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Adhesion between Metal/Polymer-Composites Irradiated by electron beam Prior to Hot-press

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Summary: *Laminations of carbon fiber reinforced epoxy polymer (CFRP) and metals of Aluminum and 18mass%Cr-8mass%Ni austenite stainless steel (CFRP/Al and CFRP/18-8) were prepared by using a new adhesion method consisting of applying low dose of homogeneous low energy electron beam irradiation (HLEBI) prior to hot-press in vacuum below 1 Pa for 2 h at 401±0.5 K after lamination assembly. This new treatment of 0.22 MGy-HLEBI prior to assembly and hot-press significantly boosts the tensile shear strength (τ_B) 437, 502 and 314 % at the accumulative probability (P_s) of 0.14 for the CFRP/18-8 joint constructed with both irradiated CFRP and 18-8 sheets (HLEBI-CFRP/HLEBI-18-8), for the CFRP/18-8 joint with untreated CFRP and irradiated 18-8 sheets (CFRP/HLEBI-18-8), and for the CFRP/18-8 joint with untreated 18-8 and irradiated CFRP sheets (HLEBI-CFRP/18-8). Consequently, compared with HLEBI to CFRP, HLEBI to 18-8 is effective to improve the adhesion force. On the other hand, 0.22 MGy – HLEBI prior to hot -press slightly increases the τ_B value 119 % at the P_s of 0.14 for CFRP/Al joint constructed with both CFRP and Al sheets (HLEBI-CFRP/HLEBI-Al). Although the τ_B value of CFRP/Al joint with hot-press without HLEBI is more than four times higher than that of CFRP/18-8 one, HLEBI effects to CFRP/18-8 prior to assembly is more effective to improve the adhesion force rather than HLEBI effects to CFRP/Al.*

1 INTRODUCTION

Techniques to increase the strength of metal/composite joints are highly sought after. Aluminum (Al) with its high electrical conductivity, shiny silver color, light specific weight and high corrosion resistance due to passivation are valuable light structural materials utilized for aerospace technology with high specific strength. In addition, Austenite stainless steel (18-8) joined with Carbon fiber reinforced epoxy polymer (CFRP) for structural applications has been widely utilized in the aerospace, automotive and shipbuilding industries, along with various day-to-day articles. CFRP with its high strength to weight ratio along with 18-8 with its high heat-resistance, high corrosion resistance and high tensile strength have been widely utilized for bullet train vehicles, automobiles, ships and airplanes. [1, 2]

It is always important to develop a joint with maximum safety enhancement adding minimal weight to the structure for low energy consumption with concern for the environment. However, methods of joining two different materials such as fasteners including bolts and rivets; and adhesive bonding processing such as welding and soldering, have always had some of the serious problems to decay the materials.

Advantages of fasteners are simple processing, high joining strength, and small scatter in the data. However, disadvantages include increase in weight due to the fasteners and low sealing performance. Moreover, the bolt holes decrease the cross-sectional area and can act as stress concentrators. It is reported drilling holes in FRP laminate composites result in breakage of the reinforcing fibers, peeling of the top plies at hole entry, resin degradation at the hole wall, and delamination of the bottom plies of the laminates. [3, 4] The resulting damage can result in generation of fatigue cracks during fatigue. [5]

For adhesive bonding processing advantages are complete sealing effect, parts are lighter since fasteners are not used, hence no stress concentration due to the bolt hole and no damage due to drilling therefore they typically exhibit higher fatigue strength than bolted joints. [5] However, disadvantages include adhesion selection is difficult for joints of different materials.

Additional steps of degreasing and etching the adhering surfaces are needed to obtain high adhesion strength.

On the other hand, chemically treated adhesive joints have the disadvantage of degradation after a few hours by oxidation decreasing bonding strength. [6] Due to these constraints, high strength adhesive joints are difficult to attain. However, a CFRP/Metal joint was developed without the use of fasteners, chemical treatment, or external adhesive by a new adhesion method. Furthermore, a double-step treatment consisting of applying low dose of homogeneous low energy electron beam irradiation (HLEBI) to the CFRP and 18-8, respectively prior to hot-pressing after lamination assembly has been proposed. 0.13 MGy-HLEBI significantly boosted adhesive shear strength (τ_B) of the CFRP/18-8 joint 503 % over the untreated.

