ONE-STEP MODIFICATION OF SPACE INTEGRATED SURFACES (OSMOSIS) FOR ADHESIVE PRIMING USING COBLAST

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ABSTRACT

ENBIO have developed a novel, green, ambient temperature blast coating technique known as CoBlast. A co-incident stream of abrasive and coating media simultaneously remove a metal's passivating layer while depositing a primer coating on the newly-exposed reactive metal surface. Previously used to apply a black thermal control coating surface, this process can be utilised to deposit various chemistries and textures.
In this work, CoBlast was used to apply a combination of organic and inorganic materials to 2024 T3 aluminium as an adhesive primer. Selective area coverage can be achieved and all materials used are chromate-free and REACH-compliant. To determine the adhesion-promotion benefits of these CoBlast surfaces, lap shear testing was conducted and samples were compared against commercial adhesive primers. Samples were prepared using a 2-part epoxy adhesive (3M™ Scotch-Weld™ EC-2216 B/A Grey) and a one-part film adhesive (Hexcel Redux 312) as per ESA recommendations. Samples were characterised using surface profilometry, SEM, EDX and cross-sectional microscopy. Bond strengths were determined for:

- As-bonded samples
- 1 week salt-fog
- 1-week humidity ageing

CoBlast-primed surfaces were shown to achieve equivalent bonded tensile strength to commercially available state-of-the-art solutions. Cohesive failure was observed in samples subjected to each ageing regime.

INTRODUCTION / SECTION TITLE

CoBlast is a surface-modification technique developed by ENBIO that is carried out at ambient temperature and pressure [1]. The technique involves the coincident bombardment of a surface with both an abrasive medium and the coating material to be deposited. The coating method uses the abrasive media to remove the surface layer of a metallic substrate in the presence of the coating or dopant material. This coating material is then free to bond to the exposed substrate metal, resulting in a strong chemical bond and the deposition of a semi-continuous layer in place of an inert oxide layer [2]. The process is used to apply a black thermal control coating called SolarBlack [3,4]. Due to the coating's ability, texture, as well as change to the surface chemistry, CoBlast has been used as a tie-layer for a secondary thermal control coating, SolarWhite [5]. With REACH regulations in effect since the 21st September 2018, the use of chemicals such as chromium trioxide and boric acid has been highly restricted by the EU. These chemicals were typically used in the priming of metals for adhesive bonding, such as chromic acid anodising. Due to the lack of successful alternative surface treatments, the aerospace industry has been granted a 7-year extension to these REACH deadlines. The ENBIO adhesive priming solution aims to replace these harsh chemical treatments that are the current SoA and soon to be highly restricted by the imminent REACH deadlines.

MATERIALS AND METHODS

2.1. Substrates and Treatments

The majority of the work was completed on Aluminium 2024 T3 substrates. Lap shear joints were constructed as per ASTM D 1002 – 10 [6]: pairs of 25.4 x 101.6 x 1.62 mm (1" x 4" x 1/16") coupons were bonded with an overlap of 12.7 mm (0.5"), as illustrated in Fig. 1.

The bonded region of these coupons was treated with either a CoBlast dopant material or a State-of-the-Art (SoA) surface treatment, as supplied by UK-based metal finishing companies. Three such SoA treatments were investigated:

- Chromic acid anodised (CAA) & Cytec BR127 primer
- Phosphoric acid anodised (PAA) & Cytec BR127 primer
- Phosphoric acid anodised & Hexcel Redux 112 primer

Additionally, lap shear joints comprising of Ti6Al4V and mixed-metal lap shear joints of 6000 series aluminium alloys and Ti6Al4V were bonded.

Honeycomb panels were constructed using a 15 mm thickness Aluminium 5052 untreated, unperforated core material from 'Easy Composites', UK (see Table I for further details). Honeycomb face plates consisted of 0.5mm Aluminium 2024 T3. State of the art comparisons were again sourced through a UK metal finishing company with a chromic acid anodised and Hexcel

Redux 112 primer finish.

