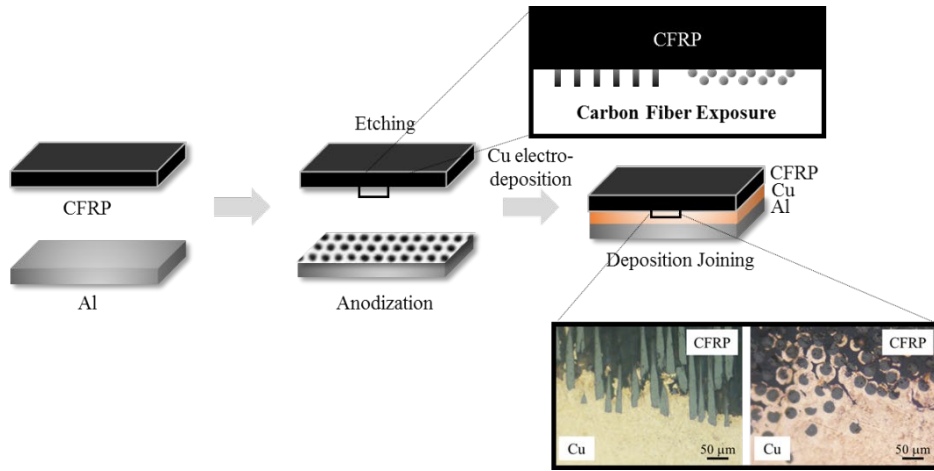


1

2



Graphical Abstract

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

3

4 Koji Naito*, Soichiro Deguchi*, Masataka Hakamada and Mamoru Mabuchi

5

6 Department of Energy Science and Technology, Graduate School of Energy
7 Science, Kyoto University, Kyoto 606–8501 Japan

8 (* Graduate student, Kyoto University)

9

10 Corresponding author, E-mail:

11 Masataka Hakamada, hakamada.masataka.3x@kyoto-u.ac.jp

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.

19

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

21

1 **1. Introduction**

2

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

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

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

4 5 **2. Experimental Procedures**

6
7 A CFRP sheet, which was composed of a plain weave roving cloth
8 prepreg (F6343B-05P) laminated using carbon fiber (T300) and a
9 120°C-curing type epoxy resin (#2500) [0/90], was purchased from
10 TORAY and it was cut to the samples with 20 mm in length, 4 mm in
11 width and 1 mm in thickness. The CFRP samples were etched by
12 immersion in a solution containing 0.2 M KMnO_4 + 4 M NaOH at 373
13 K for 45 min¹⁵⁾. After the etching, the samples were sulfonated by
14 immersion in a solution containing 14 M H_2SO_4 at 333 K for 10 min.

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

18 Cu electrodeposition was performed between the CFRP and the
19 anodized Al alloy samples with 20 mm in length, 4 mm in width and 1
20 mm in thickness under almost the same deposition conditions as those
21 in the previous work¹⁴⁾. The samples were laid with a space of about
22 200 μm between them so that the area for Cu electrodeposition was
23 10×1 mm, where other areas except the deposition area were covered
24 by an insulating tape to prevent the deposition. The Cu deposition
25 temperature and time were room temperature and 12 h, respectively.

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

8

9 **3. Results and Discussion**

10

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

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

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

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

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

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

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

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

17

18 **4. Conclusions**

19

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

1

2 **Acknowledgments**

3 The present study was financially supported by The Light Metal
4 Education Foundation, Inc. One of the authors (S. Deguchi) thanks
5 Japan Aluminum Association for the financial support. The other
6 author (M. Hakamada) also appreciates the financial aid from The
7 Japan Institute of Metals and Materials.

