International Journal of Adhesion & Adhesives 70 (2016) 142–151

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Effect of anodizing pretreatment on laser joining CFRP to aluminum alloy A6061

Zhou Zhang [a], Ji-Guo Shan [a,b,*], Xiang-Hu Tan [a], Jing Zhang [c]

[a] Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China
[b] Key Laboratory for Advanced Materials Processing Technology, Ministry of Education, Tsinghua University, Beijing 100084, China
[c] Shanghai Aerospace Equipments Manufacturer, Shanghai 200245, China

ARTICLE INFO

Article history:
Accepted 17 June 2016
Available online 22 June 2016

Keywords:
Anodizing pretreatment
Laser joining
CFRP/A6061 dissimilar joint
XPS analysis
Shear strength

ABSTRACT

Phosphate anodizing pretreatment of aluminum alloy A6061 was carried out before carbon fiber reinforced plastic (CFRP) was joined to A6061 using fiber laser. The results show that this kind of pretreatment could remarkably strengthen the joining between CFRP and A6061. With anodizing time varying between 10 min and 30 min, shear strength of over 35 MPa were achieved for the CFRP/A6061 dissimilar joints. The highest shear strength could reach 41.8 MPa under optimized joining parameters, which was approximately 8 times as high as that of the joint without anodizing pretreatment. From the observation with SEM, the nanoscale porous oxide layer that was produced on the surface of A6061 after anodizing pretreatment improved the wettability of CFRP on A6061, which leaded to a stronger mechanical anchoring effect at the interface. With the investigation of the transition layer at the interface by XPS, new chemical bonding of 'Al–O–PA6' was detected in the dissimilar joint of CFRP and anodized A6061. Therefore, it made clear that the oxide layer could strengthen the mechanical anchoring effect as well as promote the potential of chemical reaction between CFRP and aluminum.

1. Introduction

Carbon fiber reinforced plastic (CFRP) and aluminum alloys, which can reduce the weight of structure and increase energy efficiency, have attracted extensive attentions in aerospace and automotive industries [1–5]. On one hand, since aluminum is characterized by its good plasticity, relatively high specific strength and excellent corrosion resistance when compared with other engineering metals, more and more structures in aircraft and automobile use aluminum alloys instead of steels. On the other hand, CFRP merges as an innovative engineering material due to its high strength-to-weight ratio and excellent fatigue resistance. Therefore, to take full advantage of these two material, the demand for hybrid structures is increasing and the joining is inevitable [1,2]. In our study, the polyamide 6 is studied as a matrix material of CFRP owing to its low cost, ease of handling, and unusual properties including its good thermal stability, low dielectric constant, chemical inertness and high tensile strength [6,7].

Mechanical fastening [3] and adhesive bonding [8,9] are the two conventional methods to join polymer to metal. For the former method, the joining between polymer and metal is achieved by applying extra fasteners including screws, bolts and rivets, but it results in additional weight. Moreover, the holes created by fasteners would induce severe stress concentration and weaken the mechanical performance of the hybrid structures. For the latter method, a long preparation time has to be spent on spreading the adhesive on the substrates and curing reaction. This disadvantage of low efficiency makes adhesive bonding method unsuitable for massive industrial manufacture. As a result, researchers began to employ laser to join various engineering polymers including CFRP directly to commonly-applied metals such as stainless steel, aluminum and magnesium [10–12]. However, according to previous research results, the strength of the dissimilar joint between metal and CFRP or other polymer is relatively low because of their significant physical and chemical inconsistency. Jung et al. adopted a high quality CW diode laser to directly join CFRP to A5052 aluminum and conducted tensile lap shear tests to evaluate the quality of the joint at the traveling speed of 0.33 mm/s [1]. Their result indicated that the highest tension only reached 3000 N under optimized joining parameters, and the corresponding tensile shear strength was just about 8 MPa. In order to attain higher strength for wider application of this new joining technology, many pretreatment methods for polymer or metal have been

* Corresponding author at: Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China.
E-mail address: shanjg@mail.tsinghua.edu.cn (J.-G. Shan).

http://dx.doi.org/10.1016/j.ijadhadh.2016.06.007
0143-7496/

developed. Before laser joining the cyclic olefin polymer (COP) to SUS304, Arial et al. utilized UV-ozone and plasma pretreatment to modify the surface of COP [13]. These pretreatments enhanced the strength of the joint from 0 MPa to over 8 MPa, which was attributed to the generation of functional groups on the COP's surface and thus the promotion of adhesion between COP and the oxide film on the SUS304. However, the mechanism of chemical bonding at the interface was not explored thoroughly or clearly explained in their research. Apart from the modification of polymer, recent researches also focused on metal surface modification by laser. This method gained the most attention due to its controllable and flexible process. Prior to laser joining polyamide 6 (PA6) to aluminum, Heckert et al. used a continuous wave fiber laser to manufacture groove structures and large undercuts on the metal surface [14]. The highest shear strength of this dissimilar joint could reach over 25 MPa, which was much higher than that without pretreatment. Similar to their work, Amend et al. compared the effects of two types of laser structuring, grid structure and crater structure, on PA6/Al dissimilar joint, and verified that the shear strength could be up to 16.3 MPa by employing both the surface structures [15]. Considering this laser texturing method, the main principle for the improvement of the strength lies in creating a better mechanical interlocking of the thermoplastic with crater or undercuts structures. However, another controlled laser is needed to manufacture the structure on the surface of the metal before laser joining, which was both time consuming and costly. Moreover, the heat from laser modification also affects the original microstructure of the metal substrate and may deteriorate its mechanical properties. Therefore, extensive research should be done to optimize pretreatment methods for the metal joined to CFRP.

