DEVELOPMENT OF AN IMPROVED SURFACE PREPARATION FOR TITANIUM BONDING AND TITANIUM GRAPHITE LAMINATES FOR AIRCRAFT AND SPACE VEHICLE APPLICATIONS

A. Fink [1]
S. Sophabmixay [2]
W. DuMars [2]

[1] DLR, German Aerospace Center
[2] Triumph Fabrications – Fort Worth, USA

1 Introduction

The aerospace and spacecraft industry's increasing requirement for weight reductions demands the development of advanced materials which allow for a better mechanical performance, a higher structural efficiency, high reliability and better long-term behavior. In view of the wide range of the material's performance requirements, special efforts have to be made to perform an intelligent use of the diversity of engineering materials available in the present time according to their specific potentials and shortcomings.

The idea of combining different materials with very different characteristics aiming a composite material which better properties than those of the single constituents has been known from antiquity. A special configuration of these compounds represents the laminated material, which is characterized by the alternate combination of sheets or plates of dissimilar materials. Probably the earliest known reference of laminated materials improving structural properties is found in the Iliad of Homer, 800 BC referring to the Achilles shield.

Aluminum has been the most important and most widely used material for aerospace applications up to now. Recognizing the limitations of pure metal structures, which are prone to fatigue, fibre metal laminates (FML) have been conceived and developed to combine the mechanical advantages of metal and reinforced plastics, thus leading to hybrid materials with excellent fatigue behavior, damage tolerance and bourn through properties. Glare (glass fibre reinforced plastics with aluminum), Arall (aramid fibre reinforced plastics with aluminum) and TiGr (titanium graphite laminates) are the best known examples.

The advances in composite material technology have opened new perspectives in view of the increasing demand for superior structural performance and efficiency. Nevertheless, the notch and impact sensitivity, the brittleness, the limited damage tolerance, the difficult mechanical joining, the low wear resistance and the inherent degradation effects are limiting properties of composite materials in terms of their acceptance and use for primary aircraft structures. Recognizing the limitations of pure composite materials, new developments entail the hybridization with metal taking advantage of the metal's material properties to optimize the exploitation of the mechanical capacity of the composite constituent.

2 Fibre Metal Hybrid laminates

Fibre metal laminates feature alternately stacked layers of monolithic metal and fibre reinforced plastic to form a material that has potential advantages over either material alone. Starting from the deficiencies of pure fibre reinforced plastics, the hybridization with metal aims to improve, among other aspects – the thermal stability, conductivity, wear resistance, damage tolerance as well as the bearing and joint strength of composites. The hybridization of composite material has been investigated by the Institute of Composite Structures and Adaptive Systems of the German Aerospace Centre for a wide variety of applications, either as structural material for the design of panels, skins and stiffeners or as local reinforcement of composite laminates. **Fig 2.1** shows an exemplary configuration of a laminated hybrid material.

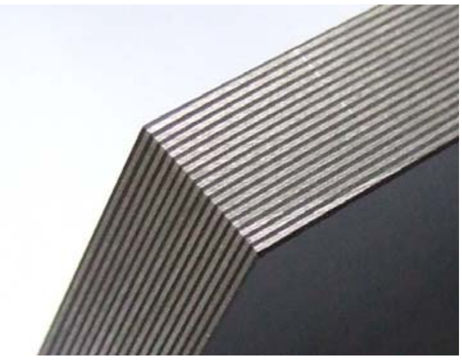

Fig. 2.1: Laminated fibre-metal hybrid material: CFRP (dark plies) and Titanium (source: DLR).

2.1 Technological aspects of CFRP-Metal hybrid laminates

The combination of dissimilar materials not necessarily leads to an addition of their outstanding properties. The exploitation of several properties of one constituent may be rather limited to a certain extent by the poor corresponding properties of its partner constituent. Hence, the tensile elongation of the hybrid laminate is expected to be restrained by the most brittle constituent, independently of the outstanding ductility of the partner. However, the impact or crash behavior of the brittle partner may be very well positively affected by the toughness of the ductile constituent within the hybrid laminate. The material combination means, in the most cases, to sacrifice some advantageous properties of the single constituents for the sake of some special properties of the hybrid material, which represent the design driver of the structural part. The combination of aluminum and GFRP in Glare leads to a lower material stiffness and lower yield strengths in comparison to monolithic aluminum. The crack growth resistance however is considerably improved, which is deemed essential for fatigue critical elements. As a result, the material combination has to be configured and the properties of the constituents be tailored in accordance to the target capabilities.

