1 Supplementary Information

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3 N-heterocyclic Carbene-Promoted Copper Powder Conditioning for

4 Thermal Spray Applications

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61 1 Experimental Section

62 1.1 Materials

63 Copper (Cu) powder was procured from Sigma Aldrich (Canada)[®] with a purity of >98.0%. HPLC 64 grade methanol was obtained from Fischer Chemical (Canada)[®] and used without any further 65 purification. The 1,3-Diisopropylbenzimidazolium hydrogen carbonate (NHC•H₂CO₃) was 66 synthesized by our collaborators at Queen University and the procedure for synthesizing 67 NHC•H₂CO₃ is described in section 1.2. The received NHC•H₂CO₃ was used without any further 68 modifications.

69 1.2 Synthesis of 1,3-Diisopropylbenzimadazolium hydrogen carbonate (NHC•H₂CO₃)

All synthetic reactions were conducted under air unless otherwise stated. Solvents were used 70 without purification except where stated. Unless otherwise noted, chemicals were purchased from 71 chemical suppliers at the highest purity and used as received. Amberlyst A26 hydroxide resin was 72 activated by sparging a solution with CO₂ for 30 minutes before use as the HCO₃ resin.¹ ¹H and 73 ¹³C[¹H] NMR spectra were recorded at Queen's University using Bruker Avance 400, 500, or 700 74 MHz spectrometers at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) and are 75 referenced to residual protonated (¹H) or deuterated (¹³C[¹H]) solvent signals. Chemical shifts of 76 known solvent impurities were referenced in the literature.² Coupling constants (J) are reported as 77 absolute values. All NMR data were processed and displayed using Bruker Topspin or 78 MestReNova software. Elemental analyses were performed at Queen's University using a Flash 79 2000 CHNS-O analyzer. Electrospray ionization mass spectra (ESI-MS) of small molecules were 80 recorded at Queen's University using a Thermo Fisher Orbitrap VelosPro mass spectrometer with 81 a heated-electrospray ionization probe. 82

1,3-Diisopropylbenzimidazolium iodide: Prepared by literature procedure with modifications.¹ 83 In a pressure tube, benzimidazole (11.84 g, 100 mmol, 1 eq), K₂CO₃ (20.80 g, 150 mmol, 1.5 eq) 84 and acetonitrile (200 mL) were added. 2-iodopropane (31 mL, 300 mmol, 5 eq) was slowly added 85 and the flask was sealed and stirred at 90 °C for 48 h. The reaction mixture was allowed to cool to 86 room temperature and was then transferred to a round-bottom flask and the solvent was removed. 87 Dichloromethane was added until just dissolved and diethyl ether was added to precipitate solid. 88 89 The solid was collected and washed with ether followed by subsequent drying under high vacuum to afford the desired colourless powder (79.4 % yield, 25.2 g). ¹H NMR (CDCl₃, 700 MHz): δ 90

91 10.92 (s, 1H), 7.81 (dd, J = 6.23, 3.15 Hz, 2H), 7.65 (dd, J = 6.30, 3.08 Hz), 5.21 (sept, J = 6.7992 Hz, 2H), 1.87 (d, J = 6.86 Hz, 12H). ¹³C NMR (CDCl3, 700 MHz): δ 139.62, 130.78, 127.04, 93 113.94, 52.45, 22.23. CHN: Calculated for C₁₃N₂H₁₉I : C: 47.29, H: 5.80, N: 8.48 Found: C: 47.75, 94 H: 5.82, N: 8.59 ESI-MS, calculated (m/z) for [C₁₃N₂H₁₉]+: 203.15; found: 203.17

1,3-Diisopropylbenzimidazolium bicarbonate: Prepared by literature procedure with 95 modifications.¹ Resin-HCO₃ (200 mL, 3 eq) suspended in water was measured in a graduated 96 cylinder and transferred to a 100 mL round bottom flask where the resin was allowed to settle, and 97 water was decanted off. The resin was washed with methanol three times. 1,3-98 Diisopropylbenzimidazolium iodide (16.5 g, 50.0 mmol, 1 eq) was dissolved in methanol (250 99 mL) and transferred to the resin. The mixture was stirred for 1 hour. The solution was passed 100 101 through a cotton plug and washed with methanol. The solvent was evaporated by the air stream 102 and the crude oily product was triturated in acetone and diethyl ether (1:1). The solvent was decanted, and trituration was repeated. Subsequent drying under a high vacuum afforded white 103 104 powder of product (57.0 % yield, 7.56 g). ¹H NMR (CDCl₃, 700 MHz): δ 8.07 (dd, J = 6.3, 3.2Hz, 2H), 7.75 (dd, J = 6.3, 3.1 Hz, 2H), 5.11 (sept, J = 6.7 Hz, 2H), 1.77 (d, J = 6.7 Hz, 12H). ¹³C 105 106 NMR (CDCl₃, 700 MHz): δ 161.42, 138.96, 132.59, 128.19, 114.97, 52.83, 22.11. CHN: Calculated for C₁₄N₂O₃H₂₀ : C: 63.62, H: 7.63, N: 10.60 Found: C: 62.41, H: 7.67, N: 10.31 107 108