HLEBI has a successful track record for improving many materials. [7-14] HLEBI is reported to improve the mist resistance and wetting of materials. [7-10] and increases polymer adhering to fibers raising impact strength in GFRP. [11, 12] These effects are mainly caused by surface energy induced by the irradiation with the formation of active terminated atoms with dangling bonds. When HLEBI improves the joining between different polymers and metals/polymers, [13, 14] rapid and safety adhesion between different polymers by using HLEBI has been successfully developed. For these reasons, the effects of HLEBI prior to lamination assembly and hot-press lamination on the tensile shear strength of adhesive CFRP/Metal laminated joints as shown in Figure 1 are being investigated.

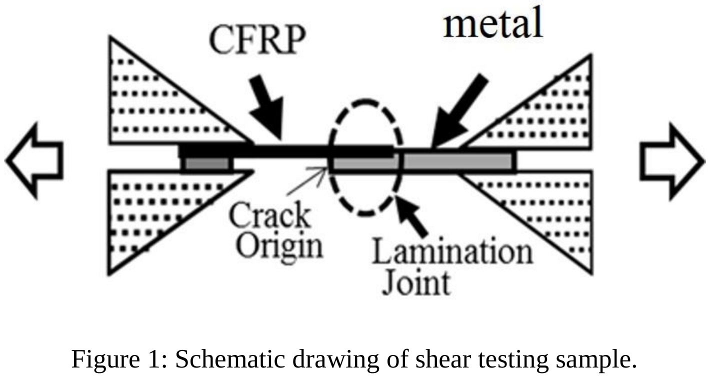

Figure 1: Schematic drawing of shear testing sample.

2 EXPERIMENTAL PROCEDURE

2.1 Preparation of CFRP/Metal

Composite sheets were constructed with 18mass%Cr-8mass%Ni austenite (18-8) stainless steel Japanese Industrial Standard 18-8 (10 mm x 40 mm x 2.0 mm, Taiho trading Co., LTD.); and CFRP (10 mm x 40 mm x 0.25 mm) (1 ply 0.25 mm in thickness). Volume of carbon fiber cross-weave reinforced epoxy polymer composite (CFRP; TR3110-331MP epoxy/CF, Mitsubishi Rayon Ltd., Tokyo) was 0.25 x 40 x 10 = 100 mm^3 with adhesive area (10 x 10 = 100 mm^2) for tensile shear test. In the CFRP sheet, V_f of carbon fiber was 60 %.

Specifically, the preparation steps of the CFRP/Metal joint samples were as follows. As Step 1, the metal and CFRP prepared were cut to size. As Step 2, is the novel part of the process: homogeneous low-voltage electron beam (HLEBI) treatment was applied to the joining surfaces of the metal and CFRP (see section 2.2) prior to lamination assembly. As Step 3, the CFRP and metal were assembled. As Step 4, the CFRP/Metal assembly was inserted into a hot press in vacuum below 1 Pa for 2 h at 401±0.5 K to cure the CFRP to adhere with the 18-8 producing the laminated joint samples. No fasteners or external adhesives were applied: the cured epoxy enhanced by the HLEBI acts as the adhesive to the 18-8.

2.2 Homogeneous low voltage electron beam irradiation (HLEBI)

To aim high reproducibility of shear strength results, the connecting surfaces of the metal and CFRP sheets were homogeneously irradiated by an electron-curtain processor (Type CB175/15/180L, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co., Ltd., Tokyo), As shown in Figure 2. [15-19] The samples were homogeneously irradiated with an electron beam through a titanium window attached to a 24 cm-diameter vacuum chamber. A tungsten filament in a vacuum was used to generate the electron beam with an electric voltage of 0.17 MeV and an irradiating current of 2.0 mA. To prevent oxidation, the samples were kept in a nitrogen atmosphere of 0.10 MPa with a residual oxygen concentration of less than 0.040 %. The flow rate of the nitrogen gas was 1.5 L/s.Given the densities (ρ) are 7.9 g・cm^{-3} for the 18-8 stainless steel; 2.7 g・cm^{-3} for Al; 1.76 g・cm^{-3} for carbon fiber; and 1.20 g・cm^{-3} for cured epoxy, the penetration depth (D_{th}) values of 0.028 mm for 18-8; 0.080 mm for Al; 0.126 mm for carbon fiber; and 0.185 mm for epoxy, respectively were estimated by assumptions of Christenhusz and Reimer. [20] The D_{th} of 0.027 mm for 18-8; 0.0176 mm for Al and 0.144 mm for the 60 % carbon fiber V_f CFRP are considered sufficient for action of dangling bonds to increase adhesion of the CFRP/Metal interface. After HLEBI the CFRP/Metal composite sheet lamination was performed by hot-press.

