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1 **A novel method for metal-diamond composite coating deposition with cold**

2 **spray and formation mechanism**

3 Barry Aldwell[1], Shuo Yin[1], Kevin A. McDonnell[2], Daniel Trimble[1], Tanvir Hussain[3] and Rocco Lupoi[1*]

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5 *[1]Trinity College Dublin, The University of Dublin, Department of Mechanical and Manufacturing Engineering,*

6 *Parsons Building, Dublin 2, Ireland.*

7 *[2]Univeristy College Dublin, School of Mechanical and Materials Engineering, Belfield, Dublin 4, Ireland.*

8 *[3]University of Nottingham, Division of Materials, Mechanics and Structure, Nottingham, NG7 2RD, UK.*

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10 **Abstract:** This paper describes the application of cold spray to the deposition of a diamond grade pre-coated

11 with Cu and Ni. This is the first time that pre-coated diamond powders are used as the sole feedstock without the

12 addition of binders (ductile phases) in cold spraying. The experimental results showed that it was possible to

13 manufacture thick metal-diamond composite coatings with high diamond fraction in the coating but without

14 phase change. Results from this paper also have demonstrated a new methodology for the deposition of metal-

15 diamond/ceramic composite coating with cold spray technique.

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18

19 Synthetic diamond coatings have been used extensively to improve the properties of various substrates for

20 manufacturing processes, due to favourable material properties such as high hardness, improved wear resistance,

21 excellent thermal conductivity, chemical inertness and low coefficient of friction. Furthermore, Diamond like

22 Carbon (DLC), which has a structure between that of diamond and graphite, has been used as a cheaper

23 alternative to synthetic diamond while still maintaining similar material properties. These coatings are

24 commonly applied using physical [1-3] or chemical vapour deposition [4]. More recently, a novel ball impact

25 process was used to fabricate DLC coatings on stainless steel substrates in an atmosphere of methane gas [5]. In

26 this technique, metal or ceramic balls and powder particles are placed inside a vibration chamber. The vibration

27 causes the balls to accelerate and repeatedly impact the inner metal surface of the chamber. As a result, the

28 metal surface is rapidly coated with the powder particles. However, the current methods to manufacture

*Corresponding author. Tel: +353 1 896 1729. Email: lupoir@tcd.ie

29   diamond-based coatings present several disadvantages. They are only suitable for small scale components with

30   limited possible feedstock/substrate combinations, they typically require complex and expensive pre-processing

31   steps, or they involve the use of toxic waste products. An industrial push therefore exists to move from current

32   technologies to alternative methods with higher efficiency.

33

34   Cold Spray (CS) is a relatively new deposition method, whereby materials can be deposited onto surfaces in a

35   solid-state manner, without heating above the melting temperature [6-8]. In this process, the feedstock material

36   (in the form of powder) is accelerated to supersonic speeds in a converging-diverging nozzle using an inert

37   carrier gas. The gas and powder mixture is fed at high pressure into the nozzle inlet and made to expand in the

38   internal channel; powder speed levels in excess of 1000 m/s can be reached at the nozzle exit. When particles

39   impact on a surface a plastic deformation process occurs. Above a critical impact velocity for the powder-

40   substrate combination the particles will bond to the surface, and form a coating. CS has been tested with a

41   number of materials, including high performance metals and alloys [6-9], composite materials [10, 11] and also

42   pure ceramics [12, 13]. Using CS it is possible to produce oxygen- and thermal- sensitive coatings on different

43   substrates without the necessity of special environmental conditions.

