METALLIZATION OF CARBON FIBRE REINFORCED COMPOSITES BY GRIP METAL™ AND COLD SPRAY

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ABSTRACT

Aerospace manufacturers incorporate an ever greater proportion of carbon fibre reinforced composites (CFRCs) in aircraft, improving strength-to-weight ratios. Yet issues regarding skin wear/erosion resistance arise, leading to swift degradation at specific locations. The issue is currently solved through costly labor-intensive methods whereby titanium sheets are shaped and glued on CFRC skins in critical areas. It is envisioned that additive manufacturing processes can offer a superior solution. Cold spray processes are low temperature additive manufacturing, suitable for heat sensitive substrate materials such as CFRCs. Cold spray also offers the possibility of creating coatings of variable thickness.

This paper reports on two different CFRC metallization techniques. Metallization occurs prior to CFRC cure in both cases. In the first technique, GRIP Metal™ plates are used as a bond coat that is combined with the uncured CFRC prepreg stack prior to cure, with subsequent cold spray on the exposed GRIP Metal™ plate. The non-exposed surface of GRIP Metal™ plates is covered with hooks which increase bonding area at the CFRC- GRIP Metal™ interface. Work on the first technique focused on consolidation and void reduction in the prepreg & GRIP Metal™ stacks, prior to coating. Aluminium bond coats and coatings were probed. In the second technique the coating is deposited on an Invar mould, followed by CFRC lay-up and cure. This technique offers straightforward integration in CFRC manufacturing. Work on the second technique focused on producing well-consolidated coatings and on developing removal methods to be used after CFRC cure. Copper coatings were probed.

The paper reports on manufacturing, microscopic characterization and mechanical testing.

1 INTRODUCTION

Aerospace manufacturers incorporate an ever greater proportion of carbon fibre reinforced composites (CFRCs) in aircraft, improving strength-to-weight ratios [1]. Yet issues regarding skin wear/erosion resistance arise, leading to swift degradation at specific locations [2, 3]. The issue is currently solved through costly labour-intensive methods whereby titanium sheets are shaped and glued on CFRC skins in critical area. It is envisioned that additive manufacturing processes could offer a better solution. Cold spray processes are low temperature additive manufacturing suitable for heat sensitive substrate materials such as CFRCs. Cold spray also offers the possibility of creating coatings of variable thickness. However, previous work has shown that it is difficult to deposit metals directly on cured CFRCs; high velocity particles erode the CFRCs, leading to breaking of fibres and chipping of epoxy matrix [4]. Nonetheless, it is believed that cold spray may be used effectively for metalizing CFRCs in alternative approaches.

The purpose of this work is to investigate two potential methods for achieving this vision. The first method features the use of GRIP Metal™ technology as bond coat for cold spray; GRIP Metal™ consists of a thin metallic plate on which strips of metal called hooks are formed by chiseling in patterned interval [5]. Hooks are formed on one side of the plate only. In this work they were exposed to the uncured CFRC stack whilst the other side was retained for spraying. Prior to curing, GRIP Metal™ was compressed into the uncured CFRC laminate, with hooks facing the laminate. The chiseled hooks increased the surface area on which epoxy from the CFRC bonds, potentially resulting in higher adhesion strength of GRIP Metal™ on the laminate when compared with simple flat sheet metal processed in the same way. The second method features a lay-up method specially developed for metalizing CFRCs with cold spray. The method consists of spraying a thin coating on an Invar mould prior to CFRC curing, then laying the uncured laminate stack onto the coating. The assembly is cured afterwards. Once curing ends, the coated laminate is demoulded.

The two methods were investigated in terms of adhesion strength and laminate quality. Laminate quality assessment differed for the two methods. For the first method, quality was evaluated in terms of presence of porosity, general consolidation and increase of adhesion strength between the bond coat and CFRC. For the second method, quality was evaluated in terms of presence of porosity and defects in the coating. Adhesion strength between the coating and CFRC remains to be tested.

Due to the high cost of titanium both in bulk and powder forms, alternative materials were selected towards proving concepts and generating knowledge transferable to case of titanium. In the first method, GRIP Metal™ Al 5052-H38 was chosen. In the second method, dendritic and spherical copper powders were used.

