Advanced diamond-reinforced copper composite coatings via cold spray and material characterization

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Diamond-reinforced copper matrix composites (DCMC) has great potentials for heat sinks applications due to their excellent thermal properties. Cold Spray, as a relatively emerging coating technique, is able to fabricate coatings or bulk materials at entire solid-state, significantly lowering the risk of oxidation, phase transformation and high thermal residual stress because of the low processing temperature. In this paper, thick DCMC coatings were fabricated via cold spray using copper-clad diamond powder or its mixture with pure copper powder. It was found that cold spray due to its low processing temperature was able to avoid the graphitization of diamond in the DCMC coatings. Using the pure clad diamond powder only, the diamond in the original feedstock was almost completely retained in the coating which contained more than 40 wt.% diamond. Such high mass fraction of diamond has never been achieved in previous cold spray works using pre-mixed powders. The mechanically mixed powder of clad diamond and copper also exhibited great retainbility for diamond; the diamond fraction in the coating was even larger than that in the original feedstock. Besides, the most important finding here is the additional copper powders acted as a buffer, effectively preventing the fracture of diamond in the coating.

1 Introduction

Copper has been widely applied as heat sinks material for a long time due to its high thermal conductivity. However, the rapid growth of the modern industry has brought an urgent demand of the heat sink materials with higher thermal performance. Diamond is known to possess much higher thermal conductivity and lower thermal expansion coefficient than copper, but it is really difficult to be machined due to the extremely high hardness, which significantly limits its direct application as heat sink material. Therefore, a kind of advanced material, metal matrix composite (MMC) consisting of copper and diamond, was developed to improve the thermal performance of pure copper heat sink. In many studies, such diamond-reinforced copper matrix composite (DCMC) exhibited excellent thermal performance, hence sparking significant interests from both science and industrial communities [1–11].

Cold Spray, as an emerging coating technique is capable to deposit metals, MMCs and even ceramics, thereby attracting great interests over decades [1]. In this process, feedstock materials in the form of micro-size powders accelerated by the supersonic driving gas through a de-Lavel nozzle, impact onto the substrate to form the coating. During the deposition process, the feedstock remains solid state without any melting; coating is formed through the metallurgical or mechanical bonding at the interface of adjacent particles and coating/substrate. Therefore, defects like oxidation, thermal residual stress and phase transformation which always appear in powder metallurgy, pressure infiltration and thermal spray can be considerably avoided in the cold sprayed coating [2]. Furthermore, with cold spray, coatings can be deposited on various similar or dissimilar substrates; also the thickness growth is almost unlimited for most metals and MMCs, which allows cold spray to act as a kind of additive manufacturing technique for producing bulk materials.

Very few attempts of diamond-reinforced metal matrix composites (DMMC) coatings via cold spray have been carried out in previous works for improving the coating wear-resistance capability [3,4], hardness and Young's module [5,6]. In these works, powders were normally mechanically mixed before spraying. By this means, the fraction of diamond in the coating significantly reduces compared with the original feedstock, which significant lowered the coating performance and resulted in a vast waste of the expensive diamond [3,4,7]. Ball milling as an alternative way is able to guarantee the minimum loss of the diamond during the deposition. But the graphitization and serious fracture of the diamond in the DMMC coating also resulted in poor-quality coating [5,6]. Besides, all the existing studies on DMMC via cold spray focused on the improvement of coating mechanical properties. In this paper, thick DCMC coating as a great potential candidate for heat sinks materials was fabricated via cold spray technique. Special copper-clad diamond powder or its mixture with pure copper powder were selected as the feedstock to fabricate the coating.

