to abrasive due to an increased amount of reinforcement. This analysis highlights a potential limitation of Archard scaling in the context of CS MMCs where changes in the reinforcement content can result in not only the hardness of the composite coating but also the defect content, the microstructure, and the wear mechanism.

Fig. 19 Experimentally measured specific wear rate versus coating hardness of CS Al-Al₂O₃ MMC and the Archard's scaling (Ref 148)

Effect of Post-spray Treatment on Wear Rate of CS MMCs

Heat treatment presents a dual effect on wear resistance of CS MMC coatings. On the one hand, bonding between the matrix and reinforcing particles can be improved, resulting in a reduction of wear rate. On the other hand, the reduction in hardness, especially at higher temperatures, leads to an increase in wear rate. Compared to the as-sprayed condition, a 33% decrease in wear rate was achieved in cBN-NiCrAl nanocomposite coatings due to enhanced inter-particle bonding after annealing at 750°C for 5 h (Ref 164). Heat treatment at 400°C in vacuum or air for 4 hr also reduced the wear rate in Al-SiC composite coatings to 30% ~ 70% of that of the as-sprayed coatings, depending on the volume fraction of SiC content. Vacuum heat treatment produced better wear resistance by reducing oxidation that impeded bonding in the inter-splat boundary (Ref 128). While moderate temperatures (800°C) in solution aging treatment led to a decrease in wear rate of CS WC-MS 300 coating due to enhanced hardness and improved bonding, higher temperature (1000°C) resulted in higher wear rates due to the reduction in the hardness of the coating (Ref 116). In MG-reinforced Cu MMC, the wear rate of the as-sprayed coating increased by a factor of 2.5 after heat treatment at 300°C for 1 hr, due to the thermal softening of the matrix (Ref 181).

Turning to post-spray mechanical treatments, FSP greatly improved the wear resistance of the Ni-Ti composite coating by a factor of ~ 2 compared to the as-sprayed coating. The improved wear resistance was attributed to the enhancement of the microhardness and the formation of the dense intermetallic structures (Ref 89). Volumetric analysis of the as-deposited and FSPed coatings following solid-liquid impingement test also showed an improved performance of FSP MMC coatings under slurry erosion conditions. Poor erosion performance of the as-deposited MMC coatings was due to agglomerated WC particles within the matrix during CS. The FSP process, on the other hand, was shown to effectively break up and disperse the agglomerates resulting in a homogenous distribution of fine reinforcing WC particles. The primary erosion mechanism in the as-sprayed condition was found to be plowing in the softer matrix alloy which subsequently exposed carbide particles to the impinging slurry. The FSPed surfaces, on the other hand, presented a reduction in WC interparticle spacing. As a result, less of the matrix alloy was exposed to the impinging slurry. Consequently, the volume loss due to erosion was lower in the FSPed specimens when compared with the as-deposited coatings (Ref 172).

In summary, a significant reduction of the wear rate of pure coatings can be achieved through the addition of

reinforcing particles. In most cases, reinforcements can provide load-bearing capacity and produce tribofilms on the surface of the wear track, offering reduced depth of friction region and more stable wear surfaces. The addition of solid lubricants can provide additional wear resistance. However, it is also worth noting that very high reinforcement contents can lead to negative impacts on the wear performance of CS MMCs due to poor interfacial bonding and severe damage caused by loose reinforcing particles. Theoretical frameworks can be adopted for predictions of wear rates of CS MMCs. The predictions are sensitive to the degree of interfacial bonding between reinforcement and matrix and require calibrations for accurate prediction. Heat treatment can improve bonding and thus improve wear resistance of CS MMC coatings. However, excessive heat treatment can lead to negative effects due to reduced hardness. Post-spray mechanical treatments such as FSP can reduce interparticle spacings of hard reinforcements and thus provide better wear resistance through reduced matrix plowing.

