



Regular Article

A novel method for metal–diamond composite coating deposition with cold spray and formation mechanism

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ABSTRACT

This paper describes the application of cold spray to the deposition of a diamond grade pre-coated with Cu and Ni. This is the first time that pre-coated diamond powders are used as the sole feedstock without the addition of binders (ductile phases) in cold spraying. The experimental results showed that it was possible to manufacture thick metal–diamond composite coatings onto an Al alloy substrate with high diamond fraction in the coating and without phase change. Results from this paper also have demonstrated a new methodology for the deposition of metal–diamond/ceramic composite coating with the cold spray technique.

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Synthetic diamond coatings have been used extensively to improve the properties of surfaces for manufacturing processes, due to favourable material properties such as high hardness, improved wear resistance, excellent thermal conductivity, chemical inertness and low coefficient of friction. Furthermore, diamond like carbon (DLC), which has a structure between that of diamond and graphite, has been used as a cheaper alternative to synthetic diamond while still maintaining similar material properties. These coatings are commonly applied using physical [1–3] or chemical vapour deposition [4]. More recently, a novel ball impact process was used to fabricate DLC coatings on stainless steel substrates in an atmosphere of methane gas [5]. In this technique, metal or ceramic balls and powder particles are placed inside a vibration chamber. The vibration causes the balls to accelerate and repeatedly impact the inner metal surface of the chamber. As a result, the metal surface is rapidly coated with the powder particles. However, the current methods to manufacture diamond-based coatings present several disadvantages. They are only suitable for small scale components with limited possible feedstock/substrate combinations, they typically require complex and expensive pre-processing steps, or they involve the use of toxic waste products. An industrial push therefore exists to move from current technologies to alternative methods with higher efficiency.

Cold spray (CS) is a relatively new deposition method, whereby materials can be deposited onto surfaces in a solid-state manner without

heating above the melting temperature [6–8]. In this process, the feedstock material (in the form of powder) is accelerated to supersonic speeds in a converging–diverging nozzle using an inert carrier gas. The gas and powder mixture is fed at high pressure into the nozzle inlet and made to expand in the internal channel; powder speed levels in excess of 1000 m/s can be reached at the nozzle exit. When particles impact on a surface a plastic deformation process occurs. Above a critical impact velocity for the powder–substrate combination the particles will bond to the surface, and form a coating. CS has been tested with a number of materials, including high performance metals and alloys [6–9], composite materials [10,11] and also pure ceramics [12,13]. Using CS it is possible to produce oxygen- and thermal-sensitive coatings on different substrates without the necessity of special environmental conditions.

A major technical disadvantage of CS is the reliance on plastic deformation for the coating formation; typically only ductile materials can be processed. The development of hard or ceramic coatings (to include diamond) is difficult and possible only with the addition of a supplementary binder to the feedstock, typically a soft metal. This binder is often required in large volume fractions. It has been reported that, in the cold sprayed metal–diamond composite coating, the fraction of diamond in the as-sprayed coating was difficult to be maintained as in the original feedstock; normally lower than 40%–50% [14,15]. A study by Suo et al. reported that ball-milled metal–diamond feedstock was able to greatly retain the fraction of diamond particles in the coating, however it led to very small-size diamond distribution in the coating at the same time [16]. In this case the large number of interfaces

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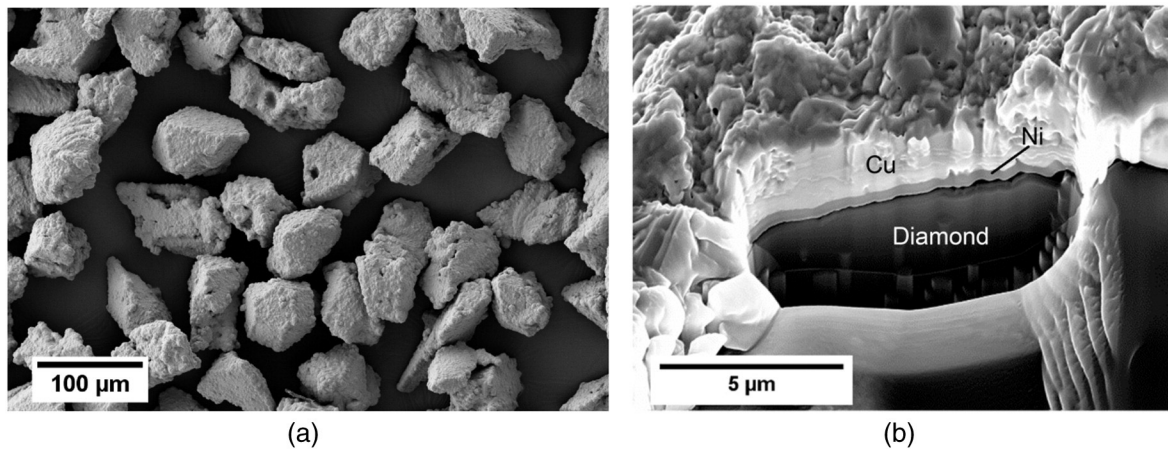