44

45   A major technical disadvantage of CS is the reliance on plastic deformation to form a coating; typically only

46   ductile materials can be processed. The formation of hard or ceramic coatings (to include diamond) is difficult

47   and possible only with the addition of a supplementary binder to the feedstock, typically a soft metal. This

48   binder is often required in large volume fractions. It has been reported that, in the cold sprayed metal-diamond

49   composite coating, the fraction of diamond in the as-sprayed coating was difficult to retain the same fraction of

50   the original feedstock, normally lower than 40%-50% [14, 15]. A study by Suo et al. reported that ball-milled

51   metal-diamond feedstock was able to greatly retain the fraction of diamond particles in the coating, while it led

52   to very small-size diamond distribution in the coating at the same time [16]. A large number of interfaces

53   between hard and soft phases in the coating would act as the barrier for thermal conduction and thus may lower

54   the coating performance. Recently, Na et al. used Ni-coated diamond powders mixed with bronze to produce

55   metal-diamond composite coating, and the result indicated that this special feedstock resulted in more uniform

56   diamond distribution and higher deposition efficiency of the diamond phase because the surrounding Ni layer on

57   the diamond surface acts as a binder to the soft phase [17]. Although the existing works have successfully

58   produced metal-diamond composite coatings, it was noticed that dilute metal powders must be used as a binder

59 phase in the feedstock leading to strong miss-matches in ration composition between the feedstock and the

60 coating. In the current work, for the first time, the dilute metal powder is not included in the feedstock. Instead

61 the hard diamond powder is pre-coated with a thin layer of ductile metal and coated directly, which was not

62 previously attempted. The rationale behind the study is directly linked to the hypothesis that the diamond alone

63 would not be processable with CS, but the addition of a ductile metal interface between particles might allow for

64 CS deposition to occur. It is demonstrated in this paper that deposition occurs in a more efficient manner when

65 compared against the conventional pre-mixing of ductile and hard-phases prior to spraying; in particular this

66 strategy has allowed to maintain practically unchanged the diamond concentration from the feedstock to the

67 coating; hence without losses in hard-phase content.

68

69 A bespoke cold spray system consisting of a commercial high pressure powder feeder (wheel type, Uniquecoat

70 Technologies, US) and a gas system capable of delivering pressure ranges of 0.5 - 3.5 MPa at the nozzle inlet.

71 The converging-diverging nozzle used for the diamond tests is an in-house design, approximately 190 mm long

72 with a throat or restriction cross-sectional diameter of 2mm, and an exit diameter of 6mm. The nozzle is made

73 out of WC, so as to minimize abrasive wear of the nozzle during spraying operations. The substrate is placed on

74 a CNC X-Y stages system, with the nozzle held stationary during spraying operations. Helium at room

75 temperature was used as a carrier gas, using a nozzle inlet pressure of 2.0 MPa, with a nozzle standoff distance

76 of 40 mm and a substrate traverse speed of 20 mm/s. The substrate material was a flat Al6082 T6 plate (3.1mm

77 thick), while the powder feeder wheel speed was set to 35% of its maximum. No surface pretreatment was

78 undertaken prior to the coating operation. A SEM equipped with EDX unit (Carl Zeiss ULTRA, Germany) was

79 used for the coating and powder observation and element analysis, while a FIB system (DB235, FEI Strata,

80 USA) was used to investigate the thickness and microstructure of the powder. The cross-section of the coating

81 was obtained by fracture, removing the need for polishing steps which would likely pull out any diamond

82 contained within the coating. Using this method it was possible to preserve and observe critical topological

83 information. The feedstock and coatings were examined by a X-Ray diffractometer system (Siemens D500,

84 Germany) operating at 40 kV and 30 mA with Cu Kα radiation at a wavelength of 0.1542 nm. The scan was

85 conducted in 2θ mode and spanned across a range of 20° to 80° with a step resolution of 0.02° per second.

86

87 The powder used in these tests is a commercial grade of diamond (Element Six, PDA C50, 270-325 US mesh)

88 with an electroless Ni and Cu clad of approximately 2-5 µm in thickness. Before adding the Cu clad, the

89 diamond is Ni coated. A SEM picture of the diamond particles is shown in Figure 1a. The metal clad on the

90 outer surface of each grit is, in reality, the combination of Ni and Cu for a total weight distribution between

91 metal phases and diamond of approximately 50-50. This ratio can slightly vary from particle to particle. Particle

92 size analysis, showed that the particles are quite large in diameter compared to typical cold spray powders, with