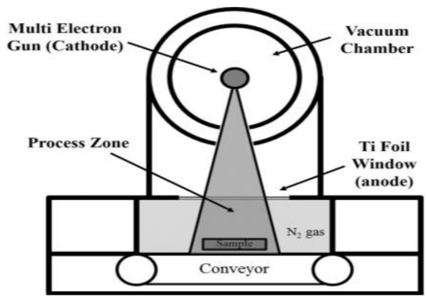

Figure 2: Schematic diagram of electron curtain processer. (Type CB175/15/180L, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co., Ltd., Tokyo).

2.3 Tensile shear strength, its strain and fracture strain

Tensile shear strength tests were performed by an Instron type tensile machine at a constant strain rate of 1 mm/min on the samples as illustrated in Figure 1 where the joint was pulled in tension, a shim being added with the thin CFRP sheet in the grips. The tensile shear stress (τ)-strain (ε) curves were obtained where the tensile shear strength (τ_B) is defined at the maximum shear stress.

Figure 3 depicts the tensile shear stress (τ) - strain (ε) curves at median- fracture strain cumulative probability, (P_s = 0.94) of CFRP/Metal lamination joints irradiated at 0.30 MGy-HLEBI prior to hot-press after lamination assembly. The initial stiffness (d_τ/dε)i, maximum stiffness (d_τ/d_ε)max, the tensile shear strength (τ_B), its strain (εs_B) and fracture strain (εs_f) are defined.

The cumulative probability (P) by the median-rank method [21] often employed in quality control (QC) is one of the widely used and convenient ways to analyze mechanical probabilities of adhesive strength [16], adhesive peeling resistance [22], along with other mechanical properties [11, 23-28]. Accumulative probabilities (P: P_i, P_{max}, P_B, $P_{S\varepsilon}$, P_{Sf}) are initial stiffness ($(d_\tau/d_\varepsilon)_i$), maximum stiffness ($(d_\tau/d_\varepsilon)_{max}$), tensile shear strength (τ_B), its strain (ε_B) and fracture strain (ε_{Sf}), which are employed here to quantitatively analyze our experimental values by the following equation. [20]

$$P = (I-0.3)/(n+0.4) \tag{1}$$

Here, n and I are total number of samples (n = 11) and rank order of each sample from weakest to strongest (1 < I < 11), respectively. When the I values are 1, 6 and 11, the P_i values are 0.06, 0.50 and 0.94, respectively.

2.4 X-ray photoelectron spectrometry (XPS)

To determine if the epoxy adhered well to the 18-8 stainless steel, fracture surface analysis was carried out by X-ray photoelectron spectrometry (XPS: Quantum 2000, ULVAC Co., JAPAN).

3 RESULTS

Figure 3 shows changes in tensile shear strength (τ_B) at accumulative probability (P_s) of 0.14. This new treatment significantly boosts the tensile shear strength (τ_B) 437 % from 1.1 to 4.8 MPa at the accumulative probability (P_s) of 0.14 for the CFRP/18-8 joint constructed with both CFRP and 18-8 sheets irradiated at 0.22 MGy prior to assembly (HLEBI-CFRP/HLEBI-18-8). Furthermore, It also boosts 502 % from 1.1 to 5.5 MPa at P_s = 0.14 for the CFRP/18-8 joint with 0.22 MGy-irradiated 18-8 and untreated CFRP sheets prior to assembly (CFRP/HLEBI-18-8). In addition, it increases 314 % from 1.1 to 3.5 MPa at P_s = 0.14 for the CFRP/18-8 joint with untreated 18-8 and0.22 MGy-irradiated CFRP sheets prior to assembly (HLEBI-CFRP/18-8).Consequently, compared with HLEBI to CFRP, HLEBI to 18-8 is effective to enhance the adhesion force.

