

Sustainable Approaches to Surface Pretreatment of Additively Manufactured Aluminium Alloys



Summary

This project aims to address the crucial need for environmentally responsible, corrosionresistant treatments for additively manufactured (AM) aluminium alloys used in aerospace, defence, automotive, and other industrial applications. Chemical conversion coatings are widely used surface pre-treatments, but the restriction on use of hexavalent chromium (Cr VI) and replacement of phosphate coatings means suitable alternatives need to be found. This project primarily focuses on identifying REACH-compliant, Cr(VI)free replacements, such as trivalent chromium (Cr III), rare earth element and silane based processes. There is also a need to understand how the performance of such pretreatments may differ when applied to AM components, compared with cast or wrought versions. Additionally, the project seeks to identify Cr(VI)-free paint systems comprising a chemical conversion coating (serving as a surface pre-treatment), primer, and top coat.

The project aims to provide industrial guidance using service-relevant data on the corrosion performance of various pre-treatments in different environments; such as neutral salt spray and accelerated exposure testing (involving a combination of cyclic conditions based on salt solution, humidity and various temperatures). Furthermore, it will include an investigation into how microstructural variations in AM aluminium alloys and traditional cast and wrought alloys influence pretreatment performance, durability, and reliability.

This project also seeks to test the REACH compliant paint systems that are compatible with REACH compliant Cr(VI) free surface pretreatments in terms of corrosion resistance, surface appearance (blisters/cracks), roughness, adhesion, thermal resistance when applied to AM, cast and wrought aluminium alloys. By evaluating the corrosion performance, adhesive bonding chacteristics, and thermal cycling resistance, the project will generate insights into suitable Cr(VI)-free surface pretreatments and REACH compliant paint systems which will enable the development of guidelines for their selection for industrial applications.

Project Concept

MOTIVATION

a) Need for REACH compliant Cr(VI)-free surface pretreatments and paint systems

Surface pretreatment of aluminium alloys for aerospace industrial applications is a key step towards improving the corrosion resistance, adhesive bonding to the substrate, and ensuring adhesion of paint systems (primers/top coats). Chemical conversion coatings are the current preferred choice as a surface pretreatment, owing to their simple and easy application and have been used for many years. The most widely used conversion coatings are based on hexavalent chromate and phosphate. However, Cr(VI) based options are identified as hazardous and are restricted in the EU (REACH, Annex XIV, SVHC list) and USA due to inherent health and environmental concerns. While their exemptions are permitted in select instances, the application process is costly and difficult. There is, therefore, a drive to find high performance, safe and environmentally benign alternatives. The most viable REACH-compliant, Cr(VI)-free replacements are either based on trivalent chromium (Cr(III)) processes (TCP) with or without a sealant, or rare earth element-based conversion coatings such as zirconium conversion coatings (ZrCCs). pre-treatments (organo-silicon Additionally, silane based



Figure 1 A cross section of a AA 2024-T3 specimen coated with AC-130 surface pretreatment, Aerodur HS 2118 primer and Eclipse Green Top Coat

chemistry) have also generated interest due to the possibility of using these compounds as "coupling agents" between metal substrates and coatings to enhance adhesion performance as well as improve corrosion performance.

There is also a clear need in the aerospace/defence sectors to identify Cr(VI)-free paint systems comprising a surface pre-treatment (chemical conversion coating (serving as a surface pre-treatment) (or) silane based pre-treatment (or) TCP) a primer, and a top coat.

b) Understanding interactions with additively manufactured components

Additive manufacturing (AM) using aluminium alloys allows for the creation of novel component designs, reduced manufacturing lead times and more efficient material usage. It can also allow for repair of components, further reducing material wastage. While extensive work has been performed developing AM technologies, little work has been dedicated to the assessment of corrosion protection mechanisms and surface pre-treatments, especially REACH-compliant pre-treatments. With the limitations on usage of Cr(VI) pre-treatments, it is necessary to identify suitable systems for corrosion protection of AM based aluminium alloys to ensure industry can exploit this strategic technology. Also, the potential for the coating to serve as a pre-treatment for bonding onto AM parts is not well understood. Identifying suitable Cr(VI)-free and REACH compliant paint systems that are compatible with Cr(VI)-free surface pre-treatments for a given AM component remains a key interest. While corrosion provention and adhesion enhancement are significant in their own right, achieving both simultaneously on AM aluminium alloys, cast and wrought version is a formidable challenge.

