Study of Advanced Composite Structures for High Temperature Applications.

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Abstract

The fibre metal laminates offer significant improvements over traditional materials for aircraft structures. The prime drivers of their development are weight reduction and improved damage tolerance characteristics, but it turns out that they have additional benefits which become more and more important for today's designers, e.g. cost reduction and improved safety. The combination of aspects typical of each constituent materials in one material is an extraordinary achievement.
This work concerns the analysis of the in-plane shear strength of Hybrid Titanium Composite Laminate developed for high temperature in aeronautical and space applications.
The Hybrid Titanium Composite laminate (HTCL) keeps the mechanical advantages of existing hybrid composite laminates such as ARALL and GLARE while extends their applications to harsh environments. HTCL has proven to possess exceptional strength and fatigue resistance.
Hybrid composite laminates, consisting of layers of Titanium grade 2 and Titanium grade 5 foils bonded together with fibre-reinforced composite plies and with carbon + PEEK plies, have been utilised in the "Single Lap Shear" tests for the analyses of the bond strength.
Special attention has been paid to surface treatments, which appear critical in Titanium bonding: both a mechanical one such as plasma spray and a chemical one such as chromic acid anodisation, have been tested on HTCL laminate in order to verify mechanical performances of the interface.
As expected, different results have been acheived for the two treatments: in particular plasma spray denoted good resistance but lower ductility compared to ionic anodisation.

1. Introduction

Composite materials are lifting off in aeronautic applications and now for the first time we are witnessing their massive use in primary aerostructures of civil passenger aircrafts. The strongest sign of the current increase in aerospace is that they are now accepted for major primary structures on both Boeing new 7E7 "Dreamliner" and the world's largest airliner, the Airbus A380, in construction. The Boeing 7E7 will have the half of its weight made of composite reinforced plastics, outclassing every other civil airliner in the use of FRP, while the Airbus A380 is the first airliner to adopt Fibre Metal Laminate (FML) for the construction of a primary structure. The use of Glare, developed at the University of Delft in the 80's, for over 400 m^2 of the A380's fuselage crown will not only secure a 25% weight saving over a conventional structure, it could also start a major new trend in aerospace material application. Composites do also provide advantages of durability, reduced maintenance, parts consolidation, increased development potential and the possibility of self-monitoring through the inclusion of 'smart' fibres and embedded sensors.
The Department of Aerospace and Astronautic Engineering (DIAA) of the University "La Sapienza" of Rome is paying much attention to the Fibre Metal Laminates (also called hybrid laminates) for their advantages respect to metals, in particular it is focusing its attention in the development of a FML for high temperature applications in aeronautics and aerospace, in order to extend the typical benefits of GLARE to high temperature environment.
A typical hybrid laminate is composed by a sequence of thin metallic layers and sheets of fibre reinforced polymeric composite. The benefits of hybrid laminates arise from the ability to tailor material properties so that the attractive aspects of the two constituent materials are kept and their

weaknesses are avoided. In the present research, the metallic layers are made of Titanium alloy, while a wide range of resins and fibres have been selected for the composite layers in order to investigate different configurations. The titanium protects the composite layers from environmental effects such as oxidation and moisture absorption as well as potentially providing improved impact resistance and bearing properties. The composite layers have higher strength and stiffness to weight ratios than monolithic titanium and is presumed to be less sensitive to fatigue effects. The combination of the two materials into a hybrid composite could potentially outperform both the two constituent materials in elevated temperature structural applications. Moreover FML will be less susceptible to fatigue than metal and less expensive than pure composite.

Fig. 1.1 – The Airbus A380 has 400 m2 of upper fuselage made of GLARE. It will permit to save up to 25% in weight respect to a conventional structure.

Fig. 1.2 – The Boeing 7E7 "Dreamliner" will be the first civil passenger airliner to use composite materials for more than 50% of its weight.

In particular the present research will be focused on the effects of the surface treatments of titanium in order to improve the strength of the interface between the composite layers and the metal ones, representing the most critical aspect in a FML. The effectiveness of the treatments will be evaluated by single lap shear tests.