109 1.3 Functionalization, Optimization, and Scale-up of NHC-treated Cu Powder

110 Immobilization of NHC on Cu powder was achieved by using the immersion method. Briefly, a 111 known amount of Cu powder (0.132 g) was taken in a conical flask followed by adding a known 112 concentration of NHC•H₂CO₃ solution (10 mM) in methanol, which generates active NHC species in-situ. The mixture was allowed to react under stirring conditions for 24 h followed by removing 113 it from the stirrer to allow the settling of Cu powder at the bottom of the flask. The settled powder 114 115 was washed multiple times with methanol to remove the unreacted and physically adsorbed NHC 116 followed by drying the powder under argon flow and thereafter stored in a desiccator connected to the vacuum. It is noteworthy to mention here that NHC is highly sensitive to both moisture and 117 environmental oxygen and therefore its proper handling is crucial before and after each 118 measurement. 119

120 To obtain the best coating, various reaction parameters such as concentration of NHC, reaction121 duration, and temperature, while stirring were optimized in detail (Table S1).

| Effect of stirring | |
|--|----------------------|
| Concentration of NHC solution (mM) | 5, 10, 20, 40 |
| Time of immobilization (h) | 12, 24, 48, 72 |
| Temperature during immobilization (°C) | r.t., 30, 40, 50, 60 |

122 **Table S1.** Optimization parameters varied during the process are shown below:

123

Depending on the amount of powder that is being treated, the volume of the NHC solution can be 124 varied to have uniform mixing among particles. Using optimized parameters, a scale-up process 125 was conducted keeping safety precautions in mind. The chosen parameters for scale-up were 10 126 127 mM NHC solution concentration, 24 h immobilization time, r.t., and continuous stirring. To coat approximately 1.5 Kg of powder, 3 x 500 ml solution of NHC•H₂CO₃ was prepared and 128 transferred to Erlenmeyer flasks, to each flask approximately 500 g of powder was added. Each 129 flask equipped with a stirring bar was placed over a stirring plate to facilitate continuous mixing 130 of NHC solution. Considering the chances of dust explosion in the case of metallic powder due to 131 higher surface energy, all the reactions were conducted in a fume hood. Once stirred for 24 h at 132 133 r.t., 3 x 500 ml flasks were allowed to settle down and the aliquot solution was separated leaving NHC-treated Cu powder at the bottom of each flask. Washing of each flask was carried out using 134 135 the appropriate amount of MeOH (4 times) and the powder was then stored under a vacuum desiccator overnight to dry the NHC-treated Cu powder. Once dried, characterization and thermal 136 spraying processes were conducted. 137

138 1.4 Thermal Spraying Process

139 1.4a Surface Preparation

For thermal spraying, 2.54 x 2.54 x 0.3 cm flat carbon steel coupons were selected and before the thermal spray process, the coupons underwent alumina grit blasting with a particle size of 20 μ m at a pressure of approximately 4 bar and an angle of 80–90°. This process was conducted to promote bonding between the coating and the substrate.³ Following grit blasting, all coupons were cleaned by ultrasonication in ethanol for approximately 15 minutes to eliminate surface impurities. The measured surface roughness for all substrate coupons was approximately 4.7 μ m before the HVAF spraying.

147 1.4b Coating Build-up Process

In the HVAF spraying process, the inner diameter (ID) gun plays an important role in depositing 148 coatings onto substrate surfaces. The process begins with the injection of fine metal powder 149 particles into the ID gun, where they enter a combustion chamber. Inside the chamber, the powder 150 particles are exposed to a high-velocity stream of mixed air and fuel, causing combustion and 151 generating a high-temperature and high-pressure flame (Figure S1B). In this case, the i7 ID-HVAF 152 spray system (UniqueCoat Technologies LLC, VA, US) was utilized both for preheating the 153 substrates and spraying operations, with propylene chosen as the fuel. As the particles pass through 154 the chamber, they are heated to elevated temperatures, softening them and preparing them for 155 accelerated deposition onto the substrate. Subsequently, the heated particles are directed toward 156 157 the substrate through an acceleration nozzle at the tip of the inner diameter gun. Upon exiting the nozzle, the particles are accelerated to supersonic speeds, impacting the substrate surface with 158 considerable kinetic energy and forming individual splats. These splats gradually accumulate to 159 form a dense and cohesive coating layer, facilitated by the high velocity and kinetic energy of the 160 161 particles. As the coating builds up, heat is rapidly dissipated, leading to the rapid cooling and solidification of the coating layer, stabilizing its microstructure and ensuring mechanical integrity. 162 163 By controlling spraying parameters, it is possible to optimize coating thickness, microstructure, and properties, with post-treatment processes further enhancing performance. Once the coating 164 165 has been built, the deposition efficiency of coatings can be calculated using equation S1.

166



167

- 168 **Figure S1.** Coating build-up process using ID-HVAF gun (A) Set-up for thermal spraying on
- 169 Carbon steel substrates (yellow box) (B) Cross-section of an ID-HVAF gun.

$$DE = \frac{(W_a - W_b)}{FR \times t} \times 100 \ \#(S1)$$

171

173 where W_a represents the mass of the specimen after deposition (in grams), W_b represents the mass 174 of the specimen before deposition (in grams), FR is the powder feeding rate (in grams per minute), 175 and t is the total time the nozzle gun is facing the substrate during the deposition process (in 176 minutes). The masses of the specimens were measured using an electrical balance (Fisher 177 Scientific, A-2000DS) with an accuracy of 0.1 mg.