Fig. 1. (a) SEM image of powder used. (b) Single particle image after FIB milling, showing Ni and Cu layers.

between hard and soft phases in the coating would act as the barrier for thermal conduction and thus may lower the coating performance. Recently, Na et al. used Ni-coated diamond powders mixed with bronze to produce metal–diamond composite coating, and the result indicated that this special feedstock resulted in more uniform diamond distribution and higher deposition efficiency of the diamond phase because the surrounding Ni layer on the diamond surface acts as a binder to the soft phase [17]. Although the existing works have successfully produced metal–diamond composite coatings, it was noticed that dilute metal powders must be used as a binder phase in the feedstock leading to strong miss-matches in composition between the feedstock and the coating. In the current work, for the first time, the dilute metal powder is not included in the feedstock. Instead the hard diamond powder is pre-coated with a thin layer of ductile metal and coated directly, which was not previously attempted. The rationale behind the study is directly linked to the hypothesis that the diamond alone would not be processable with CS, but the addition of a ductile metal interface between particles might allow for CS deposition to occur. It is demonstrated in this paper that deposition occurs in a more efficient manner when compared against the conventional pre-mixing of ductile and hard-phases prior to spraying; in particular this strategy has allowed to maintain practically unchanged the diamond concentration from the feedstock to the coating; hence without losses in hard-phase content.

A bespoke cold spray system in Trinity College Dublin consisting of a commercial high pressure powder feeder (wheel type, Uniquocoat Technologies, US) and a gas system capable of delivering pressure ranges of 0.5–3.5 MPa at the nozzle inlet was used in this study. The converging–diverging nozzle used for the diamond tests is an in-house design, approximately 190 mm long with a throat or restriction cross-sectional diameter of 2 mm, and an exit diameter of 6 mm. The nozzle is made out of WC, so as to minimize abrasive wear of the internal

profile during spraying operations. The substrate was placed on a CNC X–Y stages system, with the nozzle held stationary during spraying operations. Helium at room temperature was used as a carrier gas, using a nozzle inlet pressure of 2.0 MPa, with a nozzle standoff distance of 40 mm and a substrate traverse speed of 20 mm/s. The substrate material was a flat Al6082 T6 plate (3.1 mm thick), while the powder feeder wheel speed was set to 35% of its maximum. No surface pretreatment was undertaken prior to the coating operation. A SEM equipped with EDX unit (Carl Zeiss ULTRA, Germany) was used for the coating and powder observation and element analysis, while a FIB system (DB235, FEI Strata, USA) was used to investigate the coating thickness and structure of the powder. The cross-section of the coating was obtained by fracture, removing the need for polishing steps which would likely pull out any diamond contained within the coating. Using this method it was possible to preserve and observe critical topological information. The feedstock and coatings were examined by an X-Ray diffractometer system (Siemens D500, Germany) operating at 40 kV and 30 mA with Cu K α radiation at a wavelength of 0.1542 nm. The scan was conducted in 2 θ mode and spanned across a range of 20° to 80° with a step resolution of 0.02° per second.

The powder used in these tests is a commercial grade of diamond (Element Six, PDA C50, 270–325 US mesh) with an electroless Ni and Cu clad of approximately 2–5 μ m in thickness. Before adding the Cu clad, the diamond is Ni coated. A SEM picture of the diamond particles is shown in Fig. 1a. The metal clad on the outer surface of each grit is therefore the combination of Ni and Cu for a total weight distribution between metal phases and diamond of approximately 50–50. This ratio can slightly vary from particle to particle. Powder size analysis showed that the particles are rather large in diameter when compared to typical cold spray powders, with a D₁₀ of 56.0 μ m, D₅₀ of 73.8 μ m and D₉₀ of 96.7 μ m obtained using a size analyser by Malvern. The