2. Titanium alloy surface treatments.

At the moment, the bonding of polymer composites to titanium is a problem, which has not been fully resolved. In order to produce a strong and durable adhesive joint between different substrates, surface treatment is necessary. Certain bonding techniques provide adequate static strength, but have little durability when exposed to hot moist environments, while others are susceptible to debonding in the presence of fuels, oils and cleaning solvents commonly encountered in aircraft applications. Surface treatment increases the bond strength by altering the substrate surface in a number of ways including increasing surface tension, increasing surface roughness or changing surface chemistry. By increasing surface roughness, an increase in surface area occurs which allows the adhesive to flow in and around the irregularities on the surface to form a mechanical bond. Changing surface chemistry may result in the formation of a chemical bond e.g. between the polymer molecules in the polymer matrix composite and the metal oxide layer on the other adherent surface layer.
Mechanical, chemical, electrochemical and energetic surface treatments are used to enhance the surface of titanium alloys prior to bonding. Durability studies of Ti 6Al 4V reveal that surface preparations that produce no roughness (macro or micro) yield the poorest bond durability. Those that produce significant macro-roughness but little micro-roughness yield moderate to good durability. Finally those that produce significant micro roughness yield the best durability.
In this paper two methods of surface treatment, a novel plasma spray (PS) and chromic acid anodisation (CAA) treatments on CP2 and Grade 5 titanium alloys will be discussed. These treatments will be reviewed with respect to changes in surface morphology, surface roughness and explaining how these changes affect bond strength and durability of polymer composite titanium adhesive joints.
First we have performed plasma spray and chromic acid anodization treatments on Ti Grade 2 specimens in order to compare their efficiency in the bond strength. The lap shear tests revealed the unreliability of PS and so only the CAA treatment has been performed on Ti Grade 5 and analyses have been carried out on the roughness and morphology of the treated surface.

3. Plasma spray on Titanium Grade 2 specimens.

Little surface characterizations have been carried out on plasma spray treatment. Plasma spraying involves rapidly heating powders to a molten or semi-molten state and then spraying it with a plasma torch onto the titanium substrate at high velocity. This is a method of surface treatment employed for adhesive bonding that involves no hazardous chemicals or pollutants and it permits a high flexibility to design coatings for specific applications, insensitivity to surface contamination, indefinite shelf life prior to bonding, suitability for repair, low processing costs. It is possible to use all kind of powder or a mix of them with different composition among the thickness.
After degreasing an grit blasting, Titanium Grade 2 specimens have been treated with PS in CSM laboratory with the deposition of TiO_2 powder in Argon atmosphere with a medium thickness of the deposited layer of about 50 µm. To obtain such a thickness the process requires three subsequent expositions to the plasma flow. The deposited surface presents a high micro-roughness that receives the resin forming a good strong adhesion. During each exposition, the metallic foil is heated by the plasma over 100°C. In order to containing the heating of the specimens and to avoid excessive residual stresses between the deposited layer and the titanium substrate, it is necessary to cool the titanium with a fresh argon flow after each of the required deposition steps. After the process, the treated specimens have been stored in a clean ambient till the bonding and no primer has been applied.
As it resulted from the tests reported below in section 5, the thermo-mechanical characteristics' differences among the deposited powders and the titanium substrate, as the coefficient of thermal expansion and the stiffness, lead to a fragile adhesion between the deposited layer and the titanium substrate, that could be very dangerous in a primary aerospace structures.