The *Institute of Composite Structures and Adaptive Systems* of the DLR has been working on the combination of carbon fibre, glass fibre and aramid fibre with either titanium or steel. Thermoset and, to a smaller extent and only for special applications, thermoplastic resins have been used. Hybrid laminates have been demonstrated to be compatible with prepreg and resin infusion techniques.

The metal foil thickness and the related laminate discretization have been determined to be crucial in terms of damage tolerance, strength and delamination resistance. The mechanical performance is improved with smaller sheet thicknesses; on contrary, the handling, processing and manufacturing complexity is considerably increased. The metal sheet thickness range varies from 0.1mm to 0.5mm.

Some essential aspects affecting the compatibility of dissimilar materials are the galvanic compatibility and the CTE mismatch. The differences in thermal expansion result – especially in combination with a high material stiffness – in large residual stresses that have a negative impact on the static and fatigue characteristics. For CFRP the most suitable material choice is titanium and corrosion resistance steel. Titanium is characterized by its high specific strength and stiffness, relatively low CTE mismatch and excellent galvanic compatibility to carbon, whereas steel features high absolute strength and stiffness and low material costs but a higher CTE mismatch and specific weight.

2.2 Applications of CFRP-Metal hybrid laminates

The *Institute of Composite Structures and Adaptive Systems* is performing extensive investigation activities on fibre metal laminates following a wide variety of applications in the field of aircraft, spacecraft, automotive, transportation, energy and defense. Fibre metal hybrid materials are used on the one hand as a reinforcement approach of highly loaded composite bolted joints taking advantage of the isotropic properties of metals which simultaneously increase the bearing, shear and notched strength at a bolt loaded hole, thus allowing for high mechanical joint efficiencies. One exemplary application represents the intersegment joint of a future Ariane 5 composite booster case, whose reference design is characterized by a massive local thickening – in order to provide enough bearing and shear strength capabilities – and a two bolt row in staggered configuration. Massive steel rings with a standard clevis-tang configuration are used to join each booster segment, where the ultimate axial loads amount to about 80MN. By means of locally hybridizing with either high strength titanium or steel, the local thickening is entirely eliminated, thus avoiding secondary loading due to eccentricities, and the double-row design replaced by a single-row design resulting in mass reductions of up to half a ton per each intersegment joint. **Fig 2.2** shows the transition region between pure CFRP and CFRP/steel hybrid material. Other applications of reinforcement through hybridizing are found in the rotorcraft root joints of wind turbines, the attachment of spacecraft payload adaptors and highly loaded lug joints for aircraft structures.

Fig 2.2: Transition region between CFRP and CFRP/steel hybrid material (source: DLR)

On the other hand, fibre metal laminates are being developed as a construction material. The extremely high strength, stiffness and fatigue properties of hybrid material with 0° ply orientation allows the application of laminated hybrid material in structural parts with mainly one load direction like stringers, longerons and struts simultaneously exploiting the outstanding specific stiffness and strength and damage tolerance properties. **Fig. 2.3** shows exemplary sections of such kind of elements.

Special applications require the abrasive and wear protection of composite surfaces or the protection against degrading environmental effects like moisture absorption, oxidation or contact with hydraulics and lubricants for which the insertion of thin outer protective metal sheets have been demonstrated to be an efficient approach. **Fig 2.4** shows a composite skin protected by an inner and outer thin titanium foil, as well as a local outer titanium protection of a thick section subjected to wear abrasion.

Fig 2.3: Stringer and strut sections with hybrid CFRP-Metal material. (Source: DLR)

Fig 2.4: Skin protection with outer metal sheets (left). Abrasion protection (right). (Source:DLR)

3 Surface treatment technique

3.1 Background

One of the most critical and challenging aspects of creating reliable bonded joints is the surface preparation of the substrates. In the case of metal substrates the preparation must; 1) be compatible with the adhesive or composite matrix resins, 2) be repeatable and easy to control, 3) form bonds that can withstand stresses and harsh environmental exposures for the service life of the structure. Ideally the bond to the metal is stronger and more durable than the adhesive, bond primer or composite matrix resin. Much like phosphoric acid and chromic acid anodized replaced previous etching methods for preparation of aluminum for bonding, the Boeing Sol-Gel process is being accepted as the industry standard for preparation of titanium for bonding. Processes such as chromic acid anodize, phosphate fluoride and Pasa-Jell treatments have been shown to be hard to control and incorporate harsh chemicals such as strong acids and chromates. The Sol-Gel process is easy to control, is chromate and solvent free which have no health-safety or environmental issues. An additional feature of the Sol-Gel process as opposed to others is that it lends itself to continuous, coil to coil, processing of thin gage foil for use in titanium/graphite laminates. Sol-Gel technology is also excellent for bonded field repairs for titanium and aluminum and as a preparation of those metals for painting. Sol-Gel in conjunction with bond primer is an excellent preparation for bonding of 300 series stainless steel.