2 Experimental methodology

2.1 Coating fabrication and powders

MMC coatings were deposited on aluminium substrates using a home-made cold spray system (Trinity College, Ireland). The system consists of high pressure gas from bottles, a gas heater, a powder feeder, a CNC working platform for controlling the substrate movement, a de-Laval nozzle and a computer control system. In this work, nitrogen and helium were applied as the driving gas to deliver and accelerate the powders. Copper powders (-38+15 µm, Safina, Czech Republic), copper-claded diamond powders (-53+45 µm, Element Six, Ireland) and their mixture were used as the feedstock. Figure 1 shows the morphology and characterization of each powders observed by SEM (Carl Zeiss ULTRA, Germany). The copper-clad diamond powder is made of three different prats, namely, an inside diamond powder, a very thin interbedded nickel layer and an outside electroless copper cladding, which can be seen from Fig. 1c showing the powder cross-section prepared by the FIB (DB235, FEI Strata, USA). The reason for introducing nickel layer is because nickel provides much better bonding with diamond than copper. The thickness of the metal cladding layer is about 2-5 μm, leading to an approximate 50% mass fraction in a single grain. Detailed powders information and working conditions are provided in Table 1.

Table 1. Powders and working conditions

	Powders	Gas	P	T
P	Copper	N_2	3.0MPa	350℃
P1	Copper + Clad diamond (8:1)	He	2.0MPa	25℃
P2	Copper + Clad diamond (1:1)	He	2.0MPa	25℃
P3	Clad diamond	He	2.0MPa	25℃
P4	Clad diamond	He	2.5MPa	25℃

For convenience, coatings fabricated with different powders and working conditions were labelled as P to P5. The clad diamond fraction in the original feedstock increases from P1 to P3, while P3 and P4 are pure clad diamond without copper mixture. Note that the pure copper coating marked as ‘P’ was only used as a benchmark for the comparison with other DCMC coatings.

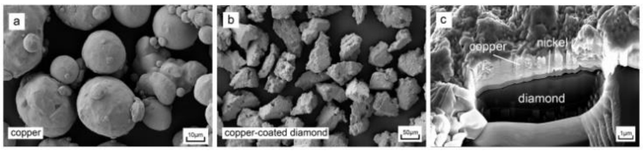

Fig. 1. Morphology and characterization of copper and copper-clad diamond powders used in this study. (a) copper, (b) copper-clad diamond and (c) cross-section of copper-clad diamond

2.2 Materials characterization

The as-sprayed coatings were examined by an X-Ray diffractometer (Siemens D500, Germany) with the Co (λ=1.789 Å) source at a current of 40 mA and voltage of 35kV to examine whether graphitization of the diamond occurs during the coating fabrication process. For analysing the coating microstructure, the as-sprayed coatings were post-processed to produce the polished and fractured cross-section. Samples for polish treatment were firstly cut, then grounded by SiC sand papers and finally polished by 0.05 μm Al_2O_3 solution. The fracture surface was obtained by bending the sample with pliers. The coating microstructures were then characterized by a SEM (Carl Zeiss ULTRA, Germany). Besides, the element analysis on the coating surface and cross-section was also performed with an EDS unit (Oxford Instruments INCA system, UK) equipping on the SEM system. In order to achieve an accurate measurement, five zones were randomly selected from the coating surface or polished cross-section and the measured data was then averaged.

2 Results and discussion

2.1 Coatings properties

Figure 2 shows the digital photos of as-sprayed DCMC coatings with different powders and working conditions. The coating thickness reached more than 5mm for each case, much higher than the CVD coating [8]. If necessary, this thickness can be further increased to form the bulk DCMC. Besides, it is obvious that the coating colour changed from red to grey as the clad diamond mass fraction increased gradually (from P to P3). To interpret this phenomenon, Fig. 3 provides the EDS element analysis on the coating surfaces. Nickel which was originally coated by copper cladding can be clearly detected on the substrate surface. This fact means that the clad diamond powder experienced large deformation during the deposition process; nickel cladding was fractured and then exposed to the outside environment. Nickel is known to present grey colour, thus coatings with clad diamond had different colour as compared to the pure copper coating. Furthermore, the nickel mass fraction on the substrate surface was found to increase gradually, while the copper mass fraction showed a revered trend. The increased nickel and decreased copper on the coating surface resulted in the coating colour to change from red to grey.