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179 1.4c Thermal Spraying Parameters

180

182

| 183 | Air flow rate (L/min) | 3401 |
|------------|---------------------------|------------|
| 184 185 | Air pressure (psi, MPa) | 128 (0.86) |
| 186 | Fuel flow rate (g/min) | 184 |
| 187 | Fuel pressure (psi, MPa) | 110 (0.78) |
| 188 | Gun travel speed (mm/s) | 1000 |
| 190 | Number of passes | 40 |
| 191 | | 40 |
| 192 | Powder feed rate (gr/min) | 25 |

181 Table S2. Summarized parameters for coating build-up process using HVAF

194

The i7 gun is a smaller version of the high-power HVAF-M3 gun, with a length of 95 mm which 195 makes it possible to spray internal diameters larger than 140 at a 50-mm stand-off distance.^{4,5} The 196 197 i7 gun can be used to spray samples positioned in both outer diameter and inner diameter fixtures as shown in Figure S1A (yellow box).⁴ A converging-diverging short-dimension nozzle with a 198 length of 26.17mm, an inside diameter of 9.2mm, and an outer diameter of 22mm provided by 199 200 UniqueCoat is used for the ID-HVAF spraying process. The copper powder was sprayed on the 201 carbon steel samples with a stand-off distance of 3 inches (7.62cm). The powder feed rate was set to 25 g/min. As reported by an IR camera used during the HVAF process, the substrate temperature 202 was 130±15°C. Other important parameters used while spraying is stated in Table S2. 203

205 1.5 Life Cycle Assessment Methodology

This study employs the Life Cycle Assessment (LCA) framework, adhering to the guidelines 206 outlined in ISO 14040:2006 and ISO 14044:2006,6,7 to comprehensively evaluate the 207 environmental impacts associated with the immersion method for N-heterocyclic carbene (NHC) 208 209 film deposition on Cu powder, and to the thermal spray (HVAF) application process. The process was then optimized and scaled to kilogram quantities and applied on the Cu surface using an HVAF 210 211 gun for mechanical and corrosion studies. Adopting a cradle-to-gate system boundary, transportation stages are excluded, aligning with established norms for laboratory-scale LCAs. 212 This strategic boundary delimitation enables the isolation and analysis of the inherent 213 environmental implications linked directly to the process itself and the used materials. 214

215 The Life Cycle Assessment (LCA) has been advocated as a foundational framework for environmental appraisal within the context of Responsible Research and Innovation (RRI). 216 217 However, its efficacy encounters constraints when applied to nascent technologies.⁸ This is because conventional LCA methodologies are tailored for assessing the environmental footprints 218 of established technologies, thus inherently retrospective in nature.⁸ To overcome this limitation, 219 scholars have devised adaptations to the LCA protocol explicitly tailored for the evaluation of 220 innovations.9-11 These methodologies encompass mechanisms for amplifying the analysis to pilot 221 scales.^{11, 12} Furthermore, advancements in prospective, ex-ante, and anticipatory LCA 222 methodologies hold the potential for scrutinizing emerging technologies.¹³ 223

The system output is defined as 1505.29 grams of NHC-modified copper powder (1500 g of copper 224 with 5.29 g of NHC) for the immersion method, representing the operational output under 225 226 examination, to thoroughly assess the environmental impacts, the LCA was conducted on the immersion methods and the thermal spray application process. Impact assessment and modeling 227 are executed utilizing OpenLCA software (version 2.1), while employing the (ReCiPe2016 228 Midpoint (H)), and (LCIA Methods (2.3.2)) for impact characterization. This analysis emphasizes 229 specific impact categories crucial to the process used in this study and conventional alternatives 230 such as global warming, mineral resource scarcity, and human toxicity (carcinogenic and non-231 carcinogenic). These categories are prioritized due to their direct relevance to the environmental 232 footprint of the examined process. 233

The Life Cycle Inventory (LCI) combines primary data from the experiments with secondary data 234 from Ecoinvent (version 3.7).¹⁴ For any reactants not available in Ecoinvent, the LCI was 235 supplemented with data from relevant literature sources.^{15, 16} This ensures a comprehensive and 236 transparent accounting of all inputs and outputs throughout the life cycle. The primary data used 237 in this study includes 1.5 kg of copper (Cu) powder, 5.286 grams (g) of Carbene, 34.56 kilowatt-238 hours (kWh) of electricity, 3 liters (L) of methanol, and a negligible quantity of Argon gas. The 239 iterative LCA methodology was employed to identify environmental hotspots and guide 240 241 optimization efforts. Initial models are constructed based on estimations, and progressively refined as empirical data becomes available. This approach ensures that the robustness of the LCA 242 framework improves as the process matures and primary data collection expands. 243

244 1.6 Physical Characterization

245 1.6a Field Emission-Scanning Electron Microscopy

SEM analysis for powder samples before and after NHC treatment was carried out using field emission electron microscopy (FE-SEM) from Hitachi Regulus 8230. The powder samples were adhered to the stage using double-sided carbon tape and were analyzed using a secondary electron and backscattered electrons detector with an accelerating voltage of 15 kV, magnitude 500x.