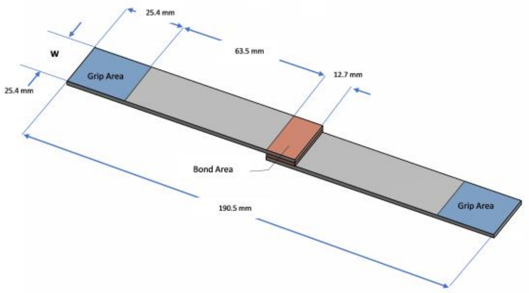

Fig. 1. Bonded lap shear joint, picture credit Admet

Table I Honeycomb core properties

Cell Size mm (inches)	Density kg/m^3 (lb/ft^3)	Foil thickness µm
3.2 (⅛)	72 (4.5)	35

2.2. CoBlast Process

The CoBlast process is described in more detail elsewhere [1]. A blend of alumina abrasive, fusion-bonded epoxy (FBE) and metal oxide corrosion inhibiting powders were fed into the blast stream using a suction fed, powder feeder system to produce the 'CoBlast Prime' surface. The blend is pneumatically conveyed through a nozzle, mounted on a 6-axis robot (Staubli TX60). This robot directs the nozzle/material stream across the material surface in such a way as to ensure an even coverage.

Surface roughness can be controlled by changing the abrasive size used. In this work a relatively small abrasive size (~12 µm) was found to perform best for film adhesives, resulting in a relatively smooth surface finish (~0.5 µm Ra). Higher roughness as achieved using larger abrasive (approximately 44.5 µm) and this was used for the 2-part epoxy tests.

2.3. Mechanical Testing

Treated lap-shear samples were bonded using both a 2-part epoxy adhesive (3M™ Scotch-Weld™ EC-2216 B/A Grey) and film adhesive (Hexcel Redux 312). The samples were bonded in accordance with ASTM D1002-10 [6] and SAE J1523 [7] test standards for determining the metal to metal overlap shear strength for adhesives. A bondline thickness of approximately 250 µm was maintained through use of a specially designed bond rig. As per the standards, a 12.7 ± 0.25 mm bond overlap length was maintained.

Samples mounted in the bonding rigs were placed in a 50L Genlab oven and allowed cure to the ESA recommended cure cycles for those adhesives (the manufacturer's cure cycle often do not account for low outgassing requirements adhesives bound for use in vacuum must meet; these ESA recommendations often run hotter and/or longer to encourage as much volatile material as possible is driven off during the cure cycle). Some additional time was added to the cure cycle to allow the entire bonding rig to come up to temperature as the steel construction served as a heat reservoir. This additional time was calculated based on results from embedded temperature probes. All lap shear tests were conducted using a Mecmesin 50i tensile tester with a 50kN load cell with wedge grips.

Following curing, the samples were allowed cool overnight, divided and subjected to one of:

- Lap shear only (to ASTM D 1002) [6]
- 1 week salt fog (to ASTM B 117) [8] followed by lap shear
- 1 week humidity ageing (56ºC, 70%RH) followed by lap shear.

Salt fog ageing was conducted in C+W SF450 salt spray chamber and humidity ageing in a Binder KBF 720 humidity chamber in accordance with:

- ECSS-Q-ST-70-14C: Space product assurance, Corrosion [9]
- ECSS-Q-ST-70-16C: Space product assurance, Adhesive bonding for spacecraft and launcher applications [10]
- ISO 9142 Adhesives- Guide to the selection for standard laboratory ageing conditions for testing bonded joints. [11]

Humidity ageing conditions (of 56ºC, 70%RH) were chosen as per previous work for ESA as part of the NeoSat project based on a modified set of conditions re-calculated using the Hallberg Peck model [12].

Climbing drum peel tests were carried out in accordance with ASTM D 1781 [13]. As per the standard, 76 mm x 305 mm (3" x 12") samples were extracted from larger panels and peeled at a crosshead speed of 25.4 mm/min (1"/min). Various combinations of CoBlasted faceplates, SoA treated face plates, CoBlasted core are to be tested. Representative results from one such peel are shown in Fig 7. for bare core and a variety of surface finishes.