3.2 The Sol-Gel Process

Sol-Gel is a contraction of "solution-gelation". It refers to the process by which a metal alkoxide solution is transformed into a polymerized "gel" network through hydrolysis and condensation reactions. The Sol-Gel solution is commercially available as kits (AC-130) of carefully controlled mixture of a zirconium compound, a silane compound, glacial acetic acid, a surfactant and water. Basically, the Sol-Gel solution leaves a thin film (20 to 300 nm) on the surface which bonds to the metal and leaves active sites for the organic primer or adhesive to attach to. The depiction in **Fig.3.1** shows the orientation of the critical constituents of the sol-gel coating which produce strong durable bonds between the metal and the organic adhesive.

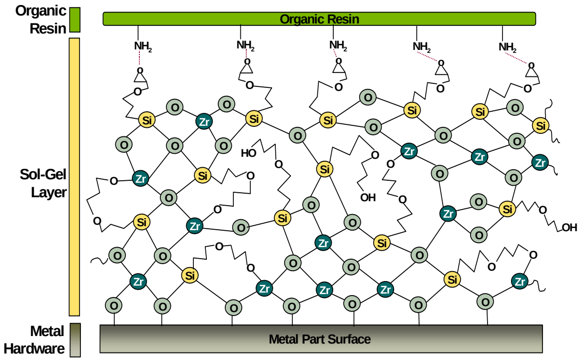

Fig. 3.1: Designed Sol-Gel interface

Typical Sol-Gel processing includes the following steps:

1. Etch- Either chemical (acid) or mechanical (aluminum oxide grit blast)
2. Rinse
3. Surface activation-50% hot Turco 5578L
4. Rinse
5. Dry
6. Sol-Gel drench
7. Dry
8. Apply bond primer or liquid adhesive

Bond primer is applied to the sol-gel surface to lock in and protect the fragile surface. It also allows for long term storage of the prepared metal and may be reactivated if contamination occurs. The most commonly used universal bond primer used in conjunction with Sol-Gel process is BR 6747-1 zero VOC chromated primer from Cytec Engineered Materials although other primers such as EC 3917 from 3M Aerospace is also approved for some applications. Test specimens used for qualifications and process control include lap shear, metal to metal peel and environmental wedge crack tested with either 121°C or 177°C (250F or 350F) cured modified epoxy film adhesives. Typical values achieved are 41.37 MPa (6000 PSI) for lap shear, greater than 4.5 kN/m (40 in.bls/in) peel and crack growths of less than 6.35mm (.25 inch) after exposure to 60°C and 95% to 100% humidity for 7 days. In all cases it is required that the failure modes are greater than 95% cohesive in the adhesive or primer. **Fig. 3.2** shows exemplarily optimal cohesive failure of peel and wedge crack (**Fig. 3.3**) specimens.

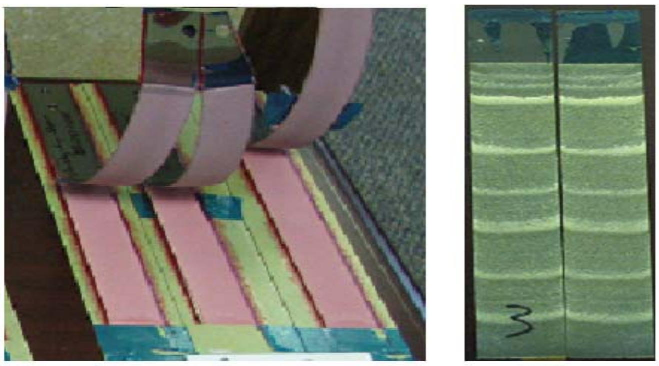

Fig. 3.2: Cohesive failure of metal-to metal peel (left) and wedge crack specimen (right). (Source:Triumph)

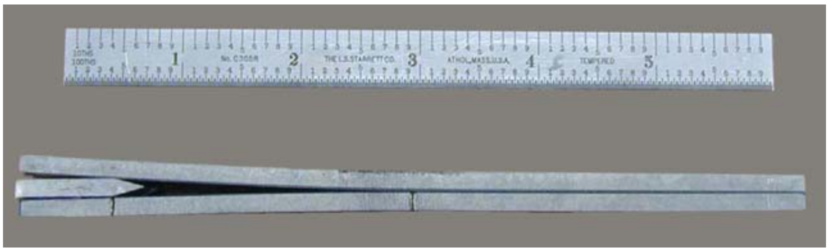

Fig. 3.3: Wedge crack specimen. (Source:Triumph)