CONCEPT

This project seeks to provide industry guidance that addresses the need for Cr(VI)-free aluminium alloy pretreatments for improved corrosion resistance and adhesion characteristics. While there are a variety of Cr(VI)free pre-treatments that are commercially available, no published study has been dedicated to comparing their performance on AM aluminium alloy substrates, benchmarking against cast and wrought alternatives. Studies on the performance of coatings (surface pre-treatments + paints) free from REACH restrictions are limited. This project seeks to provide a clear understanding of surface appearance, roughness, adhesion, coating corrosion performance and reliability of the coatings when exposed to thermal cycling and different corrosive environments (neutral salt spray and accelerated corrosion via cyclic exposure). Sponsors will select the alloys for investigation but the initial proposal is to include 1 cast alloy (eg A360/A380), 1 wrought alloy (eg AA7075-T6) and 2 AM aluminium alloys (eg AlSi10Mg, AA7075). AM processes are diverse and result in a range of microstructures. This project will select 2 AM technologies for assessment, chosen in consultation with the Sponsors.

A programme of tests will be conducted to study corrosion performance of the materials, following pre-treatment and coating (pre-treatment + paint), to assess resistance to different environments (eg neutral salt spray and

accelerated cyclic corrosion exposure, thermal cycling), adhesion performance and surface characteristics (uniformity, roughness, thickness). The results of this project seek to provide the sponsors with clear guidance as to the most promising Cr(VI)-free coating method technologies that are suitable for AM aluminium alloys. The project will also provide a benchmark against the cast and wrought alloys. The quality of the coatings in terms of durability will be assessed by means of an adhesion test (static conditions-wet and dry), exposure to corrosive conditions (salt spray test, cyclic corrosion test) and a thermal–cycling resistance test. Reliability of a coating, which refers to the ability to withstand any change or damage such as cracking, delamination or other forms of physical or chemical degradation, will be assessed by means of exposure to corrosive conditions and thermal cycling respectively.

In delivering this project, TWI will use in-house capabilities across sites, groups, sections and expertise such as:

- In-house protocols guided by the relavent standards to characterise and assess surfaces and surface treatments.
- Prior experience in the assessment of surface pre-treatments for corrosion resistance and adhesive bonding.
- TWI's testing facilities including salt spray cabinets, cyclic corrosion chambers, thermal cycling chambers, contact angle systems, adhesion testing systems etc.
- Extensive analytical instrumentation facilities including scanning electron microscopy, optical microscopy, surface profilometery and stereo microscopy.

Objectives

- Evaluate corrosion performance (MIL-STD-810G w/change 1 Method 509.6 (or) GM9540P)
 - □ Evaluate and compare the corrosion performance of combinations composed of (i) upto 5 REACH compliant Cr(VI)-free alternative pre-treatments, (ii) upto 5 primers and (iii) upto 3 top coats on 2 different AM aluminium alloy substrates (e.g. AlSi10Mg, AA7075) in corrosive environments (e.g. neutral salt spray, cyclic corrosion). Performance will be benchmarked against the cast/wrought variants and exisiting Cr(VI) treatments.
- Understand the influence AM component microstructure on pre-treatment performance
 - □ Analyse the influence of microstructure variations in AM (e.g., AlSi10Mg, AA7075), cast (A360/A380) and wrought (AA7075-T6) alloys on corrosion performance, durability, and reliability of Cr(VI)-free pre-treatments.
- Assess durability and reliability
 - □ Evaluate the thermal cycling resistance of Cr(VI)-free pre-treatments and coatings (pre-treatment + paint) on AM, cast and wrought alloys.
 - □ Measure the durability and reliability of Cr(VI)-free pre-treatments, coatings (pre-treatment + paint) on AM, cast and wrought alloys, including adhesion (according to ASTM D3359-17/ISO 4624), coating thickness (according to ISO 2808), surface energy/wettability (ISO19403-2) and following thermal cycling (MIL-STD 883H 1010.8 cycle C).
- Identify promising Cr(VI)-free coating technologies
 - □ Compare the performance of various Cr(VI)-free pre-treatments and coatings (pre-treatment + paint) to identify those suitable for AM aluminium alloys based on the data obtained from the tests conducted on corrosion resistance, durability, and reliability.
 - Provide a ranked list of pre-treatment and coating (pre-treatment+paint) options (based on the test results associated with corrosion resistance, durability, reliability, thermal cycling resistance) to the sponsors.

Benefits

- Reduced risk of corrosion damage of critical components
 - □ The project's evaluation of alternative Cr(VI)-free pre-treatments and coatings (pre-treatments+ paints) on AM aluminium alloys and traditional cast and wrought alloys will:
 - Increase confidence in commercially available REACH compliant Cr(VI)-free products and aid product selection by providing an independent assessment on the corrosion performance.
 - Reduce barriers to adoption of AM technologies, enabling the potential to produce intricate, light weight, low cost components. This will reduce maintenance costs, improve asset availability and extend asset service.
- Reduced costs by implementing sustainable and environmentally friendly solutions, with less regulatory burden and hazardous waste costs.
 - □ By focusing on REACH compliant and environmentally sustainable pre-treatments and coatings, the project aligns with industry demands for environmentally benign alternatives. The identified REACH compliant Cr(VI)-free coatings will offer eco-friendly options for industrial applications focusing on corrosion protection of AM aluminium parts, contributing to improve health & safety and reduced environmental impact.
- Increased coating durability and reliability
 - □ The project's investigation of coating adhesion, coating thickness, and thermal cycling resistance will provide an understanding of the durability and reliability of the Cr(VI)-free pretreatments/paint combinations on AM aluminium alloy parts. This will reduce unplanned maintenance costs and increase longevity of aerospace, automotive, and other industry components based on AM aluminium alloys.