2 Methodology

2.1 GRIP Metal™-CFRC

The GRIP Metal™ – CFRC assemblies were manufactured by compressing GRIP Metal™ plates into a 16-layers cross-ply Gurit SE70 carbon/epoxy CFRC laminate at room temperature under 1.0 MPa, maintaining the pressure for 5 minutes. The compression was done using an Instron 4482 testing frame. Then, the assembly was cured under vacuum at 1 atm in a controlled oven for 1 hour at 120°C, using +2°C heating and -5°C cooling rates. Once the cure was completed, samples were cut for flatwise tensile tests conforming to ASTM C297/C297M, and for optical microscopy using automated Struers saw, diamond coated blades and polisher. The tensile tests aimed at investigating the increase in adhesion where a normal force is applied to the metallized composite. Figure 1 illustrates the manufacturing process steps.

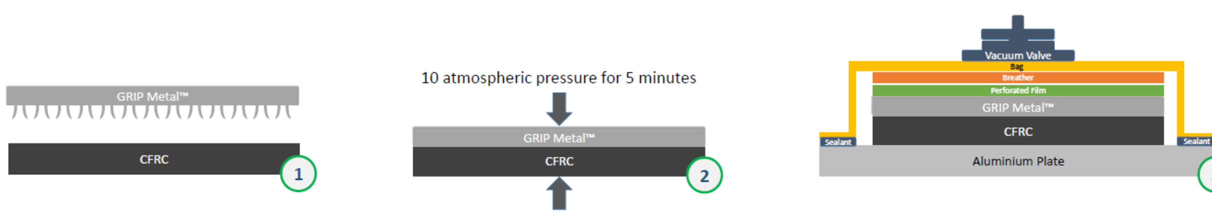

Figure 1. Manufacturing process of GRIP Metal™-CFRC: 1) Hooks face towards uncured CFRC laminate, 2) Compress GRIP Metal™ against uncured CFRC under 1,0 MPa for 5 minutes, 3) Vacuum bagging and cure

GRIP Metal™ is available in different hook sizes and curvature profiles. In this work, Al 5052-H38 "Nano" size with standard curvature was used, along with similar plates devoid of hooks. Furthermore, in some experiments the laminates were stacked as described above, while for others an additional layer of the same

Gurit epoxy resin devoid of fibres SA70 was added between the metal and CFRC. The additional resin layer aimed at mitigating porosity at the interface. Table 1 summarizes the experiments conducted.

GRIP Metal™ - Set 1.1	
Hook Size	"Nano"
Hook Curvature	Standard
Resin Layer between Metal and CFRC	No
GRIP Metal™ - Set 1.2	
Hook Size	Not applicable – Flat plate
Hook Curvature	Not applicable – Flat plate
Resin Layer between Metal and CFRC	No
GRIP Metal™ - Set 2.1	
Hook Size	"Nano"
Hook Curvature	Standard
Resin Layer between Metal and CFRC	Yes
GRIP Metal™ - Set 2.2	
Hook Size	Not applicable – Flat plate
Hook Curvature	Not applicable – Flat plate
Resin Layer between Metal and CFRC	Yes

Table 1. GRIP Metal™ – CFRC experiment configurations

2.2 Cold Spray

The Invar mould surface was ground then grit-blasted with #20 copper slag, resulting in a surface roughness of 3.9 um. Afterward, the samples were cleaned with ethanol in ultrasonic bath for 20 minutes then dried with compressed air. In a second step, copper was sprayed on the roughened surface using spray parameters listed in Table 2. An uncured 12-layers cross-ply CFRC laminate was then laid on the coating with a resin layer as medium. The assembly was then cured under vacuum in a controlled oven for 1 hour at 120°C, using +2°C heating and -5°C cooling rates. After cure, the coated CFRC was demoulded from the Invar mould. Samples were cut from the assembly for tensile tests using the Pneumatic Adhesion Tensile Test Instrument (PATTI), and for optical microscopy. Figure 2 illustrates the manufacturing process.

