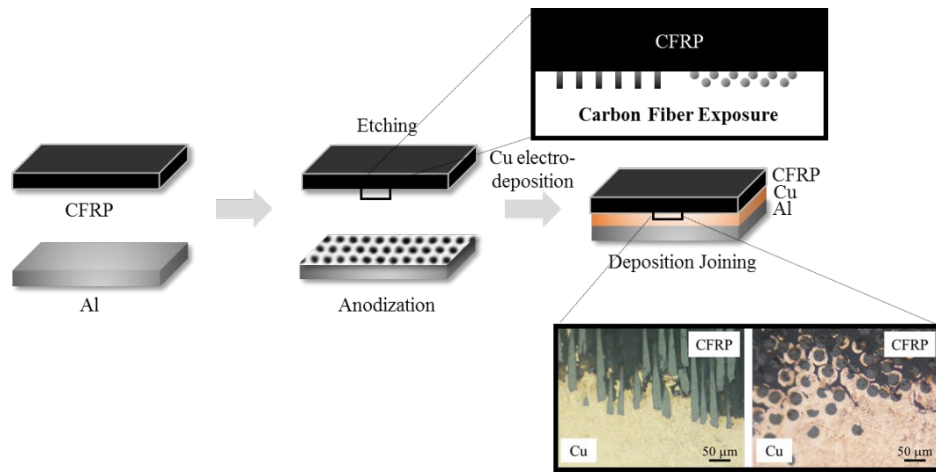


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Graphical Abstract

1 **New dissimilar joining method of CFRP/A6061 Al by Cu**
2 **electrodeposition**

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12
13 **Abstract**

14 A new CFRP-aluminum joining method has been developed by Cu
15 electrodeposition. Cu deposition was filled into the roughened CFRP surface
16 and the significant anchor effect was attained by the joining method.
17 As a result, CFRP and A6061 Al alloy were successfully joined by Cu
18 electrodeposition and a high joining strength of 67 MPa was obtained.

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20 **Keywords:** *dissimilar joining, CFRP, aluminum alloy, electrodeposition*

1. Introduction

Joining of dissimilar materials is one of important technologies for multi-materialization. In particular, joining of a carbon fiber reinforced plastic (CFRP) to a metallic material is most important for next-generation vehicles. To date, many studies have been performed on dissimilar joining of CFRP¹⁾. Because CFRP cannot be joined by direct diffusion bonding methods¹⁾, adhesives are often used for joining of CFRP. Recently, new technologies without adhesives for joining of CFRP are drawing much attention, for example, laser joining²⁻⁴⁾, friction stir lap joining^{5,6)} and ultrasonic spot welding⁷⁾. Since the bonding between a resin and a metal is weak because of non-covalent bonding, addition of functional groups has been performed for enhancing the bonding strength⁸⁻¹⁰⁾. Also, it has been demonstrated that roughening a metal surface leads to the enhanced joining strength due to the anchor effect^{2-4,11-13)}. However, the joining strength of CFRP/metal is still less than 50 MPa in spite of these achievements. In addition, the anchor effect by roughening a metal surface is less effective in joining of thermosetting resins such as epoxy resin, which is expected to be a matrix of CFRP for vehicles, than in joining of thermoplastic resins, and the joining strength of CFRP whose matrix is the epoxy resin is less than 30 MPa⁴⁾.

Recently, joining by deposition of metals was proposed, where aluminum sheets were joined by Cu electrodeposition¹⁴⁾. In the deposition joining, an anchor effect plays an important role in

enhancing the joining strength. In the present study, the deposition bonding is applied to dissimilar joining of CFRP, whose matrix is the epoxy resin, to A6061 Al alloy.

2. Experimental Procedures

A CFRP sheet, which was composed of a plain weave roving cloth prepreg (F6343B-05P) laminated using carbon fiber (T300) and a 120°C-curing type epoxy resin (#2500) [0/90], was purchased from TORAY and it was cut to the samples with 20 mm in length, 4 mm in width and 1 mm in thickness. The CFRP samples were etched by immersion in a solution containing 0.2 M KMnO_4 + 4 M NaOH at 373 K for 45 min¹⁵⁾. After the etching, the samples were sulfonated by immersion in a solution containing 14 M H_2SO_4 at 333 K for 10 min.

A6061 Al alloy sheets were anodized in the same conditions in 0.3 M H_3PO_4 as those in the previous work¹⁴⁾ to generate nanoporous structure at the surfaces.

Cu electrodeposition was performed between the CFRP and the anodized Al alloy samples with 20 mm in length, 4 mm in width and 1 mm in thickness under almost the same deposition conditions as those in the previous work¹⁴⁾. The samples were laid with a space of about 200 μm between them so that the area for Cu electrodeposition was 10×1 mm, where other areas except the deposition area were covered by an insulating tape to prevent the deposition. The Cu deposition temperature and time were room temperature and 12 h, respectively.

Four samples were prepared: non-treated sample, etched sample, sulfonated sample and etched + sulfonated sample, and the lap shear tests were conducted at room temperature to measure their joining strengths. The tests were repeated several (three-six) times and the average strength was defined as the joining strength. Cross-sections and fractured surfaces of the samples were observed by scanning electron microscopy and optical microscopy.