2.4. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was carried out using a Phenom XL (Eindhoven, NL). The Phenom XL was used to examine both the surface of the samples after treatment, as well as bond-line properties to ensure consistent preparation. Sectioned samples were cold mounted in EpoFix™ resin (Electron Microscopy Sciences Ltd. Hatfield, PA, USA), ground, and polished to a sub-micron finish.

2.5. Optical Profilometry

Surface roughness and texture measurements were undertaken using a Nanovea PS50 confocal microscope (USA) and analysed using Mountains (ver 7.4.8226) software (France). A range of properties were measured in line with ISO 4287 Geometrical Product Specifications (GPS): Surface texture: Profile method - Terms, definitions and surface texture parameters and ISO 25178-2 Geometrical product specifications (GPS): Surface texture: Areal - Part 2: Terms, definitions and surface texture parameters. Calculated parameters included surface roughness (arithmetical (Sa) and RMS (Sq) average, maximum height (Sz)), peak-to-peak density, surface area, amongst others.

RESULTS AND DISCUSSION

3.1. CoBlast summary

Initial studies were undertaken to the determine the effect of varying surface roughness on the adhesive bond strength. Further details are given in more detail in [1]. As part of this study, the ability to control the level of roughness using the CoBlast process was investigated by varying the size of the abrasive Al_2O_3 used. The particle size was varied between 13 and 525 µm. A summary of the height parameters in given in Table II.

Fig 2 a), b), c), illustrates the effect of varying abrasive size on surface roughness. The largest abrasive produces a significantly rougher surface across the key parameters measured. This high roughness may be useful for mechanical interlocking of secondary coatings or epoxies but exhibited poor adhesion due to the limited wettability of the epoxies used in this study.

The 44.5 µm abrasive (Fig. 2 b)) was found to be optimal for 2-part epoxy adhesion as it produced a uniform texture and good wettability was observed in the bonded joints. The lower roughness (Fig. 2. c)), produced with the smallest abrasive still exhibits the rolling/machining lines on the surface of the substrate and was found to be a suitable roughness range for film adhesive bonding. These abrasive sizes were selected for the production of CoBlast Prime surfaces using the FBE and metal oxide dopant materials.

Table II. Summary of roughness achieved during CoBlast processing for varying abrasive sizes

Abrasive Size	525 µm	44.5 µm	12.8 µm
Sa (µm)	8.28	0.92	0.43
Sz (µm)	110	26.3	20.0
Sq (µm)	11.5	1.31	0.59