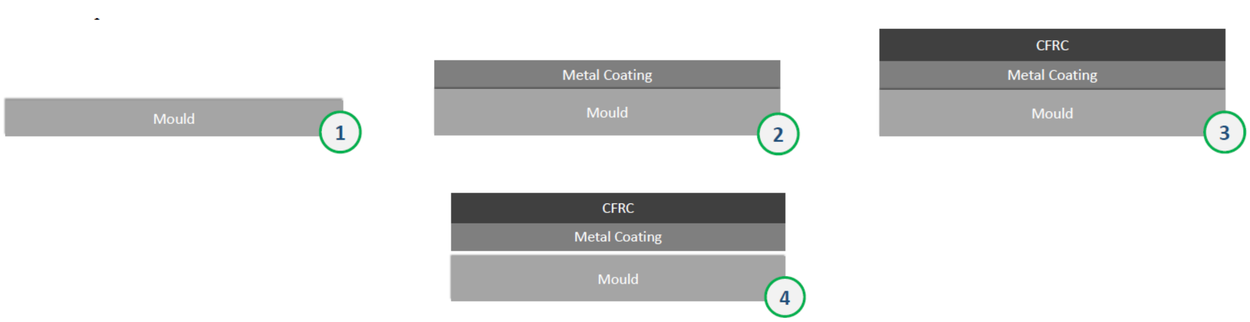

Figure 2. Manufacturing process: 1) Invar mould with roughened surface, 2) Deposition of metal coating by cold spray, 3) Mounting of CFRC laminate, 4) demoulding of coated CFRC after curing process.

Four sets of tests were conducted to investigate and characterize this technique, as presented in Table 2. Sets 1, 2 and 3 used dendritic copper SST-C5003 manufactured by Centerline Limited. Set 4 used spherical copper Cu-159 manufactured by Praxair Incorporated. Set 3 employed a two-layers approach as opposed to sets 1 and 2. The study aimed at creating coatings that barely adhere to the Invar mould, and at the same time are sufficiently dense and strong to remain intact during demoulding.

Lay-up - Set 1	
Powder	SST-C5003 by CenterLine Ltd.
Temperature	300°C
Pressure	320 Psi
Lay-up - Set 2	
Powder	SST-C5003 by CenterLine Ltd.
Temperature	500°C
Pressure	500 Psi
Lay-up - Set 3	
Powder	SST-C5003 by CenterLine Ltd.
Temperature of Layer 1 Temperature of Layer 2	300°C 500°C
Pressure of Layer 1 Pressure of Layer 2	320 Psi 500 Psi
Lay-up - Set 4	
Powder	Cu-159 by Praxair Inc.
Temperature	350°C
Pressure	250 Psi

Table 2 - Spray parameters for lay-up - Sets 1, 2, 3 and 4

3 Results

3.1 GRIP Metal™-CFRC

3.1.1 Distortion of Fibre Orientation & Resin-rich Zones

Imaging of samples' cross-sections revealed fibre distortion caused by hooks near the interface between GRIP Metal™ and CFRC. These distortions lead to large zones being filled with resin, denoted resin-rich zones. Additionally, voids were observed near and at the metal-CFRC interface as seen in Figure 3. Fibre distortion happened not only in through-thickness direction, but also in the plane of the laminate, as illustrated in Figure 4.

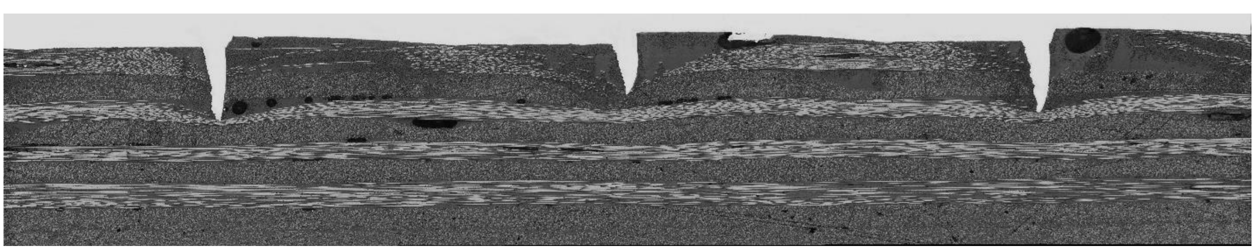

Figure 3. Sample's cross-section, GRIP Metal™ – Set 1.1

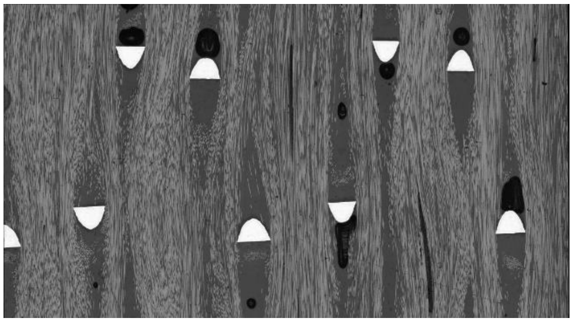

Figure 4. Sample's top cross-section, GRIP Metal™ – Set 1.1

No significant reduction in porosity was observed in samples of GRIP Metal™ - Set 2.1. Porosity still remained and could be seen near and at the interface between the metal and CFRC. Improving this aspect of results obtained from this experiment set was attempted by vacuuming the GRIP Metal™-CFRC prior to compression; no significant improvement followed.