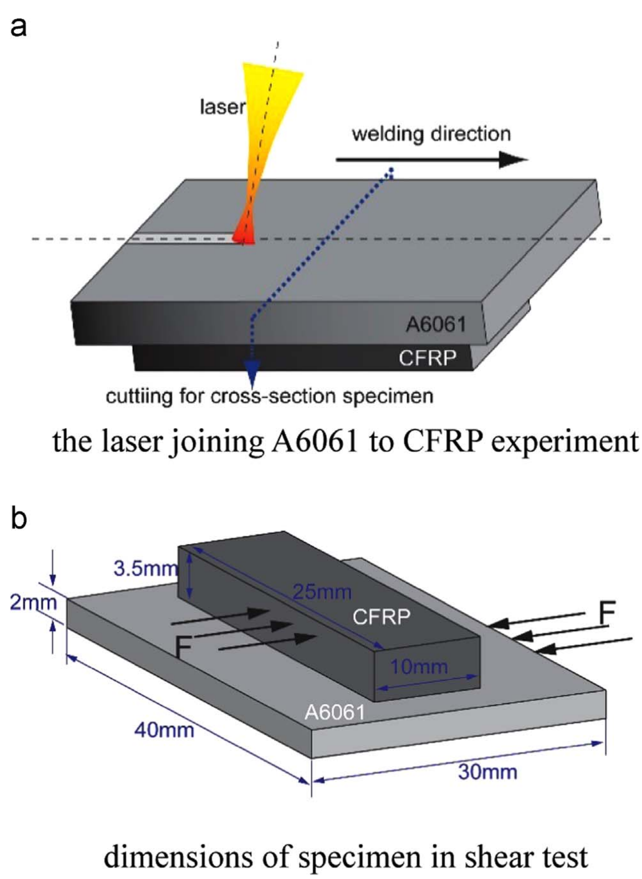

Fig. 1. Schematic diagram of the A6061/CFRP joining and shear test.

The anodizing process, a kind of electrochemistry reaction, was commonly utilized for anticorrosion treatment of aluminum in industry [16,17]. Compared with the aforementioned pretreatment methods, it has the advantages of high efficiency and low cost which is especially beneficial to mass manufacturing. In previous researches, anodizing pretreatment for aluminum is commonly applied to enhance the adhesive joint. The phosphoric/boric/sulfuric acids anodizing as a new pre-treatment for adhesive bonding of aluminum alloys were investigated by Zhang et al. [18]. The comparisons of adhesive joints with different pretreatments proved that phosphoric acid anodizing and chromic acid anodizing can lead to the highest lap-shear strength due to higher porosity of the anodic film, and it was concluded that the porous surface is beneficial for forming a composite intermediate layer and enhancing mechanical interlocking effect. Similarly, when investigating the influence of various anodizing processes on adhesion and durability of the adhesive joints, Astrid et al. also speculated that the pore size of the aluminum under different anodizing conditions might affect both glue penetration and mechanical interlocking at the interface [19]. Generally, most previous researches attributed the enhancement of shear strength of lap adhesive joint to the mechanical interlocking of porous structure or oxide protrusions of anodized aluminum [20], and systematic researches about the chemical reactions between the surface anodized aluminum and adhesives were not so much. In this research, the anodizing process was employed on the aluminum before it was laser-joined to CFRP. Shear strength was test to evaluate the effect and feasibility of this pretreatment method. The cross section of CFRP/A6061 joints and morphology of the aluminum surface were observed by means of optical microscope (OM), scanning electron microscope (SEM). Furthermore, the joining mechanisms and chemical state of different elements at the interface of the joints were studied with energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS).

2. Material and experiment

2.1. Material

The CFRP plate used in the research is composed of polyamide 6 (PA6) matrix reinforced by chopped carbon fiber with the volume fraction of 22%. The size of a CFRP plate is 3.5 mm in thickness, 25 mm in length and 10 mm in width. And A6061, common structural material in automobile, is selected as the metal in our research. The chemical compositions of A6061 are 1.0 Mg, 0.6 Si, 0.25 Zn, 0.2 Cu, and 0.15 Mn, 0. 1 Cr, 0.7 Fe and balance Al (in

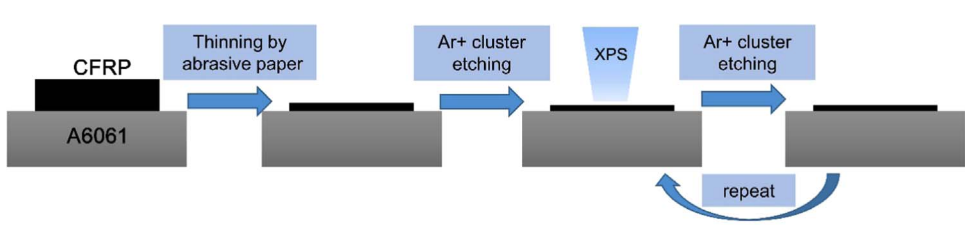

Fig. 2. XPS analysis of the interface.