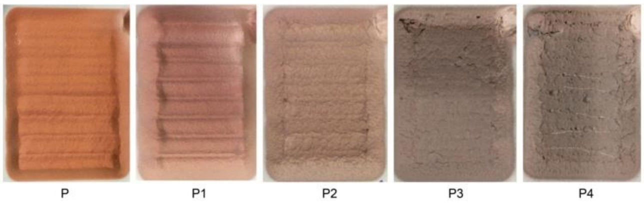

Fig. 2. Digital photos of the coatings fabricated with different powders and working conditions

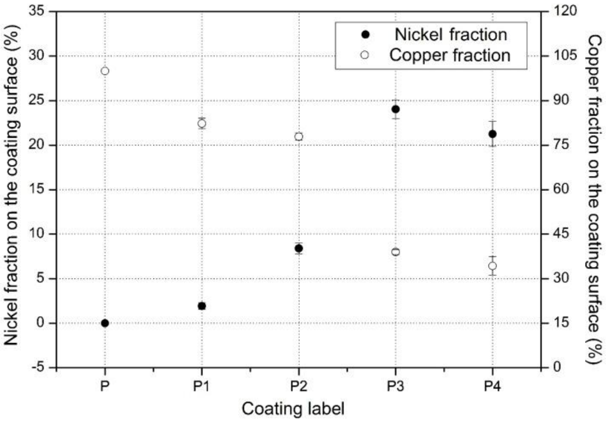

Fig. 3. EDS element analysis on the coating surface

Graphitization of the diamond during the fabrication of DCMC always occurs when using sintering or infiltration technique due to the high processing temperature [9,10,3,4]. However, the comparison of XRD spectra shown in Fig. 4 indicated that no graphitization occurred during the fabrication of cold sprayed DCMC coatings due to the relatively low processing temperature. This fact clearly showed the advantage of cold spray over other techniques in avoiding the diamond graphitization. Moreover, from Fig.4, it is also found that the peak of nickel and diamond phase exhibited significant difference, which suggested that the diamond mass fraction in different coatings must differ from each other.

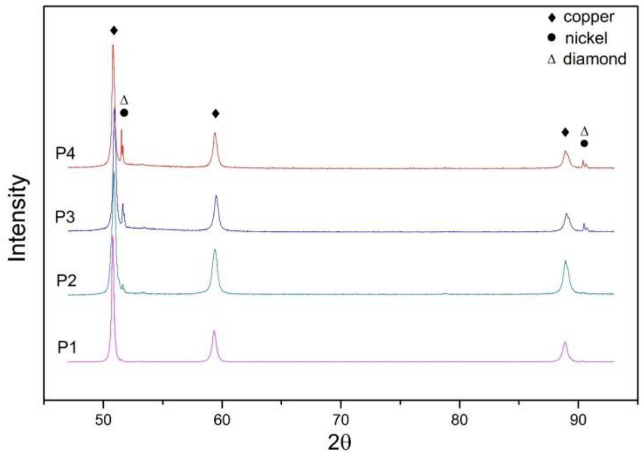

Fig. 4. XRD spectra of different coatings

Therefore, in order to quantitatively analyse the diamond mass fraction inside the coatings, Fig. 5 provides the diamond mass fraction measured at the coating cross-section by EDS. It is clearly seen that P3 and P4 coatings fabricated with pure clad diamond contained more than 40 wt.% of diamond. In comparison with the original feedstock, the diamond mass fraction in the coating was almost unchanged. Such high fraction has never been achieved in cold or thermal sprayed DCMC coatings.