4. Chromic acid anodization on Titanium Grade 2 and Grade 5 specimens.

Chromic acid anodisation oxides are reported to exhibit remarkable bond durability and provide the target bond strengths and durability for all other titanium surface treatments. For this reason it has been performed as reference for the plasma spray treatment. The superficial oxides are subjected to a gradual ageing if exposed to atmosphere, so it is necessary to preserve the formed surface with a thin layer of primer within eight hours from the treatment. Primers has other important roles that are to favor the bonding between adhesive and adherents, increasing the wettability of the surface and forming chemical bonds with adherents, and to inhibit corrosion and to increase bond strength in presence of water or water vapours. Two primers have been used and their influence on mechanical strength of the bonding compared: the EC-3960 by 3M and the Redux BR 112 by Hexcell. The first is indicated by 3M for the use in combination with the adhesive AF-163, while the BR 112 is more friendly to store and use.
Chromic acid anodisation produces a surface with significant microroughness and an oxide thickness of 40 and 80 nm depending on the applied voltage. Chromic acid anodisation has been performed as described in the following lines. The samples were degreased with MEK, pickled in 15% by volume of 70% nitric acid, 3% by volume of 50% hydrofluoric acid at RT for 30 s. They were subsequently rinsed with running distilled water for 1 min and than dried.

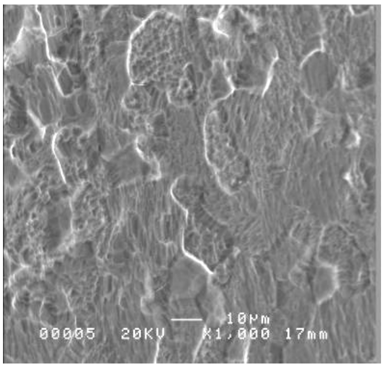

Fig. 4.1 – Titanium Grade 2 surface SEM after pickling.

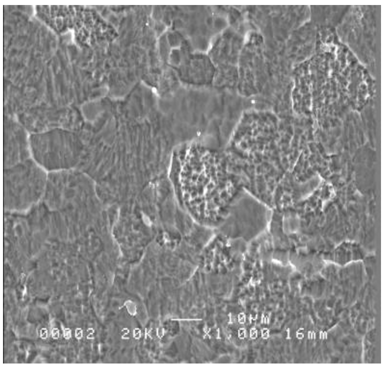

Fig. 4.2 – Titanium Grade 2 surface SEM after anodization.

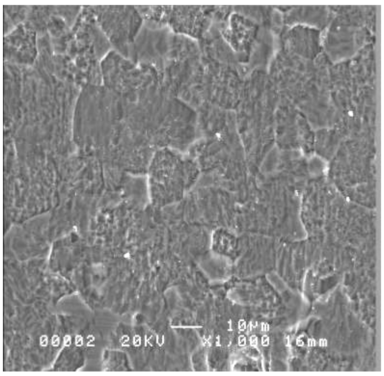

Fig. 4.3 – Titanium Grade 2 surface SEM prior to bond.

Anodization was performed in an electrolyte containing 5% CrO_3 and 0.1% NH_4HF_2 at RT. The voltage was applied with a stainless steel electrode after the specimens were immersed in the solution and was increased from 2 to 10V at a rate of 2 V/min. The voltage was held constant for 20 min. Upon removal from the solution, the samples were rinsed in running distilled water for 1 min and then allowed to dry in atmosphere. Soon after a thin layer of the selected primer was applied and left to cure as reported from the manufacturer. The excess of primer was removed with solvent prior to bond the titanium with the composite.
Samples of CP 2 Titanium and Grade 5 Titanium alloy were treated and in figures 4.1 - 4.6 SEM of the surfaces after pickling, after anodization and "prior to bond" (with primers removed) are shown.
In both cases little or no changes can be observed among the three SEM. For the CP 2 case after the anodization process, we can highlight the little increase of microroughness in some locations respect to the pickled surface. The surface "before the bonding" doesn't show traces of the removed primer, but tests showed a very important effect of the primers, so the SEM probably doesn't show the presence of the primers.

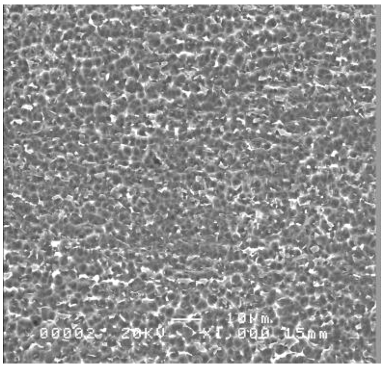

Fig. 4.4 – Titanium Grade 5 surface SEM after pickling.