3. Results and Discussion

Figure 1 shows CFRP surfaces before and after the etching process. The epoxy surface was removed by etching to expose carbon fibers parallel and perpendicular to the surface plane.

In the case that the joining is not enough, a joined sample will be easily fractured by hand and an experiment for joining strength measurement cannot be carried out. In the present study, the CFRP and Al samples were joined by the Cu electrodeposition without fracture during handling and the joining strength measurements were successfully performed for all samples. Results of the joining strength measurements are shown in Fig. 2. The non-treated sample showed a low joining strength of 3 MPa. It should be noted that etching the CFRP surface increased the joining strength to 36 MPa.

In the previous studies^{2-4,11-13}), a metal surface was roughened for the anchor effect. In such a case, the roughened metal surface was filled with resin. In the present work, however, a CFRP surface was

roughed by etching and the etched CFRP surface was filled with Cu deposition (Fig. 3). It is therefore suggested that the considerable anchor effect is related to the filling with Cu, but not with resin.

The bonding of resin and metal is enhanced by functional groups⁸⁻¹⁰). Zhu et al.⁸) showed that the joining strength was enhanced by silane coupling agent. However, the addition of the silane coupling agent did not enhance the joining strength in the preliminary experiment of the present work (data are not shown), although the reasons are unknown. An alternative is the sulfonation of a CFRP surface^{9,10}), because sulfone groups are adhered to an epoxy of CFRP surface. Therefore, the sulfonation treatment was performed on the CFRP surface. As a result, the joining strength was increased from 3 to 7 MPa by the sulfonation. However, the sulfonation was not as effective for enhancing the joining strength as the etching.

Further enhancement in the joining strength was obtained by a continuous treatment of etching and sulfonation, as shown in Fig. 2; that is, the joining strength of etched + sulfonated sample was 67 MPa. Hence, a synergistic effect of etching and sulfonation led to stronger joining of CFRP and Al.

Fracture occurred at the interface between the copper deposition and the CFRP for the etching + sulfonated sample. Figure 4 shows fracture surfaces of Al and CFRP sides after the lap shear tests. The carbon fibers parallel and perpendicular to the surface were observed for the CFRP side, while deposited Cu was rarely found (Figs 4a&b). On the other hand, deposited copper with a structure duplicated from carbon

fibers was found at the Al side (Figs 4c&d). Thus, the carbon fibers were pulled out from Cu deposition for the etching + sulfonated sample. In the conventional method for dissimilar joining of CFRP/metal, a metal surface is roughened and resin is pressed to the roughed metal surface^{2-4,11-13}). In this case, voids tend to be generated at the CFRP/metal interface by inadequate pressing. In the deposition joining, however, voids are not formed at the interface because metal is deposited from the interface. Actually, voids were not found at the Cu/CFRP surface although a few voids were generated in the deposited Cu (Fig. 3). The epoxy resin was removed at the surface and the carbon fibers were exposed by the etching (Fig. 1). This led to enough filling of Cu deposition into roughened CFRP because the carbon fibers have the high electrical conductivity, and pulling out of the carbon fibers. The present work demonstrated the joining strength of 67 MPa, which is more than twice as high as the one in the previous work⁴). The high joining strength by the deposition joining is suggested to be because the significant anchor effect is attained by enough filling of Cu deposition into roughened CFRP.

4. Conclusions

The present study demonstrated that CFRP was successfully joined to A6061 Al alloy by Cu electrodeposition. Etching and sulfonation of CFRP surface were effective in enhancing the joining strength. As a result, the high joining strength of 67 MPa was attained. It is suggested that the high joining strength is because the significant anchor effect is attained by enough filling of Cu deposition into roughened CFRP.

Acknowledgments

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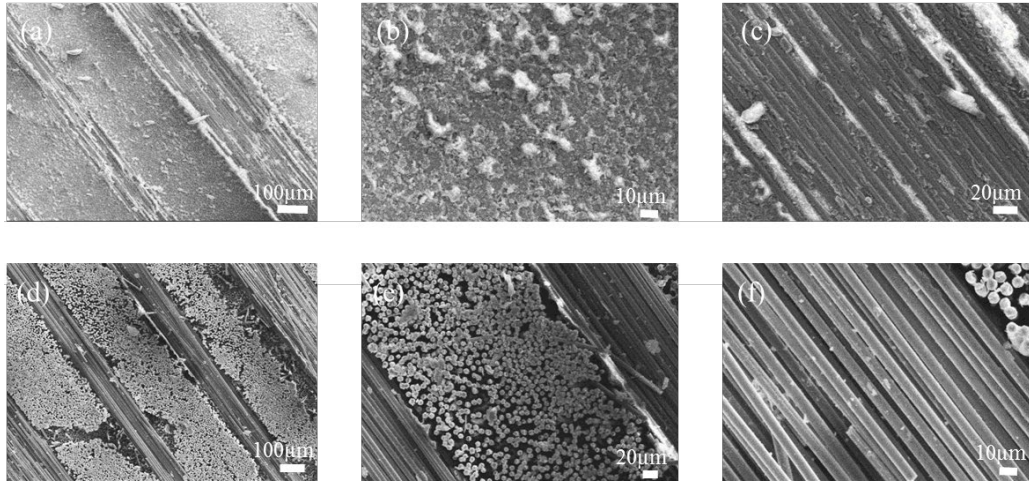
Captions List