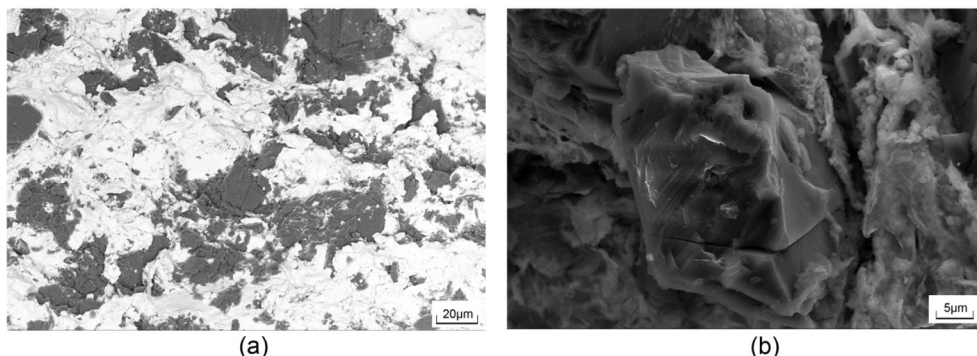


Fig. 2. (a) SEM backscatter image of coating, showing fractured diamond particles. (b) Etched coating revealing diamond grains.

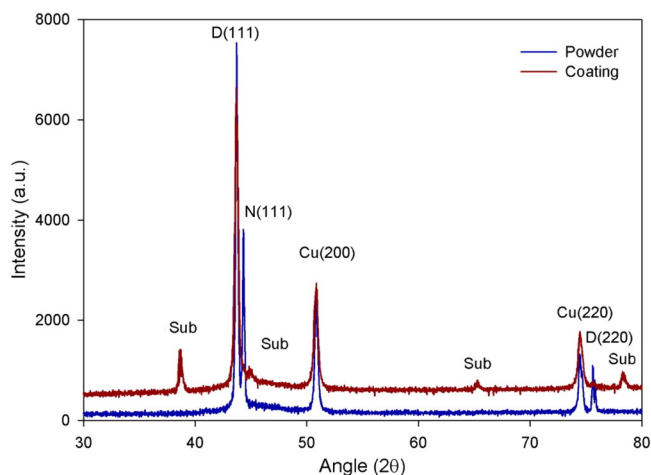


Fig. 3. Comparison of XRD spectra between feedstock and coating. Sub, D, N and Cu refer to substrate, diamond, Nickel and Copper, respectively.

thickness of the Ni and Cu layers can be seen in Fig. 1b, where the layer has debonded from the diamond particle during FIB milling, and two distinct layers can be clearly seen in the coating. EDX analysis confirms that these layers comprise an approximately 0.5 μm thick layer of Ni between the diamond and Cu, with a 1.5–2.0 μm thick layer of Cu on the surface. The density of Cu, Ni and diamond are 8960, 8908 and 3520 kg/m^3 .

It was observed in preliminary trials that for nozzle inlet pressures lower than 2 MPa no substantial deposition occurred. The peak coating thickness for a single pass coating was measured to be approximately 0.9 mm at an inlet pressure of 2.0 MPa. Fig. 2 shows a back-scattered SEM image of the coating cross-section, and a single diamond particle after chemical etching of the deposit. The darker regions indicates the abundant presence of carbon (as expected), which has a low atomic number ($Z = 6$), and lighter regions indicating Cu and Ni (the metallic coating) which have higher atomic numbers ($Z = 28, 29$ respectively). The coating density appears high in the micrographs, though no direct analysis was performed for the scope of this study. A follow on EDX analysis was carried out to reveal the chemical composition of the coating. The analysis showed that for the top surface of the coating (utmost layer) the carbon content was 45.74% by weight, with 22.15% Ni comprising 22.15% and Cu making up 29.74%, with the remainder trace elements to include a small amount of oxygen. A similar analysis for the cross-section of the coating showed 56.25% carbon, 13.56% Ni

and 25.86% Cu. The higher level of carbon in the cross-section may indicate that the diamond particles tend to embed below the surface of the metal during coating. These results are very much in agreement with the specifications provided by the powder manufacturer of 50:50 diamond:Cu/Ni by weight. This indicates that the fraction of the diamond in the coating has practically no loss. Also, the composite coating obtained in this work has the largest percentage of diamond compared to previous reported results. However, it is evident from Fig. 2a the diamond particles are of smaller size than would be expected given the particle size analysis reported earlier, which means some of the large diamond particles have fractured during the deposition process. From Fig. 2b, such fracture of the diamond particle due to the extremely large impact stress can be clearly observed. This correlates with results reported in previous studies [14]. Thermal processing of diamond can easily induce graphitization of the same; Fig. 3 shows a comparison of the XRD spectra of the feedstock and the resultant coating. The aperture size of the XRD beam was 12 mm \times 0.4 mm. The sample stage was rotated on measuring to avoid issues with specific orientations and grain sizes and hence has a spot size of 12 mm in diameter. It is clear that graphitization of the diamond did not take place during the deposition process as it was possible to keep the working temperatures low enough (CS does not require the addition of strong heat inputs). This is not typically the case; in a recent work published by Yao et al. [18] serious graphitization had occurred in diamond/Ni60 deposition using laser cladding due to the high level of temperature. From Fig. 3, there is also a reduction in the D220 in the coated sample which could be a result of the aforementioned fragmentation of the diamond during deposition. Peaks pointing to the substrate material (Sub) are also visible in the coating spectrum due to overlaps with the interface region.