On the other hand, the τ_B value of CFRP/Al joint with hot-press without HLEBI is more than four times higher than that of CFRP/18-8 one. Furthermore, 0.22 MGy – HLEBI prior to hot-press slightly increases the τ_B value 119 % at 0.22 MGy from 4.8 to 5.7 MPa at the P_s of 0.14 for CFRP/Al joint constructed with both CFRP and Al sheets (HLEBI-CFRP/HLEBI-Al). Consequently, compared with HLEBI effects to CFRP/Al, HLEBI effects to CFRP/18-8 prior to assembly is effective to improve the adhesion force.

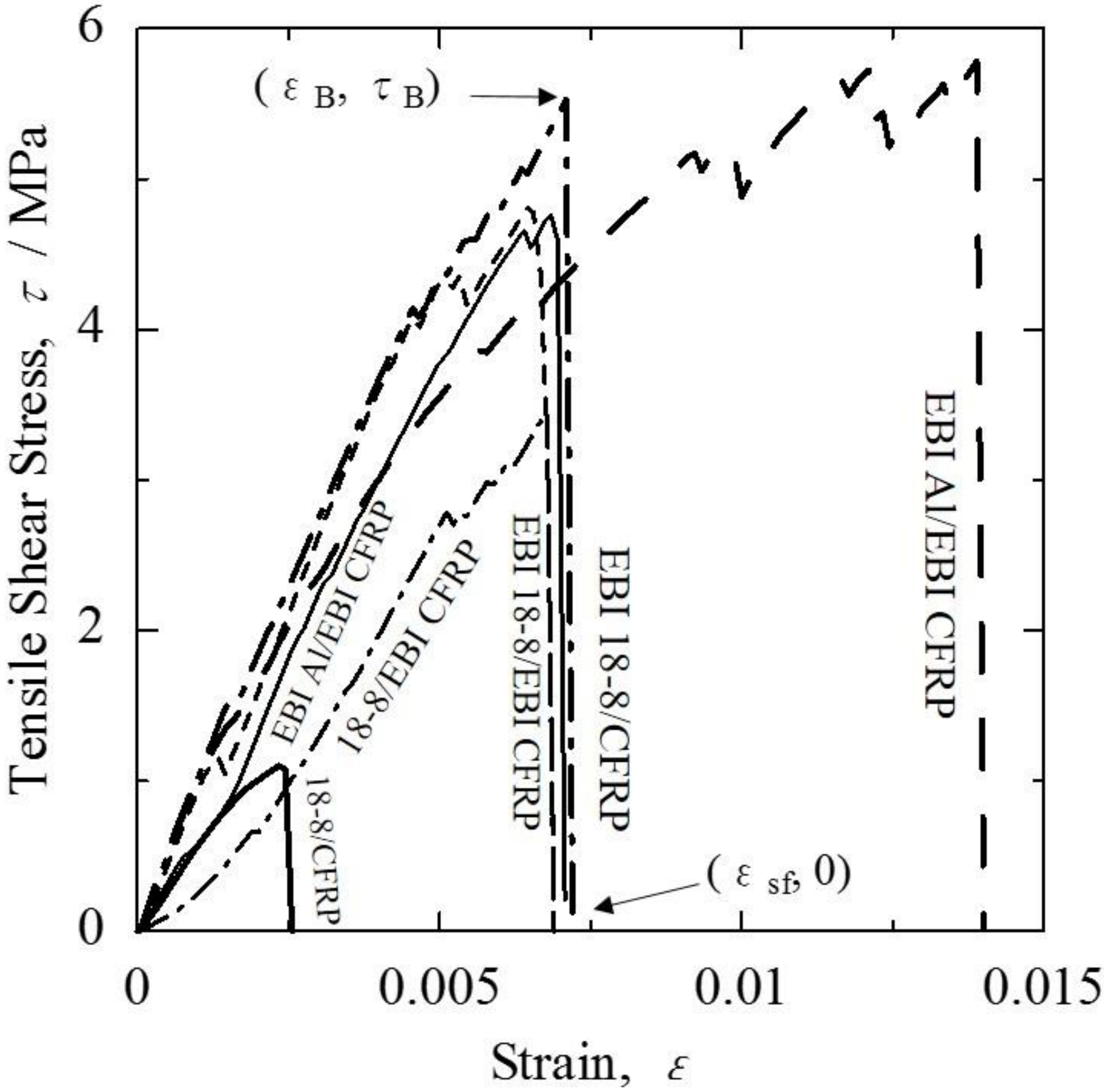

Figure 3: Tensile shear stress-strain curves at high cumulative probability of fracture strain (P_s = 0.14) of CFRP/Metal lamination joints.