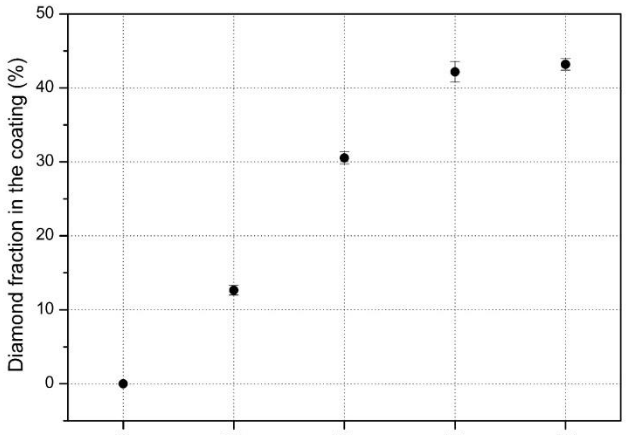

Fig. 5. EDS element analysis on the coating cross-section

In addition, for the coatings fabricated with mixed powders (copper + clad diamond), the diamond mass fraction reached 12.6 wt.% for P1 and 30.5wt.% for P2. The contents were even higher than those in the original feedstock, which implied that clad diamond was easier to deposit and had higher deposition efficiency than copper. In previous cold spray works where mechanically mixed metal-diamond powders were used as the feedstock [7,11,12], most of the diamond could not successful deposit and thus the diamond mass fraction in the coating was normally very low. The excellent performance of clad diamond in this work clearly indicated that it will be a promising feedstock and have great potential to fabricate cold sprayed DCMC coatings.

3.2 Coating microstructure

Diamond fraction and purity (non-graphitization) are critical to the coating performance, while coating microstructure is also very important and thus worthy to be further investigated. Figure 6 shows the cross-sectional SEM images of the DCMC coatings fabricated with different powders and working conditions. From Fig. 6a-d, it is clearly seen that the diamond phase was uniformly distributed in the coating for each sample. It was known that the uniformity of diamond in the DCMC has decisive effect on the final coating thermal properties. In this work, the cold sprayed DCMC coatings fabricated with the clad diamond powders exhibited excellent uniformity, providing an essential condition for the high thermal performance. Besides, an obvious difference in the diamond fraction between each sample can be found from Fig. 6a-d. P3 and P4 coatings contained more diamond than P2 coating and much more than P1 coating, which is consistent with the EDS element analysis shown in Fig. 5.

Furthermore, the magnified images of the cross-section is given in Fig. 6e-h to clarify the diamond fracture behaviour in the coating. It is interesting to find that the diamond in the coating fabricated with mixed powders (P1 and P2) was hardly fractured after deposition. Diamond in the P1 coating almost had no damage, while cracks and few small diamond pieces can be found in P2 coating. However, for P3 and P4 coatings fabricated with pure clad diamond powders, the diamond phase was significantly fractured into small pieces, particularly for the P4 coating fabricated with higher impact velocity. The reason for this difference is attributed to the additional copper powders. For P1 and P2, the soft copper powders could act as a buffer to the clad diamond powders. When diamond particles impacted on the soft copper, the kinetic energy will be absorbed through the plastic deformation of copper. The impacting stress was therefore insufficient to damage the diamond. Nevertheless, for P3 and P4 coatings, the outside metal layer was very thin, most of the impact energy was directly imposed on the inside diamond due to the absent of the buffer materials Hence, most of the diamond was fractured during the deposition. P4 coating fabricated at higher inlet pressure therefore had more fractured diamond pieces than P3 coating.

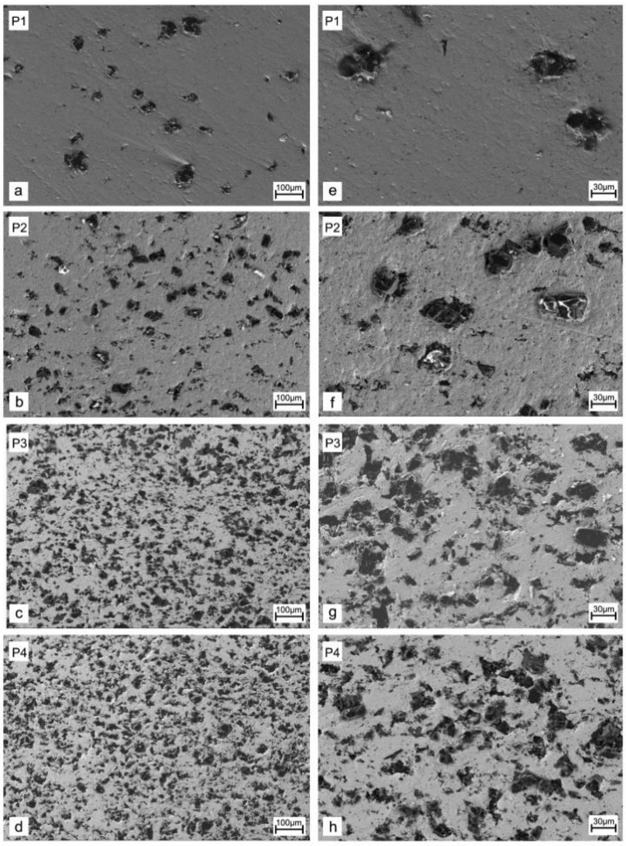

Fig. 6. Cross-sectional SEM images of MMC coatings fabricated with different powders and working conditions