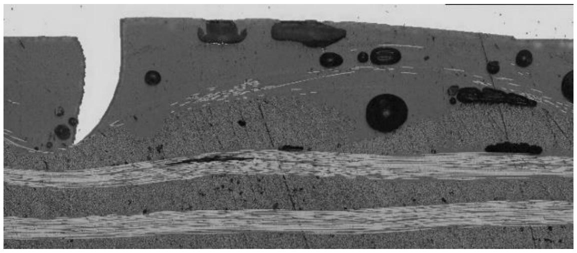

Figure 5. Sample's cross-section, GRIP Metal™ - Set 2.1

3.1.2 Adhesion Strength

Adhesion between the bond coat (GRIP Metal™ or flat plate) and CFRC was measured. The results showed that adhesion strengths of flat sheets of aluminium 5052 H-38 reached 3.17 ± 0.59 MPa, whereas GRIP Metal™ leads to an adhesion strength of 9.47 ± 4.38 MPa. For all assemblies with extra resin, the adhesion strength exceeded the capability of the glue used in tests, hence it couldn't be quantified. New testing equipment is being developed to circumvent this glue failure issue.

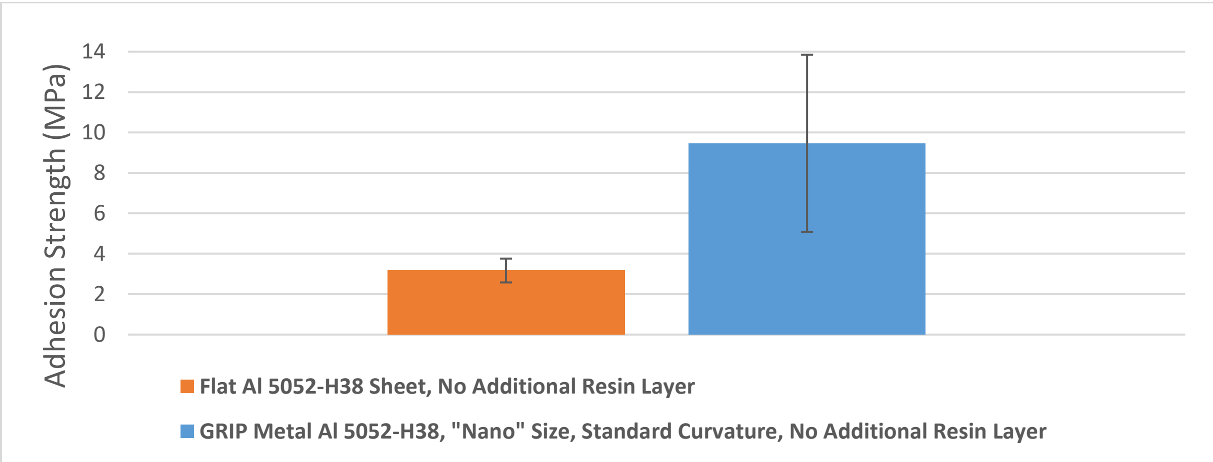

Figure 6. Performance of Al 5052-H38 GRIP Metal™ vs. Al 5052-H38 flat sheet

Most stress-strain graphs exhibited a quasi-linear profile with a sudden break when ultimate adhesion strength was reached. It was envisaged that hooks could lead to some retention after delamination; this was observed only in cases of low delamination adhesion values. However, this behavior did not appear for high ultimate delamination values. The curve on the left side of Figure 7 shows retention associated with the hooks as shown by the second peak, until ultimate adhesion; the curve on the right shows the general trend of failure happening at a higher stress level. Samples all failed at the metal-CFRC interface and showed no signs of significant damage to hooks. However, some fibres broke away from the laminate and remained on the metal interface after failure, as shown in Figure 8.