93 a D_{10} of 56.0 µm, D_{50} of 73.8 µm and D_{90} of 96.7 µm obtained using a size analyser by Malvern. The thickness

94 of the Ni and Cu layers can be seen in Figb, where the layer has debonded from the diamond particle during FIB

95 milling, and two distinct layers can be clearly seen in the coating. EDX analysis confirms that these layers

96 comprise an approximately 0.5 µm thick layer of Ni between the diamond and Cu, with a $1.5 - 2.0$ µm thick

97 layer of Cu on the surface. The density of Cu, Ni and diamond are 8960, 8908 and 3520 kg/m^3.
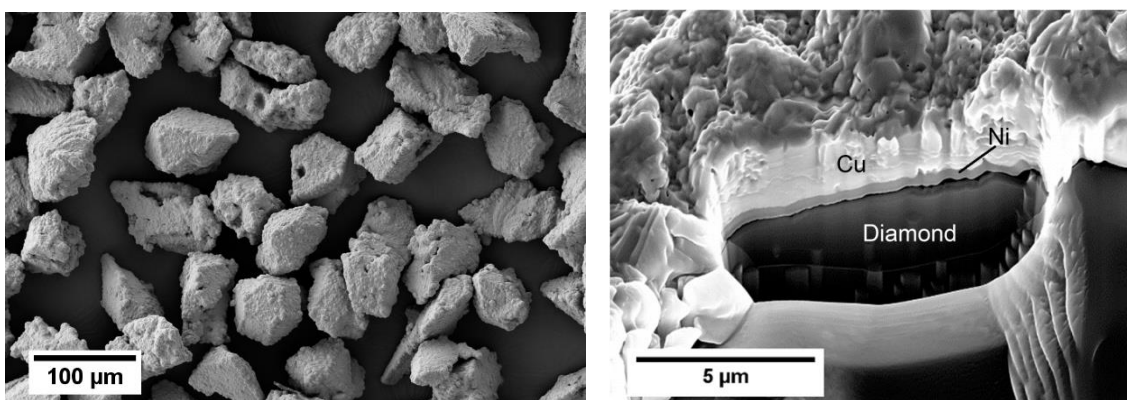
98

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

100 **layers.**

101

102 It was observed in preliminary trials that for nozzle inlet pressures lower than 2 MPa no substantial deposition

103 occurred. The peak coating thickness for a single pass coating was measured to be approximately 0.9 mm at an

104 inlet pressure of 2.0MPa. Figure 2 shows a back-scattered SEM image of the coating cross-section, and a single

105 diamond particle after chemical etching of the deposit. The darker regions indicates the abundant presence of

106 carbon (as expected), which has a low atomic number (Z=6), and lighter regions indicating Cu and Ni (the

107 metallic coating), which have higher atomic numbers (Z=28, 29 respectively). The coating density appears high,

108 though no direct analysis of coating density was performed for the scope of this study. A follow on EDX

109 analysis was carried out to reveal the chemical composition of the coating. The analysis showed that for the top

110 surface of the coating (uttermost layer) the carbon content was 45.74% by weight, with 22.15% Ni comprising

111 22.15% and Cu making up 29.74%, with the remainder trace elements to include a small amount of oxygen. A

112 similar analysis for the cross-section of the coating showed 56.25% carbon, 13.56% Ni and 25.86% Cu. The