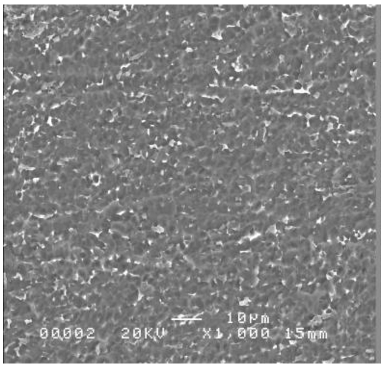

Fig. 4.5 – Titanium Grade 5 surface SEM after anodization.

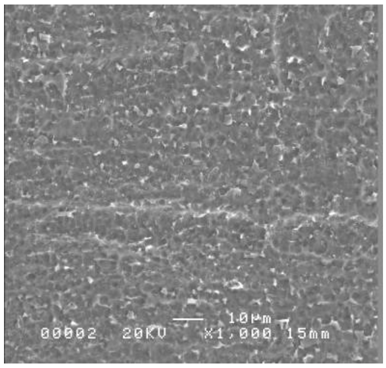

Fig. 4.6 – Titanium Grade 5 surface SEM prior to bond.

For the Grade 5 case, there are very little changes, it seems as if there was a little smoothing of the roughness due to the anodization process.
For a better evaluation of the surface changes in the process steps, superficial roughness analyses have been performed on the same samples. In table 4.1 results are reported. The values of R_a is evaluated on a length of 8 mm and it too shows little changes passing by the pickled, to the anodized and to the "prior to bonding" surface for both the CP2 and the Grade 5 titanium.

	Titanium Grade 2			**Titanium Grade 5**		
	Pickling	**Anodization**	**Bondable**	**Pickling**	**Anodization**	**Bondable**
R_a	0.58	0.60	0.60	0.52	0.55	0.56

Table 4.1 – Characteristic roughness parameters of the specimens' surfaces.

From the previous data we observe that the influence of the CAA is difficult to measure with optical or mechanical analyses, but the adhesion strength of the system titanium – primer – adhesive is undoubtedly increased by the treatment, so we can hypothesize the presence of chemical covalent bonds between oxides resulted by the CAA and the functional groups of the adhesive and primers.

5. Single lap shear tests.

Single lap shear tests were performed according to ASTM 1002 D, in order to compare the effectiveness of the two treatments and of the two primers on the Titanium Cp 2. In all the cases the specimens were prepared by stratifying the composite material and the epoxy adhesive layer directly on the treated titanium. All the specimens were then cured using vacuum bag and autoclave with a temperature of 130°C and a pressure of 5.8 Atm for 1 hour. Five specimens for each of the following configurations were tested at standard conditions. Results are reported in Table 5.1.
For the PS, Titanium Cp2 was used to realize two kinds of specimens, Titanium-Titanium and Titanium-GlassEpoxy, in order to investigate the properties of the titanium adhesive interface alone and of the whole hybrid laminate stratification. In figures 5.1-5.2 particulars of the adhesive bonds are

reported. In all the cases, the overlapping area length is 8 mm and Teflon layers were used where necessary to precisely delimitate the bonding areas, while the overlapping area width is 25 mm.

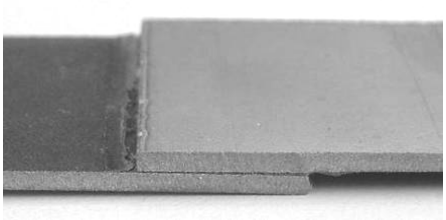

Fig. 5.1 – Titanium-AF163-Titanium single lap shear specimen.

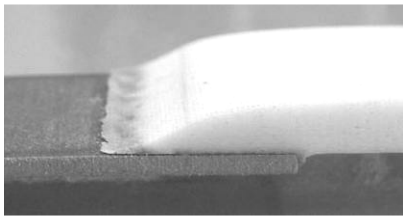

Fig. 5.2 – Titanium-AF163-Cycom 919 single lap shear specimen.