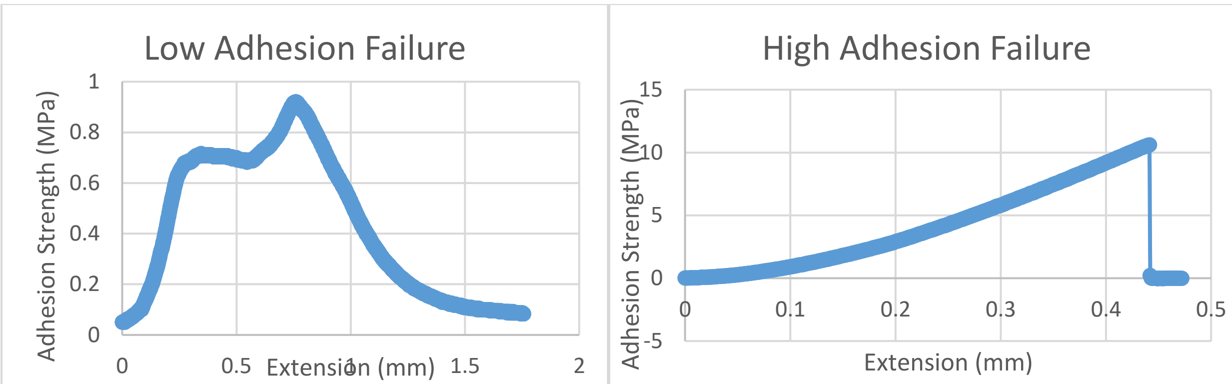

Figure 7. Low adhesion failure (Left) and High adhesion failure (Right)

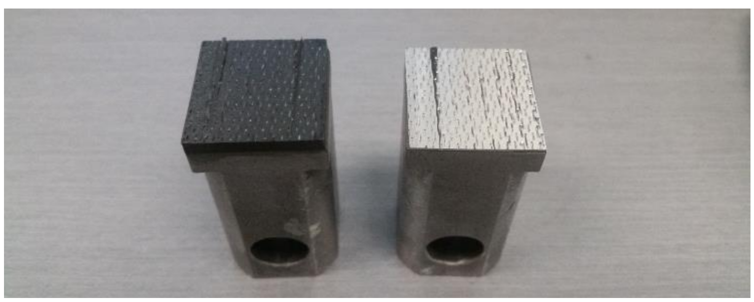

Figure 8. Example of interface after failure

3.2 Cold Spray

3.2.1 Lay-up – Set 1

In lay-up Set 1, micro-cracks were observed in coatings sprayed on the Invar mould, as shown in Figure 9. These cracks remained after demoulding of the CFRC.

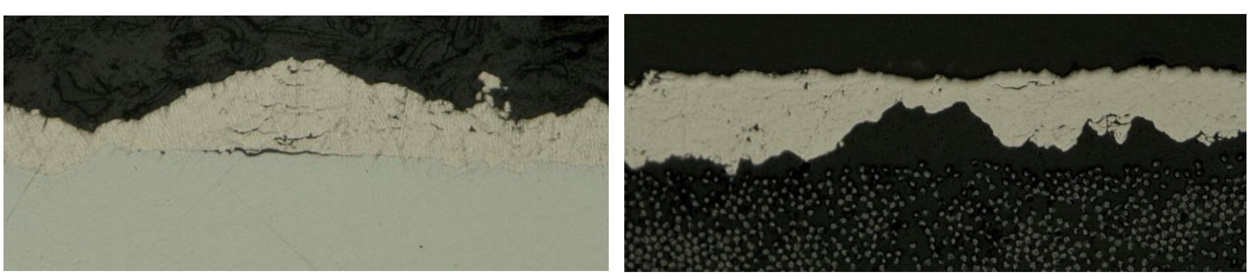

Figure 9. Copper coatings on Invar substrate, lay-up Set 1: Copper coating on Invar substrate (Left); demoulded copper coated CFRC (Right).

3.2.1 Lay-up – Set 2

In lay-up Set 2, coatings sprayed on the Invar mould were fully dense. However, severe cracking was observed in coatings after demoulding, Figure 10.