To further clarify the coating microstructure and formation mechanism, Fig. 7 provides the SEM images of the coating fracture surface. As can be seen from Fig. 7a and b, the diamond in P1 coating was intact without any damage, while P2 coating had both an undamaged diamond and a cracked diamond, which is consistent with the cross-sectional view as show in Fig. 6e and 6f. In addition, the metal jet and metallic bonding features can be clearly observed in the P1 and P2 coatings. This fact means that the bonding in P1 and P2 is based on the conventional formation mechanism in cold spraying; coating was formed through the plastic deformation and adiabatic shear of copper powders and copper cladding. However, for P3 coating shown in Fig. 7c, a seriously cracked diamond and the surrounding small diamond pieces can be clearly observed. Particularly, in the P4 coating, diamond was completely fractured into many small pieces. For these two cases, differing from the P1 and P2 coatings, bonding only occurred between the copper claddings, and the coating was formed through fractured diamond uniformly dispersing into the metal phase [13]. Besides, another interesting phenomenon is most of the fracture happened at the metal-diamond interface. This phenomenon means that the metal-to-metal bonding strength in the coating was sufficiently high although the copper cladding is very thin.

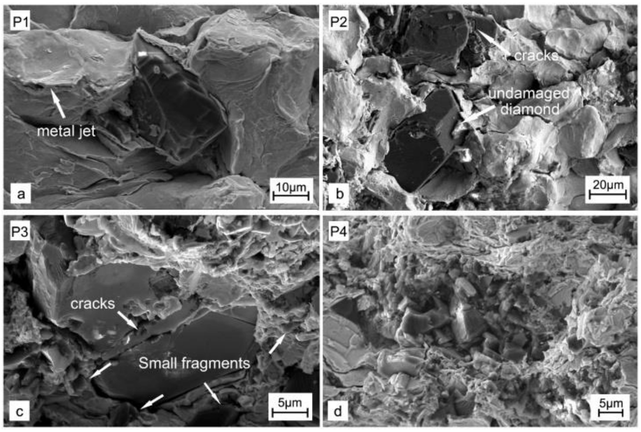

Fig. 7. SEM images of the fracture surface of MMC coatings fabricated with different powders and working conditions

Conclusions

In this paper, a range of diamond-reinforced copper matrix composites (DCMC) were fabricated via the cold spray technique using the copper-clad diamond powder or its mixture with pure copper powder. Copper-clad diamond is a novel powder consisting of an inside diamond powder, a very thin interbedded nickel layer and an outside electroless copper cladding. The experimental results indicated that all the as-sprayed DCMC coatings fabricated with different powders had thickness of more than 5 mm, much thicker than those produced by CVD. When using pure clad diamond powder as the feedstock, the coating was formed through the bonding between copper claddings and the fractured diamond uniformly dispersing into the metal phase. The diamond in the feestock was fully transfered in the coatings. . The diamond mass fraction reached more than 40 wt.%. Such level has not been achieved in previous cold spray works with conventional powders. As for the mechanically mixed powder of clad diamond and copper, the coating was formed through the plastic deformation and adiabatic shear of copper powder and copper cladding, which is similar with the conventional formation mechanism of cold spray coating. The coating also exhibited great retainbility for diamond; the diamond fraction in the coating was even larger than that in the original feedstock. Besides, because of the additional copper powders acting as a buffer, the fracture of diamond in the coating was effectively prevented. In summary, cold spray technique and clad diamond had great potential to produce the DCMC coatings.

Acknowledgments

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