8

9 **REFERENCES**

10

- 11 1) A. Pramanic, A.K. Basak, Y. Dong, P.K. Sarker, M.S. Uddin, G. Littlefair,
12 A.R. Dixit and S. Chattopadhyaya: *Composites: Part A* 101 (2017) 1-29.
- 13 2) Z. Zhang, J.-G. Shan, X.-H. Tan and J. Zhang: *Inter. J. Adhes. Adhes.* 70
14 (2016) 142-151.
- 15 3) Z. Zhang, J. Shan and X. Tan: *J. Adhes. Sci. Tech.* 32 (2017) 390-406.
- 16 4) E. Akman, Y. Erdoğan, M.Ö. Bora, O. Çoban, B.G. Oztoprak and A. Demir:
17 *Inter. J. Adhes. Adhes.* 98 (2020) 102548.
- 18 5) H.S. Bang, A. Das, S. Lee and H.S. Bang: *IOP Conf. Series: Mater. Sci.*
19 *Eng.* 369 (2018) 012033.
- 20 6) A. Tsuchiya: *J. Jpn. Inst. Light Met.* 69 (2019) 86-92. (in Japanese)
- 21 7) F. Balle, G. Wagner and D. Eifler: *Mat.-wiss u. Werkstofftech* 38 (2007)
22 934-938.
- 23 8) W. Zhu, H. Xiao, J. Wang and C. Fu: *Composite Struc.* 227 (2019) 111321.
- 24 9) C.E. Baumgartner: *Plat. Surf. Finish.* 79 (1992) 53.
- 25 10) M. Seita, M. Imanari, K. Arai, H. Nawafune, Y. Matumoto and S.

1 Mizumoto: J. Jpn. Inst. Interconnect. Pack. Electro. Circuits 11 (1996) 267-272.
2 (in Japanese)
3 11) Z. Sun and J. Huang: J. Elect. Mater. 48 (2019) 6298-6305.
4 12) B.K. Sun and T.J. O'Keefe: Surf. Coat. Tech. 106 (1998) 44-52.
5 13) H. Abe, J.C. Chung, T. Mori, A. Hosoi, K.M. Jespersen and H. Kawada:
6 Composites Part B 172 (2019) 26-32.
7 14) M. Hakamada, Y. Kohashi, Y. Yamano and M. Mabuchi: Mater. Trans. 59
8 (2018) 324-326.
9 15) S. Chen, Q. Zhu, Y. Zhao, J. He and G. Wang: Mater. Corrosion 70 (2019)
10 720-725.
11
12

1 **Captions List**

2

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

11

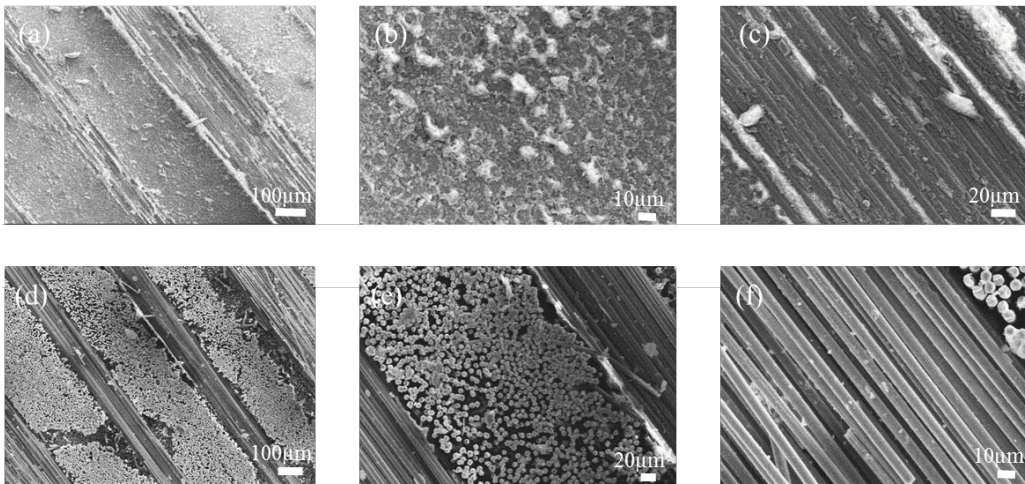
12 Figure 2 Joining strength for CFRP/A6061 alloy joined by deposition
13 joining method.