Conventional hard/soft composite cold spray coatings are created by hard particles embedding within a coating formed from a softer material. However, when the hard particles are coated with the softer material with no other dilute metal phase added, the hard particles do not have a softer coating material to embed into, as would occur in a diamond composite coating fabricated by a mechanically mixed feedstock. For the coating detailed in this work, a unique formation mechanism is proposed. Fig. 4 shows a schematic of this coating formation mechanism. When the particle impacts on the formed coating, the thin Cu/Ni layer (soft phase) experiences strong plastic deformation, causing extrusion from the central region. The diamond which was originally enclosed in the particle may impact with a diamond particle currently embedded within the coating. Modelling results have indicated that the stress during the impact process between two metal-coated-diamond particles would reach 11.32 GPa, much larger than the fracture stress of diamond (5.8 GPa) [17]. In this case, extremely high impact

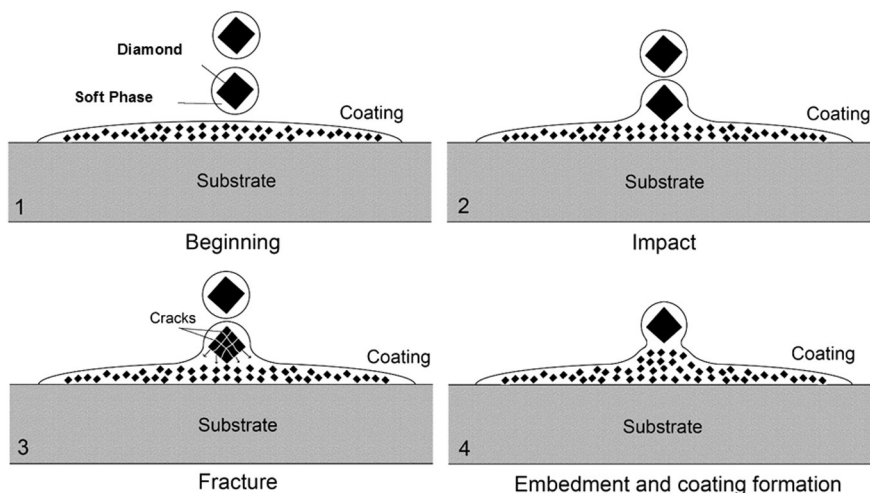


Fig. 4. Metal-coated diamond composite coating formation mechanism.

stress causes the incident diamond particle to shatter into many small pieces. These small diamond particles still possess high kinetic energy, allowing them to penetrate into and distribute in the soft metal phase of the coating, as suggested by the increased carbon percentage in the EDX results on the cross section. The metal–diamond coating is then formed in this manner, with the fracture of the diamond causing the formation of the composite coating. In the absence of the metal dilute phase it is forecasted that diamond particles would still shatter at impact (the impact energy would be roughly the same), but no coating could form under CS working conditions. In some circumstances, diamond particles were not completely fractured into pieces, as can be seen in Fig. 2. This shows that large particles also have chance to embed into the coating where the percentage of soft phase is relatively high. A very critical role is therefore played by the soft-phase. There is no doubt there will be a minimum thickness by which shattering of the diamond happens, and the coating can still form without diamond losses by rebound effects. Under this conditions the diamond % in the coating would be at maximum. However, one can think of the most extreme case where there is no soft-phase; in this scenario the diamond is not processable with CS.

In summary, a preliminary investigation into the feasibility of depositing diamond coatings onto surfaces using cold spray was carried out. It was possible to achieve diamond deposition using a new methodology onto a flat Al6082 T6 plate, using particles which had been pre-coated with a ductile phase (Cu/Ni) so as to allow for direct processing. No substrate pre-treatment was applied. SEM and EDX experimental results have demonstrated the transfer of properties from the feedstock to the coating. The measured weight fraction of diamond in the coating exceeded 50%, a result which has not previously achieved with cold spray using pre-mixed feedstocks. The coating formation mechanism was observed to depend upon the shattering of the diamond particles. Diamond has a high thermal conductivity, but is difficult to deposit

over large areas or at high deposition rates. This study has therefore demonstrated a new method for the deposition of non-ductile materials onto surfaces with the potential of leading to important applications in engineering.

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