250 1.6b Particle Size Distribution

Dynamic light scattering (DLS) was used to assess the particle size distribution (PSD) using the Spraytec-Wet cell from Malvern Panalytical[®] using a known concentration dispersed in water. The PSD values for untreated-Cu and NHC-treated Cu powder are represented in **Table S3**, where Dv(10), Dv (50) and Dv (90) values represent the size below which 10%, 50% or 90% of all particles are found.¹⁷ The overlapped PSD spectra (**Figure S2**) show the difference in particle size



256 distribution because of NHC treatment.

- 257 Figure S2. PSD curves using DLS for untreated-Cu (teal) vs. NHC-treated (red) Cu powder
- 258 explaining the difference in the distribution of particle size before and after NHC treatment.
- 259

279

| PSD parameters | Untreated-Cu Powder | NHC-treated Cu Powder |
|----------------|---------------------|-----------------------|
| Dv(10) (µm) | 6.4 | 8.5 |
| Dv(50) (µm) | 12.1 | 15.2 |
| Dv(90) (µm) | 22.9 | 27.4 |

260 Table S3. Comparison of PSD for untreated-Cu Powder vs. NHC-treated Cu Powder

261 1.6c X-ray Photoelectron Spectroscopy

Cu powder composition pre- and post-NHC immobilization was performed using X-ray 262 Photoelectron Spectroscopy (XPS). The XPS measurements were performed using a 263 monochromatic Al-Kα X-ray source (hv =1486.6 eV) from Thermo Scientific[®] under ultra-high 264 vacuum (UHV) conditions. The operating pressure of the instrument was 9×10^{-8} mbar. The 265 survey spectra and high-resolution spectra were collected at pass energy of 200 eV and 20 eV 266 respectively. The charge correction was calibrated for high-resolution spectra using C 1s peak at 267 284.8eV as a reference. Each spectrum was fitted using CasaXPS software version 2.3.26 18 and 268 Gaussian-Lorentzian function and Shirley's background was used to fit the acquired data. 269

270 Calculation of % Cu (0/I/II)

The quantification of the % loss in shakeup peak area for Cu 2p spectra for both NHC-treated vs. untreated-Cu powder was analyzed after peak fitting and the area under the curve was evaluated. The main emission line of Cu $2p_{3/2}$ around 932.5 eV has contributions from Cu (0), Cu(I), and Cu (II) whereas the shake-up peak ranging from 938eV and 946eV has contributions only from Cu (II). In the case of Cu 2p high-resolution spectra, the binding energy for Cu(0) and Cu (I) overlaps allowing us to calculate the % Cu (II) and a combined %[Cu (0) +Cu(I)] ^{19, 20} using the **equation S2** and **S3**.

$$\%(Cu(0) + Cu(I)) = (A - (A_{1s}/B_s)B)/(A + B) * 100$$
(S2)

$$\%Cu(II) = B(1 + (A_{1s}/B_s))/(A + B) * 100$$
(S3)

Here 'A' is the total area of the main peak which has been calculated by adding the area from added peaks A1 and A2, and 'B' is the total area of the shakeup peak and calculated by adding peaks B1 and B2 (example presented in **Figure S6 A** and **B**), and 'A1s/Bs' is the ratio of the main peak/shake-up peak for Cu (II) species in the sample [could be CuO or Cu(OH)₂] and value is used from literature.¹⁹

The individual percentages for Cu (0), Cu (I), and Cu (II), auger peak fitting was performed by 285 adding peaks of Cu in various oxidation states. The peak's shape for Cu LMM spectra for Cu 286 287 (0/I/II) is asymmetrical making it complicated to fit using a single peak. To imitate the actual peak shape, 7 peaks are added for Cu metal, 4 peaks for Cu(I) oxide, 4 peaks for Cu (II) oxide, and 3 288 peaks for Cu(II) hydroxide following the literature.¹⁹ The CasaXPS software allows the 289 combination of multiple peaks into one peak, making the spectra less crowded and easy to 290 291 understand and fitted data has been presented in the mentioned way (example shown in Figure S6 **D** and **E**). The fitting protocol was kept consistent for both Cu 2p and Cu LMM for all the fits 292 293 presented in the paper.

294 1.6d Laser Desorption/Ionization Spectroscopy

To confirm the presence of NHC on the NHC-treated Cu sample, laser desorption ionization-time of flight (LDI-TOF) techniques were used. The instrument was Bruker[®] MALDI Autoflex III TOF mass spectrometer in the reflector mode with Nd:YAG laser (Ytrium Aluminum-Garnet crystals doped with Neodynium) with frequency-tripling was used to generate an incident laser wavelength of 355 nm. Variable frequency was used with a maximum of 200 Hz with a laser pulse width of 5 ns, and the acceleration voltage was 20 kV. The acquisition method used was positive reflector mode. No matrix was used in any measurement.

302 1.6e ONH Analysis by Inert Gas Fusion

836 ONH analyzer from LECO company by inert gas fusion technique was used to evaluate the
bulk oxygen content of untreated-Cu and NHC-treated Cu powder after heat treatment to evaluate
the oxidation resistance as an effect of NHC treatment.