14

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

19

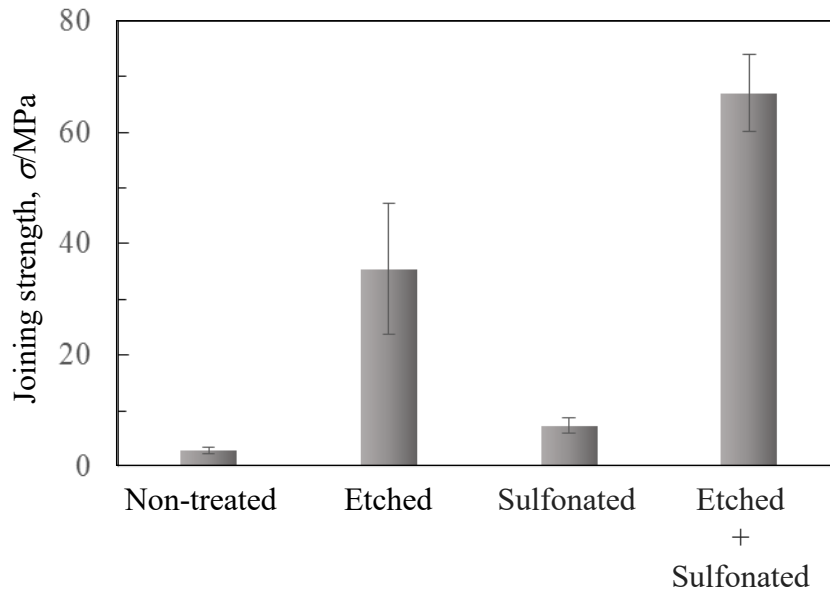
20 Figure 4 Fracture surfaces of the etching + sulfonated sample. (a)
21 Region where carbon fibers are arranged perpendicular to the surface
22 for CFRP side. (b) Region where carbon fibers are arranged parallel to
23 the surface for CFRP side. (c) Region where carbon fibers are arranged
24 perpendicular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



1

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).

2



1

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

3 joining method.

4

1

2

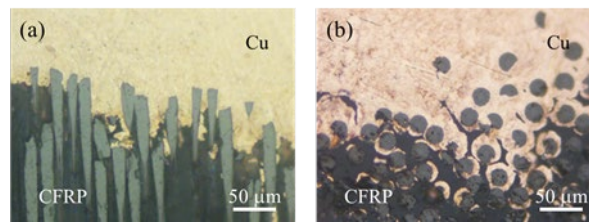


Figure 3 Cross-sectional images of the etched sample interfaces.

(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.

1
2

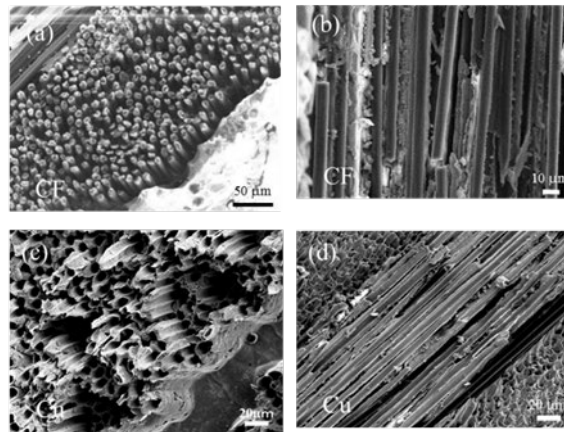


Figure 4 Fracture surfaces of the etching + sulfonated sample. (a) Region where carbon fibers are arranged perpendicular to the surface for CFRP side. (b) Region where carbon fibers are arranged parallel to the surface for CFRP side. (c) Region where carbon fibers are arranged perpendicular to the surface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