Figure 1 CFRP surfaces before and after etching treatment. (a) CFRP surface before etching. (b) Magnified image of a region where carbon fibers are arranged perpendicularly to the surface in (a). (c) Magnified image of a region where carbon fibers are arranged parallel to the surface in (a). (d) CFRP surface after etching. (e) Magnified image of a region where carbon fibers are arranged perpendicularly to the surface in (d). (f) Magnified image of a region where carbon fibers are arranged parallel to the surface in (d).

Figure 2 Joining strength for CFRP/A6061 alloy joined by deposition joining method.

Figure 3 Cross-sectional images of the etched sample interfaces. (a) Cross section of the region where the carbon fibers are arranged perpendicular to the surface. (b) Cross section of the region where the carbon fibers are arranged parallel to the surface.

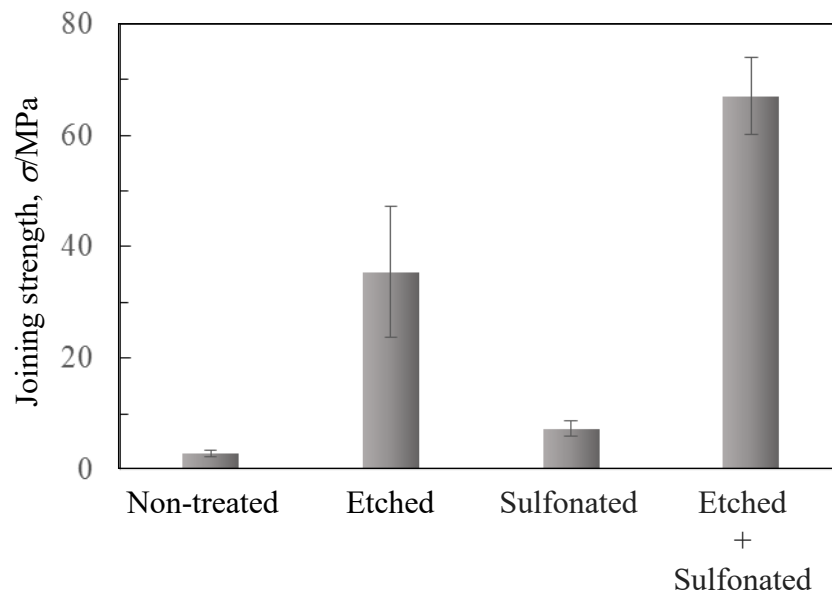
Figure 4 Fracture surfaces of the etching + sulfonated sample. (a) Region where carbon fibers are arranged perpendicular to the surface for CFRP side. (b) Region where carbon fibers are arranged parallel to the surface for CFRP side. (c) Region where carbon fibers are arranged perpendicular to the surface for Al side. (d) Region where carbon fibers are arranged parallel to the surface for Al side. CF: carbon fiber



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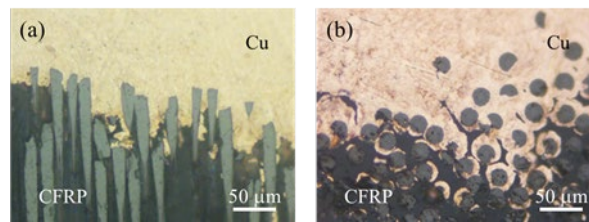


Figure 3 Cross-sectional images of the etched sample interfaces.

(a) Cross section of the region where the carbon fibers are arranged perpendicular to the surface. (b) Cross section of the region where the carbon fibers are arranged parallel to the surface.

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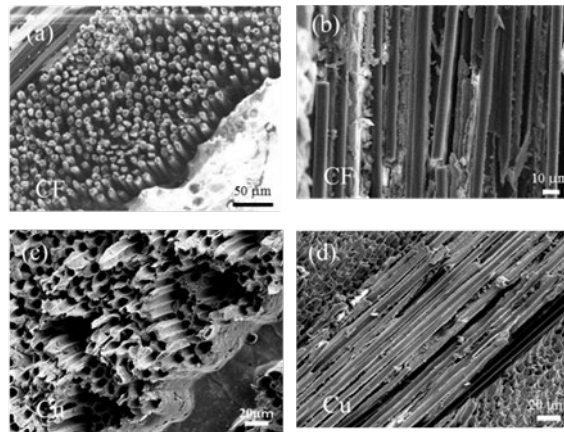


Figure 4 Fracture surfaces of the etching + sulfonated sample. (a) Region where carbon fibers are arranged perpendicular to the surface for CFRP side. (b) Region where carbon fibers are arranged parallel to the surface for CFRP side. (c) Region where carbon fibers are arranged perpendicular to the surface for Al side. (d) Region where carbon fibers are arranged parallel to the surface for Al side. CF: carbon fiber