306 1.6f Scratch Test

307 The scratch test was conducted using an Rtec multi-functional tribometer (MFT 5000) with a load 308 variation from 1 N to 6 N with a speed of 3.5 mm/min. The scratch length was kept at 2.5 mm for 309 all variants using a Rockwell diamond tip having a tip radius of 100 μ m. The schematic 310 representation of the scratch test process is shown in **Figure S3A-B**, with Cu coating built on a 311 carbon steel substrate and an indenter making a scratch. The test helps identify two types of failure: adhesive failure at the interface between the substrate and the coating, and cohesive failure withinthe coating itself.

Each sample and normal load combination was tested five times, and the average results were 314 reported. To avoid the effects of the stress field formed in the neighboring test area, the distance 315 between two test scratch tracks was kept at least five times the width of the scratch. After the 316 317 testing, an optical microscope (OM) was used to capture images of the damage that occurred in a 318 cone shape to determine the projected area of the cone (Figure S4). In the context of scratch 319 testing, the "projected cone area" refers to the area of damage observed in the material after a scratch test has been performed. When a scratch is made with a diamond-tipped stylus, the material 320 321 typically fails in a particular manner, often forming a cone-shaped damage area. This area is used to assess the cohesive and adhesive properties of the coating. Even though the projected cone area 322 323 measurement is a valuable tool for comparing thermally sprayed coatings, to fully understand the failure mechanisms, other investigations such as microscopic observation of cracks and their sizes 324 325 are necessary. The projected cone area was calculated using Image J software, and the average



326 cone area was obtained from five readings with subsequent standard deviation determination.

- 328 Figure S3. Schematic representation of (A) Scratch test conducted on thermally sprayed coatings
- 329 generated from untreated-Cu vs. NHC-treated Cu powder mounted in epoxy. (B) Graphical image
- 330 after Scratch test explaining cohesive and adhesive failure.
- 331 However, it is unclear whether the area enclosed by the side cracks should be included in the
- 332 definition of the cone area. Therefore, the cone area represents only a partial measure of the
- 333 coating's cohesion, and its evaluation is qualitative in such cases. To identify the adhesive nature

334 of the coatings, several images were taken at the interface of the coating and substrate. After

335 testing, the scratch tracks were observed using SEM (S-3400N, Hitachi High Technologies

336 America, Inc., USA) to reveal the failure mechanism.

337 The projected cone area (Acn) is calculated as a rectangular area, the formula can be expressed338 as:

$$Acn = Lx * Ly$$

340 Where:

341 • α : Cone apex angle

• Lx: Length of the cone base in one dimension.

• Ly: Length of the cone base in the perpendicular dimension.

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345

346

Figure S4. Optical microscope image of a cone fracture at the coating and resin interface, withdashed orange lines showing the projected cone area measurement.

349 1.6g NMR Spectroscopy

- 350 ¹H and ¹³C NMR spectra were recorded on Bruker Instruments (Neo-600) operating at denoted
- 351 spectrometer frequency given in megahertz (MHz) at 25 °C. ¹H chemical shifts are referenced to
- 352 the residual protons of the deuterated solvents $CDCl_3$ (at d = 7.26 ppm) and CD_3OD (at d = 3.31
- 353 ppm); ¹³C chemical shifts are referenced to the CDCl₃ and CD₃OD signals at d = 77.16 and 49.00
- 354 ppm, respectively. The following abbreviations are used to describe NMR signals: s = singlet, d
- 355 = doublet, t = triplet, q = quartet, sept = septet, and m = multiplet. Coupling constants obtained

- 356 from ¹H NMR spectra are associated with an error and reported to the first decimal point (the
- 357 digital resolution in ¹H NMR spectra and ¹³C NMR is 0.11 Hz and 0.64 Hz respectively). All data
- 358 were processed using MestReNova 11.0 software.



359 2 Results Supplementary Information

360 2.1 Surface Analysis of Cu Powder Before and After NHC Treatment

Figure S5. XPS survey scan for elemental analysis along with %atomic ratio attributed to each element (A) NHC-treated Cu powder in red and (B) untreated-Cu powder in teal.



Figure S6. LDI-ToF spectra confirm NHC presence at 203 m/z (highlighted in grey) in NHCtreated Cu powder compared to untreated-Cu powder under 10mM, 24h stirring conditions.



367 Figure S7. Deconvoluted Cu 2p XPS Spectra (A) untreated-Cu (B) NHC-treated Cu powder 368 system (C) Bar graph reflecting Cu (II) % from deconvoluted Cu 2p spectra, (D) and (E) 369 Deconvoluted Cu LMM Auger spectra for untreated-Cu and NHC-treated Cu powder system 370 respectively (F) Bar graph with individual percentage of Cu in various oxidation states from 371 Deconvoluted Auger spectra.