Overall, the successful achievement of the project's objectives will result in tangible benefits for the aerospace, automotive, defence, and other industry sectors. These benefits will positively impact the industries' competitiveness and environmental responsibility.

Approach

- WP1: Pre-treatment Selection and Characterisation
 - □ T1.1: Selection of upto 5 REACH compliant Cr(VI)-free pre-treatments
 - □ T1.2: Selection of 2 AM processes
 - □ T1.3: Selection of 2 aluminium alloys and cast and wrought alloys
 - □ T1.4: Selection and application of pre-treatments
 - □ T1.5: Characterisation of as-received pretreated samples and substrate materials
 - Cross-section evaluation, adhesion testing, surface roughess, uniformity, surface energy/wettability, chemical analysis (FTIR) etc.
- WP 2: Pre-Treatment Testing and Analysis
 - □ T2.1: Corrosion performance testing in selected environments (MIL-STD-810G w/change 1 Method 509.6 and GM9540P).
 - □ T2.2: Characterisation of pre-treated samples during and following testing (pre-macros, 168h, 336h, 1008h and after end of test)
 - Microscopy
 - Surface roughness
 - Adhesion

- **T2.3:** Correlation of microstructure with corrosion performance
 - Identify specific microstructural elements that affect the durability and reliability of Cr (VI)-free pre-treatments
- WP3: Pre-treatment Durability and Reliability Assessment
 - □ T3.1: Thermal cycling resistance testing
 - Assessment of thermal cycling performance, recording the number of cycles until pretreatment failure
 - □ T3.2: Pre-treatment durability and reliability analysis
 - Assessment of impact of the thermal cycling on pre-treatment adhesion.
 - □ T3.3: Down-selection of pre-treament/substrate combinations
 - Consideration of WP1-3 data on pre-treatement performance
 - Down-selection of most promising candidates
- WP4: Coating Selection and Characterisation
 - □ T4.1: Selection and application of upto 5 primers and 3 topcoats, all REACH compliant.
 - □ T4.2: Characterisation of as-received coated samples
 - Cross-section evaluation, adhesion testing, surface roughess, uniformity, surface energy/wettability, chemical analysis (FTIR) etc.
- WP 5: Coating Testing and Analysis
 - □ T5.1: Corrosion performance testing in selected environments (MIL-STD-810G w/change 1 Method 509.6 and GM9540P)
 - □ T5.2: Characterisation of coated samples during and following testing (pre-macros, 168h, 336h, 1008h and after end of test)
 - Microscopy
 - Surface roughness
 - Adhesion
- WP6: Coating Durability and Reliability Assessment
 - □ T6.1: Thermal cycling resistance testing
 - Assessment of thermal cycling performance, recording the number of cycles until coating (pre-treatment+paint) failure
 - □ T6.2: Coating durability and reliability analysis
 - Assessment of impact of the thermal cycling on coating adhesion.
- WP7: Identification and recommendation of promising Cr-free coating technologies
 - □ T7.1: Comparative analysis of coating performance
 - Comparison of the corrosion performance, durability, and reliability based on the data obtained from previous work packages.
 - Ranking of coating options based on their suitability for AM aluminium alloys and other traditional aluminium alloys using a list of key performance indicators.

Deliverables

The main deliverables of the project are:

- Individual Work Package reports including details of the performance for each pre-treatement and coating in terms key performance indicators - corrosion resistance (neutral salt spray, cyclic corrosion, thermal cycling), adhesion, durability and reliability.
- A final report (WP7) detailing interpretation of WP1-6 test results for Cr(VI)-free pre-treatments on each AM, wrought and cast aluminium alloy.
- Quarterly e-mail progress statements and progress meetings at six month intervals.

Price and Duration

The overall estimated price for the work is £480,000 (excluding VAT), which requires £60,000 per company per annum for a period of two years . It is anticipated that the project will commence with an reduced scope of work with a minimum of £360,000 and 3 sponsors (excluding VAT).

Further Information

For further information on how a Joint Industry Project (JIP) runs please visit:

http://www.twi-global.com/services/research-and-consultancy/joint-industry-projects/

JIP Co-ordinator: Sofia Sampethai

Email: jip@twi.co.uk

Project Leader: Ben Robinson/Kranthi Maniam

Email: <u>ben.robinson@twi.co.uk</u> | <u>k.maniam@twi.co.uk</u>