Coefficient of Friction

In CS MMC coatings, the amount of particle reinforcement or solid lubricant in the coating can significantly affect frictional behavior and alter the coefficient of friction (CoF) of the coating. One of the important mechanisms by which the addition of hard reinforcement can reduce the CoF is through the reduction of contact area between the surface and the counterbody due to increased hardness of the coating (Ref 101, 203, 204). However, the surface roughness of the composite coating, as well as the bonding between matrix and particles, can be affected by the addition of reinforcement too, both of which can adversely influence the CoF (Ref 95, 106). Another important mechanism that can be exploited to reduce CoF is self-lubrication by adding solid lubricants as reinforcement to the matrix (Ref 20, 158, 159, 196, 204, 205). Application of solid lubricants, such as hexagonal boron nitride (h-BN) (Ref 205) and MoS₂ (Ref 158, 159, 196), can decrease the coefficient of friction by introducing a layer of lubricating tribofilm.

In Al-based CS MMCs, lower CoF was achieved in both CS pure Al and Al-Al₂O₃ composite coatings when compared with pure Al bulk metal (Ref 118). This can be due to the enhanced hardness of the CS coating compared to the bulk material. At microscales, coatings with 25 and 50 wt.% of Al₂O₃ showed comparable CoF to that of pure Al coating (~ 0.3), while coatings with 75 wt.% Al₂O₃ provided a significant improvement in CoF (below 0.1). This can be attributed to higher hardness along with reduced plowing of the Al matrix at higher reinforcement content. Addition of ~ 38 vol.% TiN into Al2319 coating resulted

in a ~ 43% reduction in CoF and a ~ 15 times smaller wear rate compared to that of pure coating (Ref 98). The adhesion between the coating and the 100Cr6 steel sliding ball was found to be the dominant wear mechanism in the case of pure Al2319 coating. In the composite coating, on the other hand, third-body abrasion by fine TiN particles between the sliding ball and the coating was shown to be responsible for lowering both the friction coefficient and the wear rate (Ref 98). CoF of the Al-AlSi composite coatings was also found to monotonically reduce from 0.80 to 0.23 with an increasing amount of AlSi alloy reinforcement from 0 to 100% (Ref 97). The addition of 10 wt.% Al₂O₃ particles significantly reduced the CoF of the cold-sprayed A380 alloy coating from ~ 0.5 to ~ 0.3 (Ref 95). However, an increased amount of Al₂O₃ to 20, 30, and 40 wt.% increased CoF to around 0.4 (Ref 95). The reason was found to be an increase in the contact area between Al₂O₃ particulates and the counter tool due to the fragmentation of Al₂O₃ particles (Ref 95). CoF can also be sensitive to the applied load. In Al5056/SiC coating, at a normal load of 2 N, the CoF showed an initial increase from 0.72 to 0.96 followed by a decrease to 0.77 as the SiC content increased in the range of 0 to 41.4 vol.% (Ref 151). At a higher normal load of 10 N, however, an initial plateau at 0.52 was followed by an increase to 0.73 in the CoF in the same range of reinforcement content (Ref 151). The different trends were attributed to different wear mechanisms at different load levels. Since the amount of the contribution of the two phases to wear resistance is different, at the lower load Al matrix mainly resists wear, but at the higher load, participations from both phases occurred. Different reinforcement contents also contributed to the change in wear mechanism due to the change in interfacial bonding strength.

In Cu-based coatings, effects of both hard reinforcements such as W, Al₂O₃, and AlCuFeB quasicrystal as well as solid lubricants such as MoS₂ on friction behavior of CS MMCs have been studied. In CuSn8-based composite coating, the CoF decreases slightly from ~ 0.72 to ~ 0.65 with the increase of AlCuFeB quasicrystal (QC) phase from 0 to 57.6 vol.% (Ref 101). The slight reduction in COF was attributed to the decreased adhesion between the sliding pairs with increasing QC particle fraction (Ref 101). The amount of W as reinforcement, however, did not change the CoF for 70Cu-30 W compared to 50Cu-50 W coatings, as there was not a major change in wear mechanism (Ref 198). CoF was found to slightly increase with the addition of 2.36 to 7.22 vol.% Al₂O₃ to pure Cu coating due to more asperities exposed to the surface during the wear process at higher contents of reinforcement (Ref 100). A significant reduction of the CoF in Cu coating from 0.7 to 0.14–0.15 was achieved with the addition of 1.8 ± 0.99 wt.% MoS₂ which acted as a solid lubricant (Ref 159).