372 2.2 Optimization Results

373 2.2a Effect of Stirring

The effect of stirring was studied during the immobilization process by performing a control 374 experiment without using stirring conditions vs. the stirred one and probed by collecting XPS and 375 LDI-ToF spectra. Stirring retains the Cu powder morphology and leads to minor changes in Cu 376 (II) % considering the Cu 2p and Cu LMM fittings (Figure S8). The system with stirring has 377 average of 41% of Cu (II) whereas without stirring has 46% of Cu (II) (Figure S8C). The Cu 378 LMM fitting reveals 44% Cu (II) in stirred samples versus 48% in unstirred ones (Figure 2A) 379 showing a good agreement between Cu 2p ad Cu LMM Auger fitting results. Stirring facilitates 380 uniform mixing of NHC with Cu powder leading to an intense peak at 203 m/z in LDI spectra 381 382 (Figure S9) compared with the unstirred sample. Therefore, stirring conditions only assist in the NHC immobilization process vs. the stagnant conditions. 383



384

Figure S8. Influence of stirring on oxide reduction: Deconvoluted Cu 2p XPS Spectra (A) Stirring (B) No Stirring (C) Bar graph reflecting Cu (II) % from deconvoluted Cu 2p spectra, (D) and (E)

387 Deconvoluted Cu LMM Auger spectra for stirring and no stirring system respectively.



Figure S9. LDI-ToF spectra using 40mM NHC solution for 48h duration NHC-treated Cu sample 398 with stirring and without stirring 399

2.2b Effect of NHC Concentration 400

401 The next varied parameter was NHC concentration, from 0 mM to 40 mM during immobilization 402 with 48 h stirring at room temperature. LDI spectra (Figure S10) show increased peak intensity 403 for NHC (m/z = 203) with higher concentrations. Before further increasing the NHC concentration, the LDI results were verified using XPS and ruled out if physisorption had played 404 a role. The deconvoluted Cu 2p spectra (Figure S11) show the maximum reduction in the 405 406 shakeup peak area when the NHC concentration increased from 5 to 10 mM, and no significant reduction was observed after that. The Cu LMM Auger fitted spectra (Figure S12) show a 407 22.7% decrease in Cu (II) and Cu (0) has increased from 7% to 21% (Figure 2B) with 10 mM 408 the optimal NHC treatment, stating it as 409 concentration. 411 40 mM 412 20 mM Intensity [a.u.] 413 10 mM 414

- 415
- 416

417



Figure S10. LDI-ToF analysis of concentration variants confirming the presence of NHC at 203
 m/z.



Figure S11. Deconvoluted Cu 2p spectra for different concentration variants (A) Ref. (B) 0 mM 426 (C) 5 mM (D) 10 mM (E) 20 mM (F) 40 mM (G) Line graph reflecting Cu (II)% for mentioned



Figure S12. Deconvoluted Cu LMM spectra for different concentration variants (A) Ref. (B) 0
mM (C) 5 mM (D) 10 mM (E) 20 mM (F) 40 mM

438 2.2c Effect of Immobilization Time

The time of immersion varied from 12 to 72 h while stirring the solution in 10 mM NHC (previously optimized parameter) at room temperature. NHC peak at 203 m/z was present at all periods (Figure S13), making XPS Cu 2p and Cu LMM analysis crucial. The maximum reduction in the shakeup peak (43% to 31%) is observed for the 24 h variant beyond which no significant change in the Cu 2p spectra was observed (Figure S14) which was also verified further using auger peak fitting (Figure S15). The Cu LMM analysis (Figure S15) also showed a 7% to 17% (Figure 2C) increase in metallic Cu for the 24 h variant. Percentages for other time variants shown

447 in Figure 2C conclude that a longer immersion period increases surface oxide which could be due
448 to the moisture-absorbing nature of methanol leading to NHC degradation.²¹



Figure S13. LDI-ToF spectra of different immobilization periods (a) Ref. (b) 12h (c) 24h (d) 48h
(e) 72h Cu powder samples using 10mM NHC concentration along with stirring.

451



453 Figure S14. Deconvoluted Cu 2p spectra for different time variants (A) Ref. (B) 12 h (C) 24 h (D)
454 48 h (E) 72 h (F) Line graph reflecting Cu (II)% for mentioned concentration variants.



458 Figure S15. Deconvoluted Cu LMM spectra for different time variants (A) Ref. (B) 12 h (C) 24 h
459 (D) 48 h (E) 72 h

460 2.2d Influence of Temperature

The final parameter investigated was the effect of temperature from room temperature to 60 °C, 461 using previously optimized conditions, and NHC presence was confirmed using LDI-ToF (Figure 462 S16). As the temperature increased, the color of settled powder particles changed to blue (Figure 463 S17) indicating the formation of oxidized Cu species. The results align with Cu 2p fitted (Figure 464 465 S18) and Cu LMM fitted spectra (Figure S19). The calculation from Cu LMM shows that the room temperature variant has the lowest percentage of Cu (II) (37.3%) and the highest % of Cu 466 467 (0) (18%) vs. the ones at higher temperatures (30, 40, 50, and 60 °C) which can be related to moisture interference leading to a reaction making more Cu (II) species at higher temperatures. 468

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473 Figure S16. LDI-ToF spectra of various temperature variants (A) Ref. (B) r.t. (C) 30°C (D) 40°C
474 (E) 50°C (F) 60°C using 10mM NHC concentration for 24h along with stirring



Figure S17. Influence of increasing temperature on settled color particles in methanol, the particle
 color changes to blue at higher temperatures reflecting the formation of oxidized Cu species.