113 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 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 Figure 2a that some of diamond particles are of smaller size than would be expected given the particle size analysis earlier, which means some of the large diamond particles have fractured during the deposition process. From Figure 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; Figure 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 x 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 graphitization of the diamond did not take place during the deposition process as it was possible to keep the working temperatures low enough (CS typically does not require the addition of strong heat inputs). This is not typically the case; in a recent work published by Yao at al. [18] serious graphitization had occurred in diamond/Ni60 deposition using Laser Cladding due to the high level of temperature. From Figure 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.
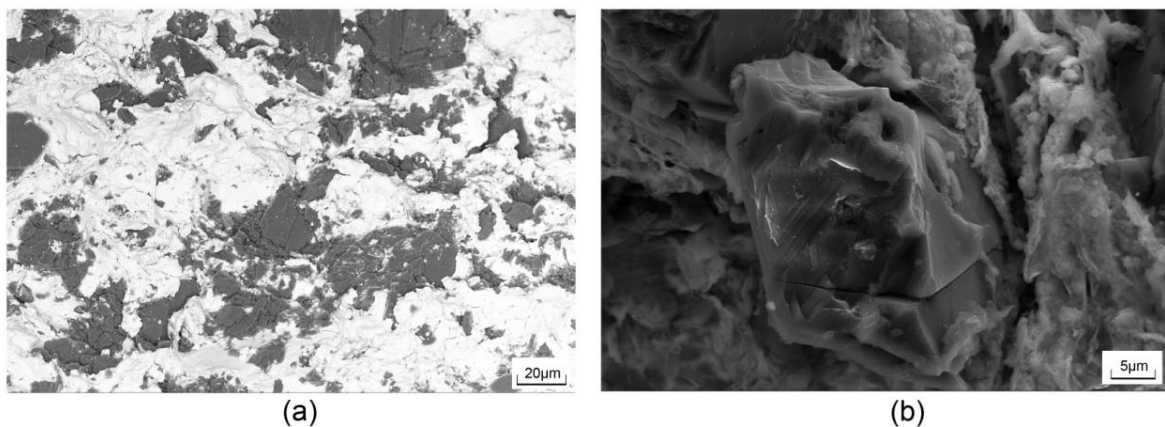
Fig. 2 (a) SEM backscatter image of coating, showing fractured diamond particles. (b) Etched coating revealing diamond grains.

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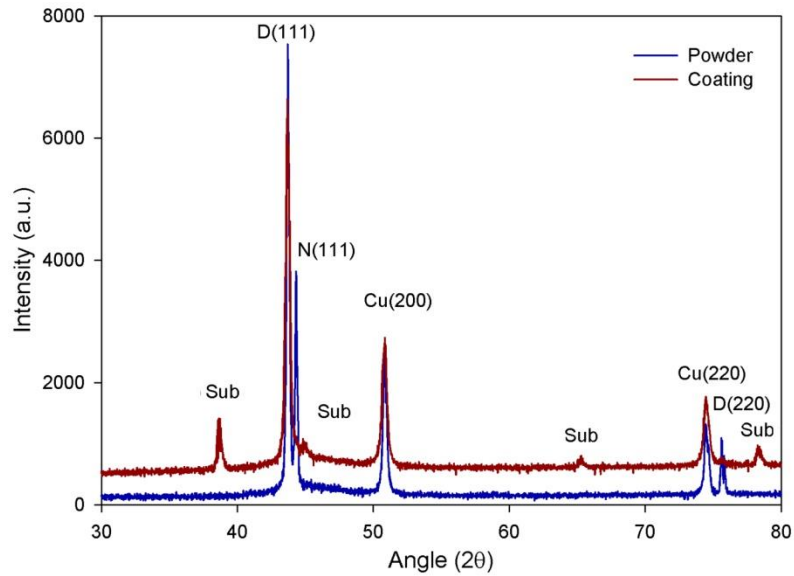
Fig. 3 Comparison of XRD spectra between feedstock and coating. Sub, D, N and Cu refer to substrate,

diamond, Ni and Cu, respectively.

Conventional hard/soft composite cold spray coatings are created by hard particles embedding within a coating formed from the 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 mechanically mixed feedstock. For the coating detailed in this work, a unique coating formation mechanism is proposed. Figure 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. Previous modelling results have indicated that the stress during the impact process between two metal-coated-diamond particles would reach 11.32GPa, much larger than the fracture stress of diamond (5.8GPa) [17]. In this case, extremely high impact 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 Figure 2. This shows that large particles also have chance to embed into the coating

156   where the percentage of soft phase is relatively high. <mark>A very critical role is therefore played by the soft-phase.</mark>

157   <mark>There is no doubt there will be a minimum thickness by which shattering of the diamond happens, and the</mark>