However, the CoF is not stable throughout the wear test, due to frequent detachment of Cu creating deep grooves along the wear track (Ref 158). It is through the addition of WC that CoF was stabilized since WC resisted detachment of Cu and MoS₂ particles. For Cu-MoS₂ and Cu-MoS₂-WC composite coating, CoF of Cu-MoS₂-WC against alumina was lower than the composite without WC reinforcement (both lower than pure Cu coating). CoF was also more uniform throughout the wear track on Cu-MoS₂-WC composite (Ref 158).

The effect of reinforcement on CoF was also studied in Ni- and Fe-based coatings. The addition of 0.15 wt.% graphene nanoplates (GNP) into IN718 composite coatings resulted in 16% and 13% lower CoFs than IN718 substrates and pure IN718 coatings, respectively. This was achieved due to sliding and lubricating effects activated by the exfoliation of the GNPs, increasing the wear resistance of the composite coatings (Ref 106). In CS-Ni-WC coatings, the presence of WC particles in the coating stabilized CoF, while fluctuations were noticed in the case of pure Ni coating. The fluctuations of CoF in pure Ni coating were attributed to material removal which was significantly reduced with the addition of WC reinforcements (Ref 103). In CS 316L-Ni/SiC coating, only a slight reduction of CoF was observed with the addition of 30 wt.% Ni/SiC particle reinforcement in 316L matrix (Ref 162).

Mechanisms discussed above strongly depend on matrix/reinforcement material types, presence and density of defects, surface distribution of reinforcements, as well as experimental conditions. The strong dependency could be the reason why a clear trend may not be easily discerned when comparing the CoF values that we have gathered from across the literature and plotted as a function of reinforcement content in Fig. 20. We highlight that the test conditions, such as counterpart material, load, sliding distance, speed, and the length scale (micro/macro), are different from one study to another causing significant scattering in the plot. The emphasis here is the general CoF trend for each material system represented by the same symbol and color rather than cross-comparison of the CoF values from different studies. The beneficial effects of

Fig. 20 Coefficient of friction (CoF) of select MMC coatings as a function of reinforcement volume fraction (Ref 37, 97, 98, 101, 116, 151, 152, 158, 161)

reinforcing particles in the reduction of the CoF appear to be the more dominant trend in Fig. 20. It is also interesting to note that the steepest decrease in CoF among all of the composite coatings shown in Fig. 20 is related to the addition of self-lubricating particles as reinforcement.

In summary, the addition of hard reinforcements that can reduce the contact area between the surface of the coating and counterbody, as well as incorporation of solid lubricants can effectively decrease the coefficient of friction in CS MMC coatings. In some cases, significantly reduced coefficients of friction can be found. However, there also exist cases where reduction of CoF is less obvious or nonexistent. Large reductions of coating CoF are usually achieved by significant shifts in the underlying wear mechanisms.

Conclusions and Future Research Directions

In this review article, we have discussed various aspects of cold spray metal matrix composites from processing science to mechanical and tribological properties. We started

the review with a discussion on bonding mechanisms and highlighted the surface activation and tamping effects of ceramic particles combined with the cushion effect of the metallic particles in a co-deposition scenario. The tamping effect is an efficient mechanism in closing defects and reducing the porosity of the deposited layers. While deposition efficiency increases with increasing the reinforcement content, impacts of ceramic particles onto ceramics become more probable at a relatively larger volume fractions of reinforcement which in turn reduces the deposition efficiency. A maximum deposition efficiency can be generally achieved with a volume fraction of ceramic particles in the range of 20–40%.