Figure S18. Effect of temperature on Cu oxide species: Deconvoluted Cu 2p spectra for different temperature variants (A) Ref. (B) r.t. (C) 30°C (D) 40°C (E) 50°C (F) 60°C (G) % Cu⁺² for

mentioned temperature variants.



504 **Figure S19.** Effect of temperature on Cu oxide species: Deconvoluted Cu LMM spectra for 505 different temperature variants (A) Ref. (B) r.t. (C) 30°C (D) 40°C (E) 50°C (F) 60°C (G) % Cu⁺²

506 for mentioned temperature variants.

507 2.3 Stability test of NHC film on Cu powder

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510 Figure S20. Stability test of NHC-treated Cu powder in 0.1M NaOH (Red) and 0.1 M HCl (Blue)

511 solution for 5h w.r.t NHC-treated Cu powder acting as reference (Magenta). LDI-ToF spectra

512 showing the presence of 203m/z peak even after immersing NHC-treated Cu powder in harsh

513 conditions.

515 2.4 Characterization of Cu powder after scale-up



Figure S21. Characterization of scaled-up NHC-treated Cu powder vs. untreated-Cu powder (A)
LDI-ToF representing NHC presence in NHC-treated Cu powder (B) and (C) Deconvoluted Cu2p
XPS spectra and (D) and (E) Deconvoluted Cu LMM spectra of untreated-Cu and NHC-treated
Cu powder respectively (F) Bar graph representing % of Cu in various oxidation states from Cu
LMM spectra fitting.

528 2.5 Characterization of Cu-sprayed Coatings



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530 **Figure S22.** EBSD analysis using Cross-section to compare mechanical properties and 531 crystallographic orientation for (A) and (B) untreated-Cu powder (C) and (D) NHC-treated Cu 532 powder.

533 EBSD Phase Maps

The EBSD phase maps in Figures 5A and 5B illustrate two distinct phases: metallic copper (Cu) 534 535 in red and black regions representing oxide phases or pores. These black regions arise from oxide 536 formation and are typically found at grain boundaries, voids, or regions with severe deformation.²² 537 In Figure 5A, coarser grains, with more prominent black regions likely due to increased oxidation in black areas at grain boundaries or interfaces. The coarser microstructure suggests greater 538 susceptibility to oxidation, possibly due to the process temperature²² or the feedstock's native oxide 539 layer. Coarser grains generally result in weaker mechanical properties, such as lower yield 540 strength,²³ as they provide fewer grain boundaries to impede dislocation motion. Furthermore, the 541 larger grain sizes in Figure 5A can lead to poorer surface integrity and higher oxidation rates, 542 543 which can degrade the material's performance over time.^{22, 23}

544 On the other hand, Figure 5B displays the microstructure consists of finer, more uniform grains,

545 which result in fewer black regions. This indicates minimal oxidation and better phase resolution.

546 Finer grains enhance diffraction quality by providing more uniform and smaller crystallites.

547 Additionally, finer grains offer advantages such as improved mechanical properties, including

548 increased strength and better resistance to creep and fatigue. The reduced oxidation observed in

549 this case also highlights the enhanced surface stability of finer grains.^{24, 25}



551 Figure S23. Image of thermally sprayed coupons using HVAF obtained after spraying untreated-



- 552 Cu and NHC-treated Cu powder.
- **Figure S24.** XPS survey spectra of coatings generated from NHC-treated Cu (red) and Untreated-Cu (teal) for quantitative surface oxygen analysis (O 1s highlighted in grey).
- 555 Table S4. Comparative analysis of oxygen (%) for coatings generated from NHC-treated and
- 556 Untreated Cu powder. The table below provides quantitative analysis using XPS survey spectra
- 557 for surface oxygen and ONH elemental analysis using the inert gas fusion technique for bulk
- 558 oxygen analysis.

| El ana ant | % Atomic ± St. Dev. | % Atomic ± St. Dev. |
|--------------|---------------------|---------------------|
| Element | (NHC-treated Cu) | (Untreated Cu) |
| XPS Survey | 31.7±0.6 | 32.5±0.1 |
| ONH analysis | 0.461±0.0108 | 0.443±0.0136 |

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560 Thermogravimetric Analysis of NHC

NHCs are volatile organic species that are removed from the surface when exposed to 561 temperatures exceeding their glass transition point. During the thermal spray (HVAF 562 process using i7 gun) coating process, where a temperature of 1000-1700 °C is applied, the 563 NHC layer on the coated Cu powder is effectively eliminated without leaving any residues 564 on the surface. This observation is strongly supported by thermogravimetric analysis 565 (TGA) measurements (Figure S25) and corroborates with Lomax et al.,²⁶ which confirms 566 the complete removal of NHC molecules at higher temperatures. The carbene evolves 567 around 215°C and leaves a clean metallic surface. A similar mechanism is expected for 568 NHC-treated Cu powder when exposed to higher temperatures during thermal spray. Since 569 the particles used in the HVAF process are relatively fine (average size = $12\mu m$), their 570 higher surface-to-mass ratio allows them to heat more easily, causing them to melt or 571 partially melt. In other words, the particles reach the copper melting temperature of 572 1080°C. That being said, NHC likely dissipates from the Cu particle surfaces but still has 573 an effect, as it helped reduce the initial native oxide layer. This results in a slightly denser 574 coating and improved corrosion resistance. 575

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577

578 **Figure S25.** Thermogravimetric analysis of NHC to understand the decomposition and evolution 579 of NHC during thermal spraying.