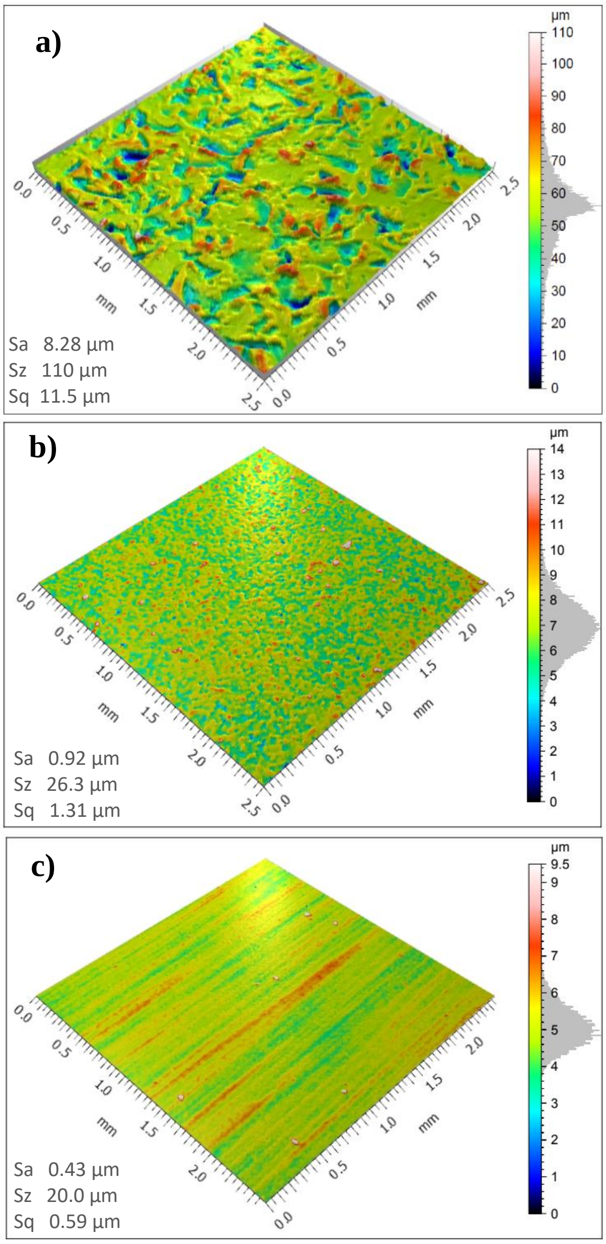

Fig. 2. Surface roughness profiles for CoBlast Prime deposited using a) 525 µm abrasive b) 44.5 µm abrasive c) 12.8 µm abrasive.

3.2. Lap-shear testing

Initial studies were undertaken using a wide range of CoBlast coating materials and compared against SoA and grit-blast surfaces [14]. To output surface of these studies was a combination of FBE and metal-oxide called CoBlast Prime, cross-section seen in Fig. 3. These surfaces were shown to achieve equivalent bonded tensile strength to commercially available SoA solutions for both 2-part epoxy and film adhesive systems, as seen in Fig. 4. The failure mode is cohesive failure/tearing of the adhesive, seen in Fig. 5.

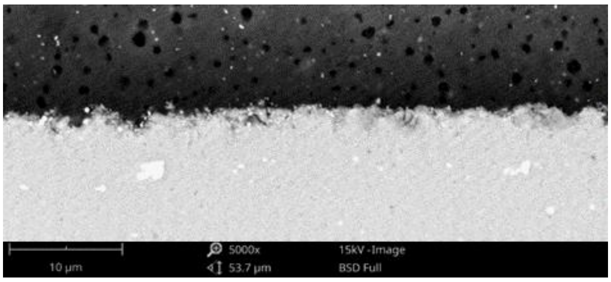

Fig. 3 SEM image of CoBlast Pime cross-section on Aluminium 2024 T3

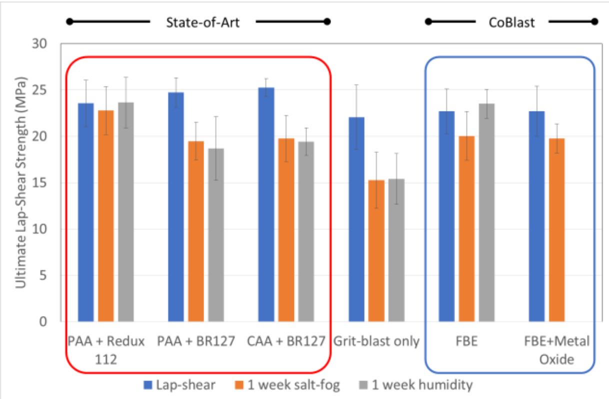

Fig. 4. Lap-shear results for Scotch-Weld 2216 2-part epoxy comparing SoA, grit-blast and CoBlast surface treatments

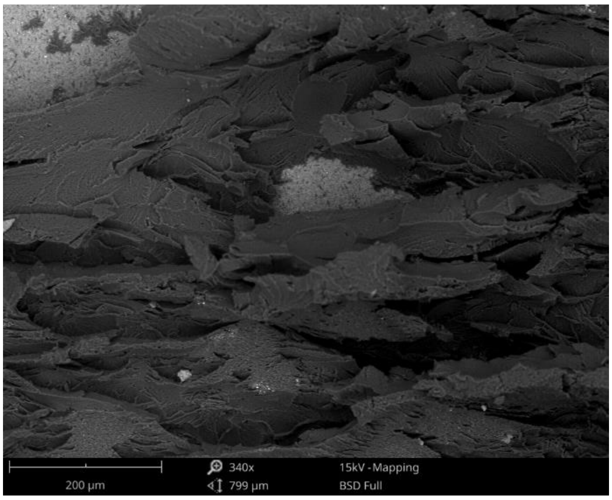

Fig. 5. SEM image of post-failure adhesive surface, showing adhesive tearing.