The chosen adhesive was the 3M Af-163, it is a modified epoxy structural adhesive with or without nylon support, commonly used in aeronautical applications, while the composite material is the Cycom 919 prepreg, consisting of epoxy resin and 7781 glass fibre fabric.
As reported in table 5.1 and showed in Figures 5.3-5.5, in all the tests with PS treatment the failure occurred in the interfaces between the deposited powder layers and the titanium, highlighting the poor affidability of the PS treatment. In particular, while the pure strenght performances are sensibly inferior in respect to ACC ones, the main problem is that interfaces between deposited layer and titanium substrate failure abruptly. Moreover the differences of CTE and Young's modulus among them could amplify this characteristic after service life cicling loads. A difference of 15% is observable among the two configurations and it could be a consequence of the different flexural stiffness of titanium and glass reinforced epoxy. In the above cases the supported adhesive AF-163-2k was used.

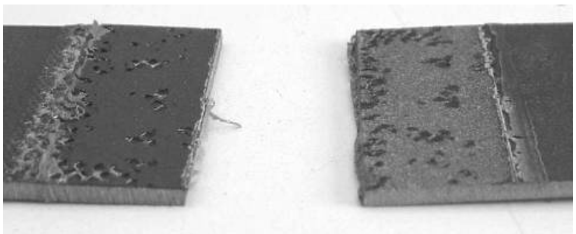

Fig. 5.3 – Failure of the Titanium-Powders interface layer in Ti-AF163-Ti specimens.

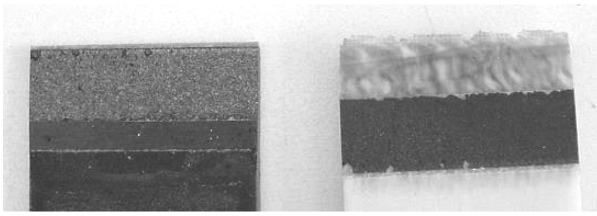

Fig. 5.4 – Failure of the Titanium-Powders interface layer in Ti-AF163-Cycom 919 specimens.

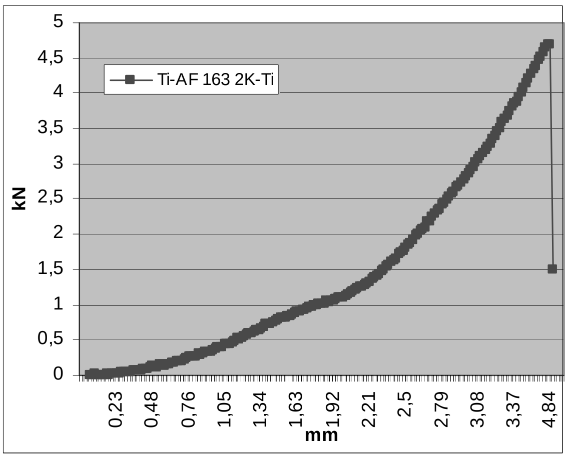

Fig. 5.5 – Load vs displacement in Plasma Spray Ti-AF163 2K-Ti specimens.

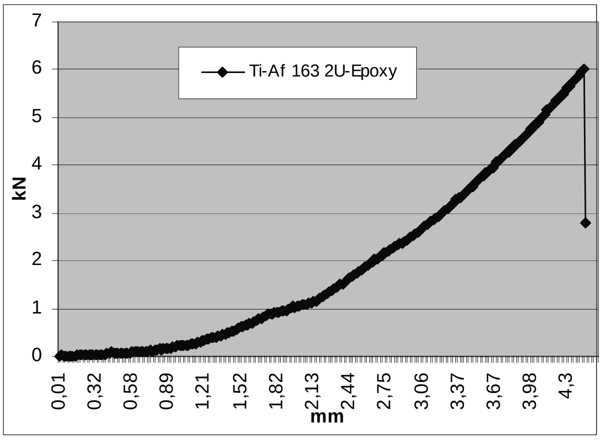

Fig. 5.6 – Load vs displacement in AAC Ti-AF163 2U-Cycom 919 specimens.