580 To address the effect of NHC on coating composition, XPS analysis was conducted on thermally 581 sprayed coatings generated from NHC-treated Cu and Untreated-Cu powder. The % N was 582 calculated using XPS from survey spectra. The survey analysis provided similar % N in coatings 583 generated from NHC-treated vs. Untreated-Cu powder, which reflects the successful removal of 584 NHC during thermal spraying.

Table S5. Influence of NHC on the composition of Cu coatings post-thermal spraying has been evaluated using N% from XPS survey spectra and has been reported below: -



Mass

Figure S26. Electrospray ionization-mass spectrometry (ESI-MS) analysis of aliquot solution 588 collected after NHC treatment showed the presence of oxidized NHC species at 219.15 and 221.16

mass. ESI-MS analysis reflects that free carbene successfully interacts with the oxidized Cu

- 590 surface, reducing the Cu surface and simultaneously producing oxidized carbene species.

606 3 References

- C. M. Crudden, J. H. Horton, M. R. Narouz, Z. Li, C. A. Smith, K. Munro, C. J. Baddeley,
 C. R. Larrea, B. Drevniok and B. Thanabalasingam, *Nature Communications*, 2016, 7,
 12654.
- 610 2. G. R. Fulmer, A. J. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E.
 611 Bercaw and K. I. Goldberg, *Organometallics*, 2010, 29, 2176-2179.
- J. Yang, J. Yang, Q. Wang, K. Qu and J. Xie, *Journal of Materials in Civil Engineering*,
 2020, **32**, 04020260.
- 614 4. S. Kuroda, J. Kawakita, M. Watanabe, K. Kim, R. Molak and H. Katanoda, *Future*615 *Development of Thermal Spray Coatings*, 2015, 163-206.
- 616 5. A. Verstak and G. Kusinski, 2012.
- 617 6. I. ISO, Environmental management—life cycle assessment—principles and framework,
 618 2006, 235-248.
- 619 7. I. O. f. Standardization, *Environmental management: life cycle assessment; requirements* 620 and guidelines, ISO Geneva, Switzerland, 2006.
- 621 8. S.-E. Jakobsen, A. Fløysand and J. Overton, *Journal*, 2019, 27, 2329-2343.
- J.-P. Schöggl, R. J. Baumgartner and D. Hofer, *Journal of Cleaner Production*, 2017, 140, 1602-1617.
- W. H. Motta, L.-R. Issberner and P. Prado, *Journal of cleaner production*, 2018, 187, 1103 1114.
- J. Martínez-Blanco, S. Forin and M. Finkbeiner, *The International Journal of Life Cycle Assessment*, 2020, 25, 311-331.
- 628 12. S. Matos and J. Hall, Journal of operations management, 2007, 25, 1083-1102.
- M. Villares, A. Işıldar, C. van der Giesen and J. Guinée, *The International Journal of Life Cycle Assessment*, 2017, 22, 1618-1633.
- G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz and B. Weidema, *The International Journal of Life Cycle Assessment*, 2016, **21**, 1218-1230.
- 633 15. I. Vogel, *Practical organic chemistry*, Citeseer, 1974.
- I. Binns, X.-D. Liu, P. Dalladay-Simpson, V. Afonina, E. Gregoryanz and R. T. Howie, *Physical Review B*, 2017, 96, 144105.
- H. G. Merkus and H. G. Merkus, *Particle Size Measurements: Fundamentals, Practice, Quality*, 2009, 13-42.
- N. Fairley, V. Fernandez, M. Richard-Plouet, C. Guillot-Deudon, J. Walton, E. Smith, D.
 Flahaut, M. Greiner, M. Biesinger and S. Tougaard, *Applied Surface Science Advances*, 2021, 5, 100112.
- 641 19. M. C. Biesinger, Surface and Interface Analysis, 2017, 49, 1325-1334.
- 642 20. M. C. Biesinger, B. R. Hart, R. Polack, B. A. Kobe and R. S. C. Smart, *Minerals Engineering*, 2007, 20, 152-162.
- 644 21. A. Al Rashed, Queen's University (Canada), 2018.
- 645 22. T.-H. Fang, C.-C. Huang and T.-C. Chiang, *Materials Science and Engineering: A*, 2016,
 646 671, 1-6.
- 647 23. G. Demeneghi, B. Barnes, P. Gradl, J. R. Mayeur and K. Hazeli, *Materials Science and* 648 *Engineering: A*, 2021, **820**, 141511.
- J. Escobedo, D. Dennis-Koller, E. Cerreta, B. Patterson, C. Bronkhorst, B. Hansen, D.
 Tonks and R. Lebensohn, *Journal of Applied Physics*, 2011, 110.

- 651 25. C. Gu, M. Hoffman, L. S. Toth and Y. D. Zhang, *Materials Characterization*, 2015, 101, 180-188.
- 653 26. J. T. Lomax, E. Goodwin, M. D. Aloisio, A. J. Veinot, I. Singh, W.-T. Shiu, M. Bakiro, J.
- Bentley, J. F. DeJesus and P. G. Gordon, *Chemistry of Materials*, 2024.