The rate of increase in elastic modulus of CS MMCs with the addition of the reinforcing particles is not constant as suggested by the rule of mixture. The rate, instead, increases as reinforcement content increases. Tamping effect and dispersion strengthening are the origins of the enhanced hardness of CS MMCs when compared to monolithic CS deposits. Experimental measurements of hardness as a function of reinforcement content generally lie in the space confined with the inverse rules of mixture (lower bound) and the rule of mixture (upper bound). Surface activation, tamping, and roughening effects of ceramic particles are also effective in improving the cohesion and adhesion strengths in CS MMCs. At a relatively high amount of reinforcement, the cohesion and adhesion strengths can be adversely affected due to reduced effective contact area between metallic particles in the coating or between metallic matrix and substrate surface. Plasticity and plowing in the matrix and fracture in the reinforcement combined with interfacial fracture are the important mechanisms governing the wear behavior of MMC CS coatings. The positive effects of reinforcing particles on wear resistance at lower contents and the deteriorating effects at higher contents are likely due to the load sharing of the particles in the former and the higher probability of particle debonding in the latter. Our theoretical treatment of specific wear rate in CS MMCs compared with the experimental measurements suggests that there is significant room to improve the tribological properties of CS MMCs. Reinforcement of CS matrix can be exploited as an effective strategy to reduce the coefficient of friction directly through self-lubricating reinforcements or indirectly through the reduction of the contact area between the

surface and a counterbody due to increased hardness. In general, the flexibility in matrix/reinforcement material selection combined with a wide range of possible reinforcement contents can be exploited to span orders of magnitude for wear rate, a wide range of coefficient of friction, and hardness.

The effect of cold spray processing parameters on deposition efficiency and porosity of CS MMCs is similar to that of monolithic CS coatings. The higher levels of plastic deformation due to thermal softening and increased impact velocities result in higher deposition efficiencies and lower porosities. Post-spray treatments can be exploited to modify the microstructure and properties of CS MMCs. Post-spray heat treatments can reduce the defect content and significantly enhance the ductility by improving inter-splat bonding, recovery, grain growth, and recrystallization. It can be also used as a processing strategy to form intermetallic reinforcement post-deposition in which case the hardness of the coating can be increased as well. Post-spray mechanical treatments are also very effective in increasing coating hardness due to microstructural and morphological refinement as well as improved material mixing and bonding.

In writing this review, we have also emphasized on a predictive understanding of the mechanical and tribological properties of CS MMCs as a function of the corresponding properties of the constituent phases. Despite our general ability, as a community, to explain and rationalize experimental measurements, some pieces are yet missing for a comprehensive predictive understanding. In our view, this is a critical step toward a theory-driven optimization of CS MMCs in terms of mechanical and tribological properties. In preparing this review, we have identified a few areas with pressing research needs that we offer as future directions of research for the field of CS MMCs.

Perhaps the largest outstanding question about the mechanical properties of CS MMCs is the extent to which each phase contributes to the overall load-bearing capacity of the material. While the collective response of CS MMCs to external load has been widely investigated in the field, the phase-specific response of these materials is much less understood. With the recent advances in cold spray processing as an additive manufacturing technique and the possibility of making bulk free-standing MMC deposits, the phase-specific mechanical response is becoming a

pressing question. Load-bearing behavior of the composite coatings is fundamentally dictated by the load partitioning between the two, often soft and hard, phases. The state of stress and strain in each phase can be dramatically different from what is measured at the macroscopic level. Advanced characterization techniques, e.g., in situ x-ray diffraction, are needed to resolve the phase-specific response and enable bridging the underlying microscale mechanisms and phase interactions to the continuum level behavior of MMCs.

The interfacial fracture toughness was discussed to be an important parameter governing the wear mechanism and rate. Low interfacial fracture toughness can result in particle removal, whereas high interfacial fracture toughness can favor other mechanisms such as plowing of the matrix material or fracture of the particle to be the dominant wear mechanisms. Despite its importance, interfacial fracture toughness in CS MMCs is an area that is yet to be investigated. Small-scale mechanical testing such as in-situ nanoindentation and microcantilever beam fracture can be employed to study the fracture toughness of metal-ceramic interfaces. Of particular interest to the cold spray community is to understand how interfacial fracture toughness is related to the characteristics of the reinforcement (material, size, volume fraction) and cold spray process parameters.