4 DISCUSSION

Fracture surface analysis by X-ray photoelectron spectrometry (XPS) indicates HLEBI acts to produce strong adhesion in the CFRP/Metal lamination three CFRP/Metal laminated sheets, which 18-8 and CFRP are treated with and without HLEBI prior to hot-press after lamination assembly, where fracture generally occurred at the shear-fractured interface of CFRP/Metal lamination. The higher intensity peak for the HLEBI treated specimen at 276.5 eV indicates excess residual carbon adhered to the metal interface from the epoxy increasing the adhesive force.

When HLEBI creates increased adhesion at CFRP/Metal interface, residual epoxy deposition in the form of increased intensity C (1s) peak is found to be retained on the 18-8 sheet by inter-matrix fracture of epoxy resin further into the CFRP thickness near the carbon fibers. This can be explained by the adhesion force of CFRP/Metal being stronger than the cohesive force of epoxy polymer in the CFRP itself.

By applying HLEBI, electrons probably undergo polarization and bond or exhibit intermolecular coulomb attractive forces with the carbon fiber or metal making the CFRP/Metal bond stronger increasing the τ_B of the joint.

The XPS Carbon (1s) signal in metal fracture surface of CFRP/Metal lamination sheet constructed with irradiated metal and untreated CFRP is higher than that constructed with both irradiated metal and CFRP, and is also much higher than that of irradiated CFRP and untreated metal. When this XPS results are indicated by Epoxy-CFRP/Metal adhesion, the results of tensile shear strength can be explained. The strength approximately corresponds to the XPS signal height.

5 CONCLUSION

Up to now, adhesion of 2-layer laminated CFRP/Metal sheets without our treatment of homogeneous low energy electron beam irradiation (HLEBI) prior to hot press after lamination assembly has not been observed in the literature. However, strong adhesion of the CFRP/Metal was created from the new treatment applying low dose ≦0.30 MGy-HLEBI to the CFRP and metal prior to hot-press in vacuum below 1 Pa for 2 hr at 401±0.5 K after lamination assembly.

1:This new treatment significantly boosts the tensile shear strength (τ_B) 437 % from 1.1 to 4.8 MPa at the accumulative probability (P_s) of 0.14 for the CFRP/18-8 joint constructed with both CFRP and 18-8 sheets irradiated at 0.22 MGy prior to assembly (HLEBI-CFRP/HLEBI-18-8). Furthermore, It also boosts 502 % from 1.1 to 5.5 MPa at P_s = 0.14 for the CFRP/18-8 joint with 0.22 MGy-irradiated 18-8 and untreated CFRP sheets prior to assembly (CFRP/HLEBI-18-8). In addition, it increases 314 % from 1.1 to 3.5 MPa at P_s = 0.14 for the CFRP/18-8 joint with untreated 18-8 and0.22 MGy-irradiated CFRP sheets prior to assembly (HLEBI-CFRP/18-8).Consequently, compared with HLEBI to CFRP, HLEBI to 18-8 is effective to enhance the adhesion force.

2: Although the τ_B value of CFRP/Al joint with hot-press without HLEBI is more than four times higher than that of CFRP/18-8 one, 0.22 MGy – HLEBI prior to hot -press slightly increases the τ_B value 119 % at 0.22 MGy from 4.8 to 5.7 MPa at the P_s of 0.14 for CFRP/Al joint constructed with both CFRP and Al sheets (HLEBI-CFRP/HLEBI-Al). Consequently, compared with HLEBI effects to CFRP/Al, HLEBI effects to CFRP/18-8 prior to assembly is effective to improve the adhesion force.

3: Surface analysis by XPS detected carbon on the shear fractured metal interface indicating the residual epoxy adhered well to the metal by the HLEBI. In comparison, a smaller signal was observed in the untreated sample, laminated by hot-press but not HLEBI treated. The increased peak intensity is probably a result of adhesion force of CFRP/Metal being made stronger than the cohesive force of epoxy polymer in the CFRP itself by the HLEBI.

4: With careful consideration to optimize dose level, the new treatment applying HLEBI prior to lamination assembly and hot press proves a viable method for quick lamination of metals with passive films and epoxy CFRP without the use of external adhesives or fasteners.

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