A further set of lap-shear comparison studies were undertaken using Redux 312 film adhesive. For this adhesive, the smoother CoBlast Prime surface was used. Similarly to the 2-part epoxy tests, the CoBlast Prime surface demonstrated equivalence to the SoA treatments (Fig. 6). Titanium surfaces were also treated alongside the Aluminium to demonstrate the multi-metal applicability of the process. Significantly higher lap-shear strengths were achieved on Ti6Al4V substrates, indicated in Fig 6 (right side). These higher strengths are likely due to the higher Young's Modulus of Titanium versus the Aluminium substrate, resulting in less plastic deformation and a truer measure of the adhesive itself.

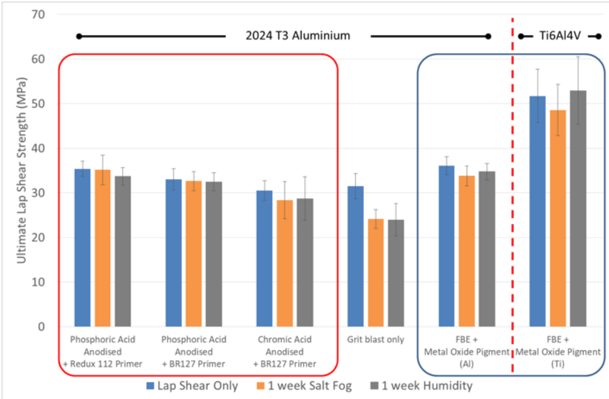

Fig. 6. Lap shear results with Redux 312 adhesive film comparing CoBlast, grit blast and SoA surfaces.

3.3. Honeycomb panel testing

Honeycomb panels were manufactured using treated and untreated aluminium face-plates, 15mm thickness Al 5052 core and Redux 312L adhesive. CoBlast Prime face-plates were compared against CAA with Redux 112 primer. Initial results from honeycomb panel testing demonstrates that the CoBlast surface is compatible with Autoclave vacuum-bagging assembly and demonstrates equivalent performance to SoA surface treatments, as seen in Table III. The peel-force profile is similar for both SoA and CoBlast treated panels, see Fig. 7.

Table III. Average peel forces during honeycomb peel testing

	Average (N)	Std. Dev (N)
SoA (CAA+Redux 112)	639.25	63.00
CoBlast (FBE+metal oxide)	626.92	59.63
Untreated face-plate	200.65	5.98
Face-plate only	187.12	4.60

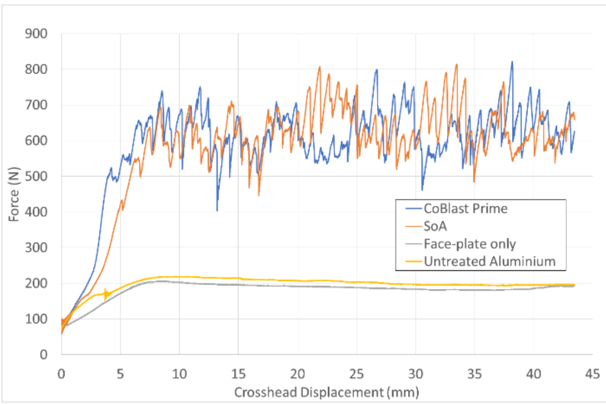

Fig. 7. Load Profile for honeycomb panel tests

Although the load profile exhibits fluctuations, this is indicative of the honeycomb area in contact with the adhesive during peeling. No flexion of the panel was observed during testing (Fig. 8). Untreated aluminium exhibited almost no adhesive strength, exhibiting similar properties to a face-plate only test. Storage and salt-fog testing will be completed in the coming months.

Fig. 8. Climbing drum honeycomb peel adhesion test

CONCLUSIONS

CoBlast Prime has been shown as an alternative treatment to achieve adhesive properties as current SoA treatments that are subject to REACH legislation. In lap-shear testing, CoBlast Prime demonstrates equivalent mechanical properties and exhibits cohesive failure during testing, before and after ageing for both 2-part epoxy and film adhesion systems. In honeycomb peel testing, CoBlast Prime demonstrates equivalent peel forces to current SoA chromate-based technologies.

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