Computational efforts, both atomistic and continuum, can be extremely helpful to further understand deposition mechanisms and mechanical performance of CS MMCs. In terms of deposition behavior and bonding, it is highly desirable to understand the details of surface activation, tamping, and cushion effects in the co-deposition of CS MMCs. Is there a threshold velocity for ceramic particles impact to activate metallic surfaces? How can we quantify the extent of tamping and cushion effects? Systematic finite element simulations can be developed to tackle these questions. Molecular dynamic simulations can be also used to understand the state of interfaces, e.g., the nature of metal-ceramic bonding in CS MMCs. In terms of mechanical performance, finite element simulations can be used to predict the collective behavior of the composite material from the known properties of the constituent phases. Dispersion strengthening and its correlations with reinforcing particle spacing, size, morphology, volume fraction can be further understood.

As a solid-state process, cold spray is offering a unique space in the areas of composite fabrication and additive manufacturing of structural materials. A widespread deployment of CS MMCs as load-bearing components

would not be possible before a comprehensive understanding of the bulk failure modes including fatigue. There are several important questions regarding the fatigue behavior of CS MMCs that need thorough understanding. For instance, among various types of defects (pores, interfacial cracks or particle cracks, etc.) that could be present with various densities in CS MMCs, which one may dominantly govern the response of the material under cyclic loading? How does the load partitioning between the two phases evolve during cyclic loading? To what extent various reinforcements can deflect a propagating crack and provide toughening mechanisms for MMCs?

The impact of metallic particles onto metallic substrates has been widely investigated in the field of cold spray. Fundamental phenomena, including plastic dissipation, thermal softening, large interfacial strains, and jetting, are relatively well understood, and the transitions from rebounding to bonding or erosion are theoretically well-documented for metal-on-metal impact. The same level of understanding, however, is lacking for the impact of ceramic particles onto ceramic and/or metallic substrates. With the absence of plasticity in ceramic particle impact onto ceramic substrates, at what threshold velocity rebound gives way to fracture and fragmentation? What is the relationship between that threshold velocity and physical and thermomechanical material parameters? How can the tamping effect in ceramic particles impacting metals be quantified? These are a few fundamental questions that could be tackled by single-particle impact studies, either through wipe tests or through laser-induced particle impact tests.

These are just a few among an extensive list of potentially impactful directions for future research in the field of CS MMCs. With the recent proliferation of CS MMCs in structural applications, advanced characterization techniques, and new researchers trained in this field, we look forward to rapid progress in understanding these questions.

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Appendix

As an addition to the discussion presented in the paper, we have prepared Table 1 where CS MMCs are grouped based on the matrix material. We have reported the reinforcement

Table 1 A classification of CS MMCs studied in the literature based on material systems, post-spray treatments, and studied mechanical or tribological properties