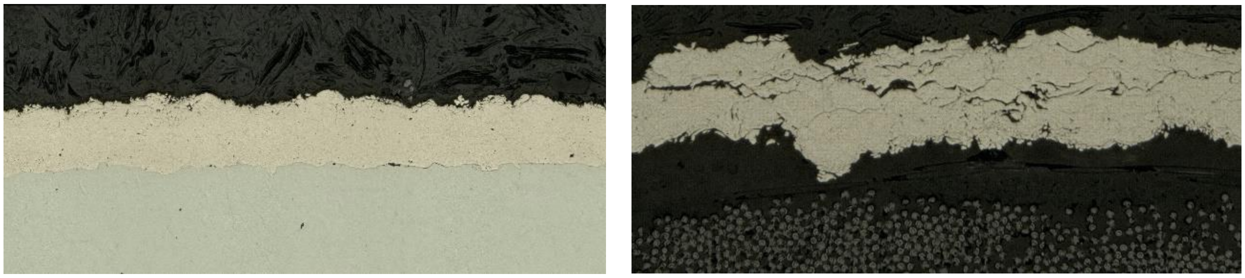

Figure 10. Copper coatings on Invar substrate, lay-up Set 2: Copper coating on Invar substrate (Left); demoulded copper coated CFRC (Right).

3.2.1 Lay-up – Set 3

In lay-up Set 3, coatings sprayed on the Invar mould were fully dense and no distinction between the 1st and 2nd sprayed layers were observed. After demoulding, some areas remained fully dense but others contained cracks propagating from the 1st layer towards the 2nd. Cracks seemed to decline in intensity as they propagated through the 2nd layer, as can be seen in Figure 11.

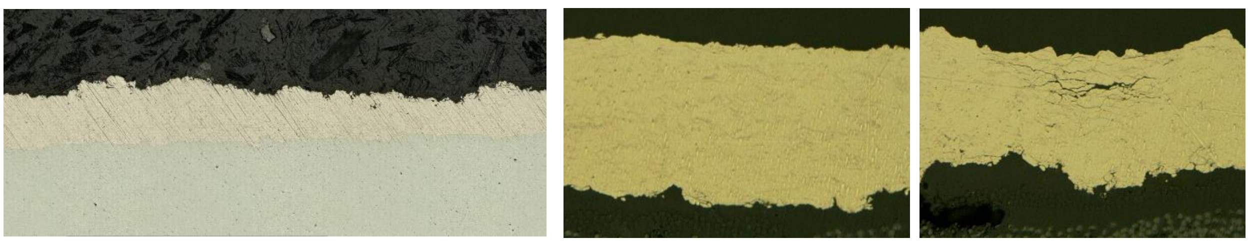

Figure 11. Copper coating on Invar substrate, lay-up Set 3: Copper coating on Invar substrate (Left); demoulded copper coated CFRC (Right).

3.2.1 Lay-up – Set 4

In lay-up Set 4, coatings sprayed on the Invar mould were mostly fully dense with minor porosity, and remained dense after demoulding. Nonetheless, small crack propagation was observed at locations where porosity occurred, as shown in Figure 12.

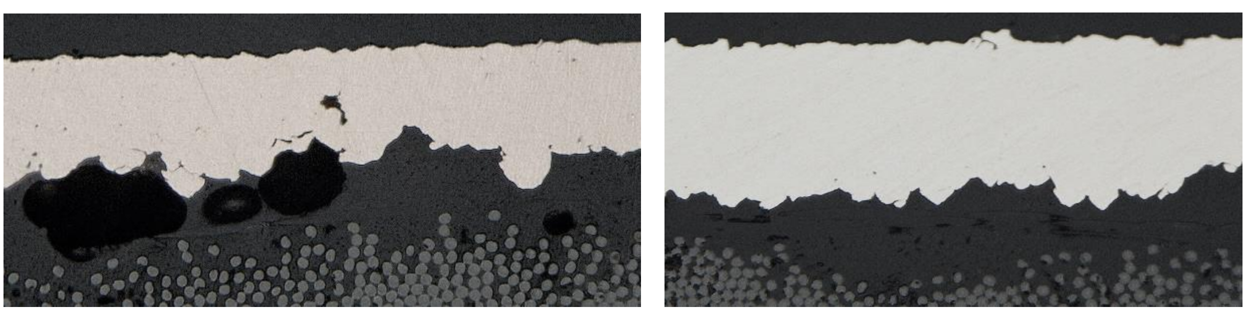

Figure 12. Copper coatings on CFRC substrate, lay-up Set 4: demoulded copper coated CFRC.