3.3 Titanium Foil Processing for Laminates

Triumph Fabrications - Fort Worth (*www.triumphgroup.com*), one of the Triumph Group companies, developed continuous foil process capabilities as a joint venture with Boeing to support design concepts for titanium graphite laminates. The capabilities include processing up to 305mm (12 inch) wide coils of foil of thicknesses between 0.025 and 0.254mm (0.001 and 0.010 inch) at line speed of 1.52 meters (5 feet) per minute. For material requirements outside these parameters and for hardware TFFW has the capability to batch process of sizes up to 1.2 and 5.5 meters (4 by 18 feet).

Continuous foil process steps include:

1. MOD 1- Grit Blast **(Fig 3.4)**
   a. Aluminum oxide slurry robotic grit blast
   b. Two stage rinse
   c. Dry
2. MOD 2- Sol-Gel **(Fig 3.5)**
   a. Spray treatment of hot Turco 5578L
   b. Three stage reverse osmosis (RO) water rinse
   c. Spray application of Sol-Gel
   d. Dry Sol-gel Coating
3. MOD 3- Adhesive or application **(Fig 3.6)**
   a. Dip application of selected adhesive
   b. Heat set
   c. Application of separator plastic film

Fig. 3.4: MOD-1: slurry grit blast.

Fig. 3.5: MOD-2: etch and Sol-Gel.

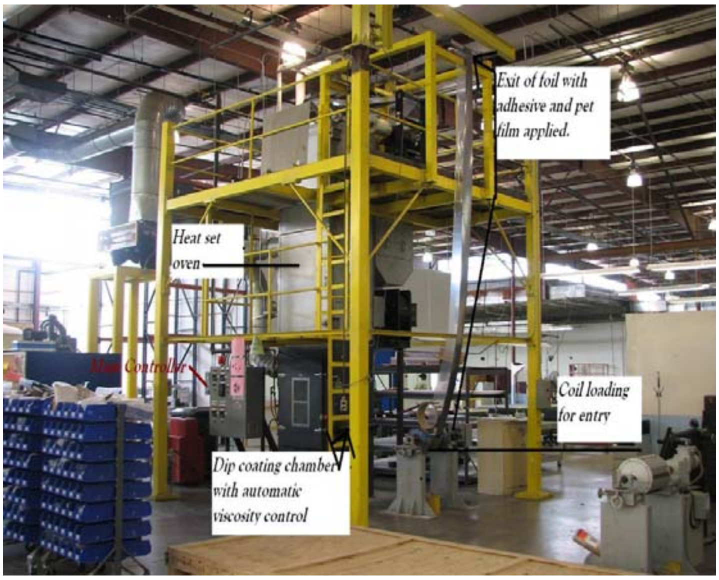

Fig. 3.6: MOD-3: Adhesive application.

3.4 Actual industrial applications

The Sol-Gel process for preparing titanium for structural bonding is a mature process and is accepted by most aerospace companies. Examples of current production applications include titanium spars for F-35 composite flight control surfaces, primary structure on 787 titanium to composite hardware, lightning protection straps on rotorcraft and foil for rain erosion protection of large composite 787 parts. The approval process is proceeding for many other fixed wing and rotorcraft applications.

4 Summary and Conclusions

Metal treatment prior to bonding is a key factor for both the adhesive strength and its long-term environmental durability. Conventional surface treatment techniques of preparing metal surfaces for bonding, like anodizing and etching, are characterized by complex processes and use hazardous materials. Sol-Gel techniques have been proven to provide an environmentally compliant, high-performance, simple and cost-efficient approach for metal surface preparation. The outstanding process and performance properties of So-Gel techniques enable numerous applications in the design of composite structures in aeronautics, transportation, automotive and energy. The hybridization of composite laminates with metal helps to overcome specific mechanical shortcomings of composites thus optimizing and extending its use in lightweight design. The use of Sol-Gel technologies helps to open new research fields of metal-composite hybrid laminates and introduce them into a wide variety of industrial applications. The *Institute of Composite Structures and Adaptive Systems* of the *German Aerospace Center DLR* has been researching on metal-composite hybridization and its multifaceted use on composite structures under the use of Sol-Gel techniques for metal surface treatment experiencing a high reliability and performance of Sol-Gel techniques. Metal foil processing has been carried out in collaboration with Triumph Fabrications - Fort Worth, who performs Sol-Gel treatments of metal foil within a continuous process.