Coating matrix	Coating reinforcement	Substrate	Post-spray treatment	Mechanical properties	Tribological properties	Reference
Ag	SnO ₂	Cu	HT	✓	✓	(Ref 166)
Al	Al ₂ O ₃	Steel	N/A	✓	✓	(Ref 206)
Al	Al ₂ O ₃	Al 6061	N/A	✓	✓	(Ref 93)
Al	Al ₂ O ₃	AZ91D	N/A	✓	N/A	(Ref 79)
Al	Al ₂ O ₃	S235JR Steel	MAC	✓	N/A	(Ref 207)
Al	Al ₂ O ₃	AZ91	N/A	✓	✓	(Ref 118)
Al	Al ₂ O ₃	AZ91	N/A	✓	N/A	(Ref 91)
Al	Al ₂ O ₃	...	N/A	✓	N/A	(Ref 9)
Al	Al-Si	Al 6061	N/A	✓	✓	(Ref 97)
Al	B ₄ C	Al 6061	HT, HR	✓	N/A	(Ref 180)
Al	B ₄ C	Al 6061	HT, HR, HC	✓	N/A	(Ref 176)
Al	B ₄ C	Al 6061-T6	HT	✓	N/A	(Ref 109)
Al	Cu	...	N/A	✓	N/A	(Ref 129)
Al	Si	AZ31/mild steel	N/A	✓	N/A	(Ref 208)
Al	SiC	Al	HT	✓	✓	(Ref 128)
Al	Ti	Ti2AlNb	HT	✓	N/A	(Ref 111)
Al (A380)	Al ₂ O ₃	AZ31	N/A	✓	✓	(Ref 95)
Al (A380)	Al ₂ O ₃	Al 6061	N/A	✓	✓	(Ref 133)
Al (A380)	Al ₂ O ₃ of different shapes	Al 6061	HT	✓	N/A	(Ref 110)
Al (A380)	Si	Steel	HT, HR	✓	N/A	(Ref 179)
Al/Al 6061	Al ₂ O ₃	AZ91E	HT	✓	✓	(Ref 149)
Al 2024	Al ₂ O ₃	Cu	FSP	✓	N/A	(Ref 171)
Al 2024	Al ₂ O ₃	Cu	FSP	✓	✓	(Ref 209)
Al 2024	Al ₂ O ₃	Al 2024-T3	N/A	✓	N/A	(Ref 94)
Al 5056	SiC	Al	N/A	✓	N/A	(Ref 83)
Al 5056	SiC (different ratios)	Al	N/A	✓	✓	(Ref 151)
Al 7075	B ₄ C/SiC	Al 6061-T6	N/A	✓	✓	(Ref 150)
Al 7075	TiB ₂	Al 7075-T6	N/A	✓	N/A	(Ref 114)
Al/Ni/Cu/Co	Al ₂ O ₃ /BN/Al ₂ O ₃ /SiC	SS-316/IN718/SS-316/Co	N/A	✓	N/A	(Ref 96)
Al-12Si	SiC	Al 6061-T6	N/A	✓	N/A	(Ref 84)
Al-12Si	B ₄ C	Al 6061/SS-316L	N/A	✓	✓	(Ref 130)
Al 2319	TiN	Al	N/A	✓	✓	(Ref 98)
Al ₂ O ₃	CNT	Al alloy	N/A	✓	✓	(Ref 163)
AZ91D	SiC (different particle sizes, different ratios)	AZ31	N/A	✓	N/A	(Ref 108)
Co	WC	Al 7075-T6	N/A	✓	✓	(Ref 113)
Co	WC	Al 7075-T6/carbon steel	N/A	✓	✓	(Ref 11)