4 Discussion

4.1 GRIP Metal™-CFRC

4.1.1 Distortion of Fibre Orientations & Resin-rich Zones

Distortions were primarily induced by the inability of hooks to penetrate entirely through the laminate, forcing fibres near the impelling hooks to marry their profile. This lead to the development of large voids at the interface, prior to curing, which filled with resin contained within the prepreg. Most often, the voids could not be fully filled with resin and remained as voids after curing. Porosity at the interface between GRIP Metal™ and the CFRC might lead to early delamination, as pores act as crack initiation and propagation sites.

Adding an additional layer of resin at the interface of the metal and CFRC did not lessen porosity by an quantifiable amount. Even using vacuum upon consolidation could not solve the issue. It is thought that whilst vacuum may displace entrapped gas, this does not lead to a collapse of the physical spaces created upon consolidation; instead, it may only reduce pressure in these spaces. Also, if air bubbles remain present inside the bag, these bubbles may become small under 1.0 MPa but expand again under cure which is conducted under atmospheric pressure at 0.1 MPa. Overall, experiments conducted in this work indicate that it may be difficult to eliminate the voids.

4.1.2 Adhesion Strength

Hooks form additional surfaces to which epoxy may bond and increase adhesion. It was conjectured that the presence of porosity near and at the interface would reduce performance. However, GRIP Metal™ – Set 1 samples outperformed those featuring flat metal sheet of the same type. All failures happened suddenly at the interface between the metal and CFRC, with a linear increase in adhesion stress. However, when metal delaminated at very low stress levels, hooks offered retention ability and led to higher total delamination strength. GRIP Metal™ adhesion strength of 9.47 ± 4.38 MPa represents significant improvement over flat metal sheet, but further work will be required to rein in variability.

GRIP Metal™ – Set 2 samples could not be tested satisfactorily due to adhesive strength of the metal on CFRC exceeding the adhesion strength of available glues. It is believed that adhesion strengths will surpass those measured with samples from Set 1. More work is forthcoming.

4.2 Cold Spray

4.2.1 Lay-up Sets 1, 2 and 3

Set 1 shows that low spray parameters generated cracked as-sprayed coatings on the Invar substrate. In an attempt to improve coating cohesive strength by using higher spray parameters (Set 2), coatings bonded more firmly to the Invar substrate, leading to severe structural shattering upon demoulding from the Invar mould. A trade-off was observed between coating quality and adhesion strength on the substrate.

Set 3 attempted to leverage advantages seen with Sets 1 and 2 and identify a solution that could potentially lessen the trade-off of previous trials, by combining one layer of each Set 1 and 2. The results from Set 3 showed mitigation on crack propagation. Most cracks originated from the 1st layer and propagated towards the 2nd wherein a decline in branching was observed. Nonetheless, it was observed that some cracks could initiate within the coatings at defect locations and from the surface of the 2nd layer where particles bonding benefited from deformation by impacting particles (hammering effect) coming from the gas stream.

4.2.2 Lay-up - Set 4

Set 4 used a spherical powder in an attempt to achieve better coating cohesive strength. Cross-section images of the final product showed promising results wherein coatings were fully dense, both before layup and after demoulding of CFRC, with minimal presence of cracks. No severe crack propagation was observed. This indicates that spherical copper powders lead to better cohesive properties than dendritic copper powders. Porosity near the interface of metal-CFRC was due to improper laying of CFRC on the coating. Adhesion strength of the coating on CFRC remains to be tested.

5 Conclusion

Overall, GRIP Metal™ acting as a bond coat potentially provides superior adhesion to a flat sheet of the same material, without need for extra resin at the metal-CFRC interface. An adhesion strength of 9.47 ± 4.38 MPa was obtained from flat-wise tensile tests for the following configuration: aluminium 5052-H38, "Nano" size, standard curvature and no additional resin layer. Nonetheless, hooks induced fibre distortion and resin-rich zones that lead to voids to be partially filled by resin. Regardless of the addition of resin at the metal-CFRC interface, porosity remained present. GRIP Metal™ offers more hook profiles, straight and over-bent, that may perform differently. These alternative configurations will be tested in the future to evaluate the effect of hook profile on adhesion strength.

For cold spray lay-up method, low coating adhesion strength on substrate and high coating cohesive strength are key to minimize cracks. From experiment sets 1, 2 and 3, it is concluded that a trade-off exists when varying spray parameters. Dendritic copper has a cohesive strength that is too low to be further considered as a main coating, as it cracks either in as-sprayed coatings or after demoulding; the spherical powder offers better cohesive strength. Adhesion tests for spherical copper powder coatings remain to be conducted.

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