158   <mark>coating can still form without diamond lossess by rebound effects. Under this conditions the diamond % in the</mark>

159   <mark>coating would be maximum. However, one can think of the most exterme case where there is no soft-phase; in</mark>

160   <mark>this scenario the diamond is not processable with CS.</mark>

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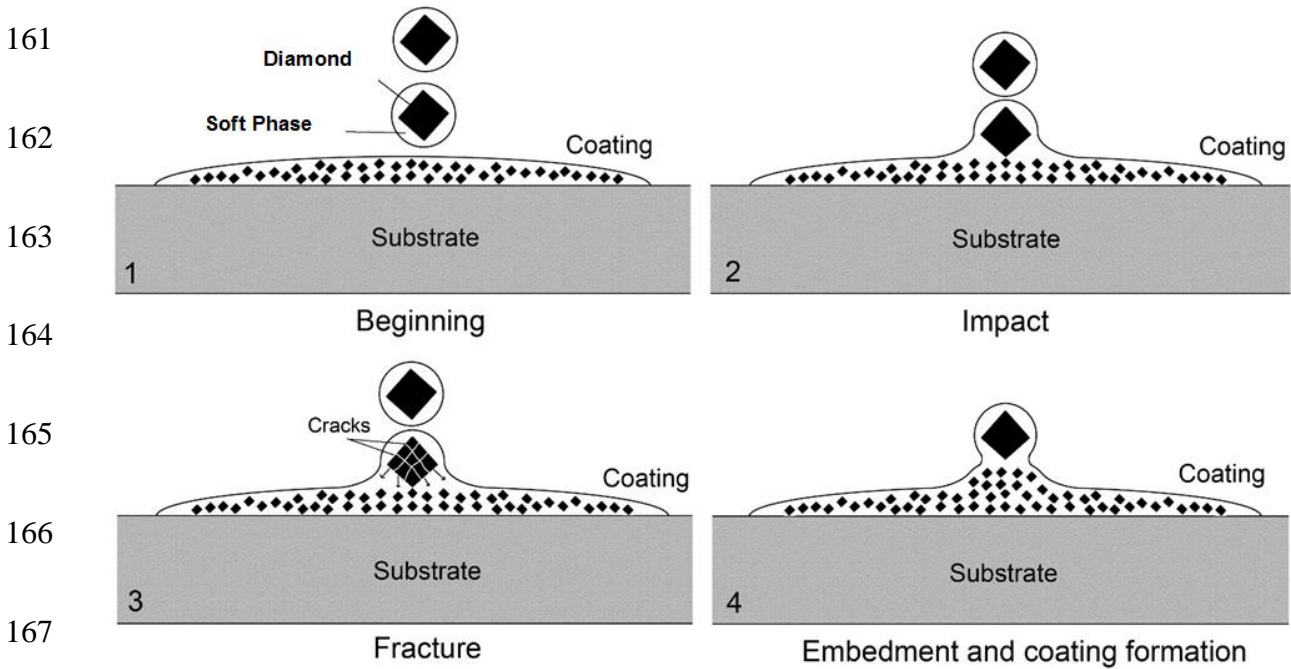
168   **Fig. 4 Metal-coated Diamond composite coating formation mechanism**

169   In summary, a preliminary investigation into the feasibility of depositing diamond coatings onto surfaces using

170   cold spray was carried out. It was possible to achieve diamond deposition using a new methodology, using

171   particles which have been pre-coated with a ductile phase (Cu/Ni) so as to allow for direct coating using cold

172   spray. SEM and EDX experimental results have demonstrated the transfer of properties from the feedstock to

173   the coating. The measured weight fraction of diamond in the coating exceeded 50%, a result which has not

174   previously achieved with cold spray using pre-mixed feedstocks. The coating formation mechanism was

175   observed to depend upon the shattering of the diamond particles. Diamond has a high thermal conductivity, but

176   is difficult to deposit over large areas or at high deposition rates. This study has therefore demonstrated a new

177   method for the deposition of non-ductile materials onto surfaces.

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