Table 1 continued

Coating matrix	Coating reinforcement	Substrate	Post-spray treatment	Mechanical properties	Tribological properties	Reference
Co	WC	Stainless steel	HT	✓	N/A	(Ref 43)
Co	WC	Stainless Steel	N/A	✓	✓	(Ref 188)
Co, CoCr	WC	Al	N/A	✓	N/A	(Ref 210)
CoCr, NiCr	WC, Cr ₃ C ₂ , Al ₂ O ₃	Al 5083	FSP	✓	✓	(Ref 172)
Cu	Al ₂ O ₃	Al 2017	N/A	✓	✓	(Ref 100)
Cu	CNT, SiC	Cu	N/A	✓	✓	(Ref 102)
Cu	Cr	Cu	N/A	✓	✓	(Ref 155)
Cu	Diamond (copper clad powder)	Al alloy	N/A	N/A	✓	(Ref 197)
Cu	MoS ₂	Al 6061	N/A	✓	✓	(Ref 159)
Cu	MWCNT	Mild steel	N/A	✓	✓	(Ref 144)
Cu	Ni	AZ31D	USSP	✓	N/A	(Ref 156)
Cu	W	Al	N/A	✓	✓	(Ref 198)
Cu	ZrCuAlNiTi metal-glass	...	HT	✓	✓	(Ref 181)
Cu, Ni, Zn	Al ₂ O ₃	AZ31B	N/A	✓	✓	(Ref 157)
Cu60Zn40	SiC and Al ₂ O ₃	Al 2017	N/A	✓	✓	(Ref 154)
CuSn8	AlCuFeB quasicrystal	Mild Steel	N/A	✓	✓	(Ref 101)
Cu-MoS ₂	WC	AA 6061	N/A	✓	✓	(Ref 158)
Cu-MoS ²	WC	AA 6061	N/A	✓	✓	(Ref 196)
Cu-MoS ₂	WC	AA 6061	N/A	✓	✓	(Ref 195)
CuSn5	Al ₂ O ₃	Al 7075-T651	N/A	✓	✓	(Ref 99)
Ni	Al ₂ O ₃	Steel	HT	✓	✓	(Ref 165)
Ni	B ₄ C/TiC/WC	Low-carbon steel	N/A	✓	✓	(Ref 174)
Ni	Cr ₃ C ₂	15Cr-5Ni stainless steel	N/A	✓	N/A	(Ref 41)
Ni	Fe-9.6%Si-5.4%Al	Stainless steel	N/A	✓	N/A	(Ref 132)
Ni	FeSiAl	Stainless steel	N/A	✓	✓	(Ref 173)
Ni	In718	Stainless steel	N/A	✓	✓	(Ref 153)
Ni	Ni ₃ Al	Al 6061	N/A	✓	N/A	(Ref 131)
Ni	Ni ₃ Al	Al	N/A	✓	N/A	(Ref 88)
Ni	Ti	Al	HT, FSP	✓	✓	(Ref 89)
Ni	WC	Mild steel	N/A	✓	✓	(Ref 204)
Ni	WC	Mild steel	N/A	✓	✓	(Ref 37)
Ni	WC	Steel	N/A	✓	✓	(Ref 37)
Ni	WC of different particle sizes	Mild steel	N/A	✓	✓	(Ref 104)
Ni	WC-17Co	Al alloy	N/A	✓	✓	(Ref 152)
Ni20Cr	Cr ₃ C ₂	Al 7075	N/A	✓	N/A	(Ref 175)
NiCrAl	BN	Stainless steel	HT	✓	✓	(Ref 164)

Table 1 continued

Coating matrix	Coating reinforcement	Substrate	Post-spray treatment	Mechanical properties	Tribological properties	Reference
IN718	Graphene nanoplates	IN718 alloy	N/A	✓	✓	(Ref 106)
Stainless steel—316L	Cu/Triballoy T-700	Al	N/A	✓	N/A	(Ref 107)
Stainless steel—316L	Ni-coated SiC	AZ80	N/A	✓	✓	(Ref 162)
Steel—MS 300	WC	304 stainless steel	HT	✓	✓	(Ref 116)
Steel—MS 300	WC	304 stainless steel	N/A	✓	✓	(Ref 177)
FeAl	Al ₂ O ₃	Stainless steel	HT	✓	N/A	(Ref 90)
Ti	Hydroxyapatite	Ti	N/A	✓	N/A	(Ref 211)
Ti	TiC	Ti6Al4V	N/A	✓	✓	(Ref 115)
Ti	TiC	Mild steel	N/A	✓	✓	(Ref 160)
Ti & NiCrAl	TiAl ₃ & BN	Ti6Al4V/IN718	N/A	✓	N/A	(Ref 117)
Ti6Al4V	TiC	Mild steel	N/A	✓	✓	(Ref 161)
Zn/Al	Graphene	Low-carbon steel	N/A	✓	N/A	(Ref 212)

HT heat treatment, MAC machining, HR hot rolling, HC hot compression, FSP friction stir processing, USSP ultrasonic shot peening

and the substrate materials and marked the properties studied by each work as well as possible post-spray treatments for readers to quickly narrow down the studies that may interest them.

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