For CAA, Titanium CP2 was used to realize different configurations of lap shear specimens, Titanium-AF163 2U-Cycom 919, Titanium-Cycom 919 and Titanium-AF163 2K-Peek. The first was used to compare PS and CAA treatments' efficiency, the second to evaluate the effective efficiency of epoxy adhesive and the last to analyze the interface with carbon fiber reinforced Peek.

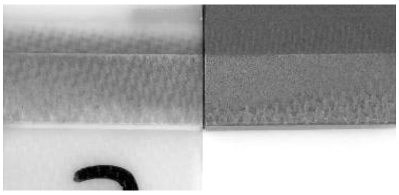

Fig. 5.7 – Failure in Ti-AF163-Epoxy specimens.

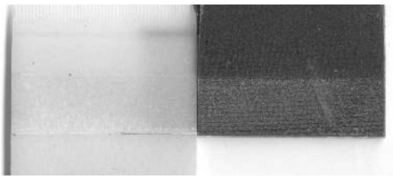

Fig. 5.8 – Failure in Ti-Epoxy specimens.

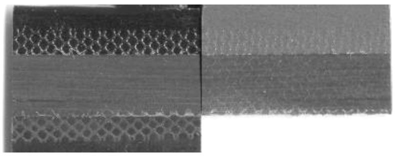

Fig. 5.9 – Failure in Ti-AF163-Peek specimens.

In figures are shown failure surfaces of specimens with CAA titanium while the figure 5.6 shows a typical load vs displacement curve in the lap shear tests on Ti-Af 163 2U-Epoxy specimen. Results in the table 5.1 highlight as the primer Redux BR-112 by Hexcell outperformed the EC3960 by 3M in these conditions, with differences of about 30% when using structural adhesive and of about 40% when no adhesive is present. Moreover, the use of structural adhesive increases the failure shear stress for more than 50% with both primers. This it is an important result, because highlight the deep improvement of bonding layer strength and it confirms the need of an adhesive layer in HTCL stratification.
In the case of Ti-AF163 2K-Peek , the difference among the two primers is not so big as in the previous cases and is about 6% in favour of Redux BR-112. The failure appened into the composite, while the adhesive layer remains bonded to titanium, in some cases a pull out of carbon fibres from composite has been noted.

	Plasma Spray		Chromic Acid Anodization					
	Ti-AF-Ti	Ti-AF-Epoxy	Ti-AF-Epoxy		Ti-Epoxy		Ti-AF-Peek	
Primer			3M	Hex	3M	Hex	3M	Hex
Load (kN)	4.57	4.21	4.37	5.99	2.88	3.67	5.73	5.65
Shear Stress (Mpa)	22.83	21.05	21.68	28.26	13.64	18.81	27.31	28.97

Table 5.1 – Failure loads and failure shear stresses of single lap shear tests, performed at standard conditions.

6. Conclusions.

Two surface treatments on titanium alloy have been performed and their action evaluated by different tests. The Plasma Spray on CP 2 Titanium revealed a critical adhesion of the deposited powders on the titanium substrate. This treatment doesn't assure bonding strength as high as the Chromic Acid Anodization and it appears substantially inadequate for primary aeronautical structures subjected to high fatigue loads. The CAA on CP 2 Titanium revealed in the lap shear tests a very high adhesive strength in all the analyzed cases, in particular the combination of structural adhesive with the Hexcell primer has shown the best performance. Tests of superficial roughness and SEM analyses on both CP 2 and Grade 5 Titanium treated with CAA have been carried out in order to highlight the effects of the chemical treatment, but they did not show big changes.
In particular lap shear results on the Titanium-Adhesive-Peek have showed the possibility to bond in a very strong way, if compared to the strength of the composite itself, materials with a high service temperature. It could be possible to realize a high temperature fibre metal laminate that could outperform standard materials in strength to weight ratio and in fatigue resistance.
It remains to investigate the properties of the Chromic Acid Anodization in a harsh environment, with exposition to hot/wet conditions and to high temperature.

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