

Effects of NaCl Concentration and Solution Temperature on the Galvanic Corrosion Between CFRP and A516Gr.55 Carbon Steel

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CFRP (Carbon Fiber Reinforced Plastics) is composed of carbon fiber and plastic resin, and is approximately 20 - 50% lighter than metallic materials. CFRP has a low density, higher specific stiffness, specific strength, and high corrosion resistance. Because of these excellent properties, which meet various regulation conditions needed in the industrial fields, CFRP has been widely used in many industries including aviation and ship building. However, CFRP reveals water absorption in water immersion or high humidity environments, and water absorption occurs in an epoxy not carbon fiber, and can be facilitated by higher temperature. Since these properties can induce volume expansion inside CFRP and change the internal stress state and degrade the chemical bond between the fiber and the matrix, the mechanical properties including bond strength may be lowered. This study focused on the effects of NaCl concentration (0.01 - 1% NaCl) and solution temperature (30 - 75 °C) on the galvanic corrosion between CFRP and A516Gr.55 carbon steel. When NaCl concentration increases 10 times, corrosion rate of a specimen was not affected, but that of galvanic coupled carbon steel increased by 46.9% average. However, when solution temperature increases 10 °C, average corrosion rate increased approximately 22%, regardless of single or galvanic coupled specimen.

Keywords: CFRP, Carbon steel, Galvanic corrosion, NaCl concentration, Temperature

1. Introduction

About 20 ~ 50% of typical carbon fiber reinforced plastic is lighter than metals, and CFRP has excellent properties, including low density, high strength and high corrosion resistance [1,2]. Because of these excellent properties of CFRP, composite materials which meet various regulation conditions needed in the industrial fields, have been widely used in the many industries including aircraft, transportation, ship building, and automobile etc. [3,4].

However, CFRP reveals water absorption in water immersion or high humidity environment, and water absorption occurs in an epoxy not carbon fiber, and can be facilitated by higher temperature. Since these properties can induce volume expansion inside CFRP and change the internal stress state and degrade the chemical bond between the fiber and the matrix, the mechanical properties including bond strength may be lowered [5,6]. When CFRP contacts to metallic materials, galvanic corrosion

can be occur because of the potential difference between them [7,8].

Galvanic corrosion is known to occur when two dissimilar materials are jointed together. In general, the less noble material experiences accelerated corrosion [9]. Corrosion of metallic materials varies with the exposure time in the environments, and it depends upon the formation of protective passive film and microstructure [10] and the ratio of cathode and anode, corrosivity, and temperature etc. [11].

Our group has recently reported the galvanic corrosion between GECEM (Graphite Epoxy Composite Materials) and aluminum/carbon steel [12-14]: In galvanic couple between aluminum and carbon steel bolt, their corrosion rates were higher than those of single specimen. In galvanic couple between GECEM, aluminum, and carbon steel, corrosion behavior of carbon steel bolt and aluminum was changed due to different corrosion mechanism in tap water and chloride solutions. On the other hand, it is well known that a strong galvanic couple can be formed between CFRP and steel rivets if the joint is exposed to a corrosion environment. In general, CFRP is cathodic and performs

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as a noble material. The steel rivet is anodic and acts as an active material for corrosion. The galvanic coupling was formed in between CFRP damaged fiber and rivet base metal boron steel [15,16].

Corrosion of metallic materials can be influenced by pH, dissolved oxygen, chloride, humidity, temperature, microorganism in atmosphere, soil, seawater environments [17-19]. Among these corrosion factors, the effect of chloride on the corrosion of carbon steel can be summarized as follows; increasing chloride concentration, corrosion potential of the steel gradually decreases and this means the acceleration of anodic dissolution of the steel by chloride ion. In the case of dilute and medium chloride solutions, chloride ion can penetrate into the metal and then the electrical conductivity of the solution will increase and corrosion rate increases. However, very high chloride concentration may reduce the solubility of oxygen and thus reduce the corrosion rate of metals [20]. Increasing the temperature of the solution, corrosion rate also increases with temperature and the maximum rate is shown at 80 °C in an open system. The lower corrosion rate above 80 °C is related to a marked decrease of oxygen solubility in water as the temperature is raised, and this effect eventually overshadows the accelerating effect of temperature alone. In a closed system, on the other hand, oxygen cannot escape, and the corrosion rate continues to increase with temperature until all the oxygen is consumed [21,22].

In order to reduce the weight of the machinery, alloy materials for some parts have been replaced from metals to CFRP. Galvanic corrosion between CFRP and metals has gradually issued, in special, in the case of machinery used in the outdoor exposure. In marine atmospheric environments, chloride concentration varies with the distance from the coast area and the wet/dry condition by temperature change can be formed. This work focused on the effects of NaCl concentration (0.01 ~ 1% NaCl) and solution temperature (30 ~ 75 °C) on the galvanic corrosion between CFRP and A516Gr.55 carbon steel.

2. Experimental methods

2.1 Materials

Commercial CFRP and carbon steel (A516Gr.55) were used in this work, the chemical composition of the A516Gr.55 was Fe-0.26C-0.60~1.20Mn-0.15~0.40Si.

CFRP specimen was used as 'as-cut' or 'polished' state, because the surface of CFRP was coated with epoxy (All test used 'polished' specimen, except the resistance measurement test). As for CFRP, the resistance measurement on the surface and cross section were performed to know the electrical connection and the water absorption.

2.2 Polarization test

Specimens were cut to a size of 1.5 mm × 1.5 mm and the surface was ground using #600 SiC paper and the specimen was electrically connected with a rubber coated Cu wire, and the surface of the specimen was coated with epoxy resin, except for an area of 1cm². Polarization tests were performed using a potentiostat (Gamry co. Interface 1000, DC105). The reference electrode was a saturated calomel electrode (SCE), and the counter electrode was high-density graphite rods. The test solution was deaerated using nitrogen gas at the rate of 200 ml/min for 30 min and the scanning rate was 0.33 mV/s. NaCl concentration was controlled as 0.01, 0.1, and 1% NaCl and solution temperature was maintained as 30, 50, and 75 °C.

2.3 Immersion corrosion test

Carbon steel specimen was cut to a size of 15 mm × 20 mm × 1.5 mm and each surface was ground using #120 SiC paper. Every specimen was weighed and immersion test was performed during 10 days. Test solution was no-deaerated and after the test, corrosion rate was calculated and the surface appearance was observed.

2.4 Galvanic corrosion test

Specimens were cut to a size of 1.5 mm × 1.5 mm and the surface was ground using #600 SiC paper and the specimen was electrically connected with a rubber coated Cu wire, and the surface of the specimen was coated with epoxy resin, except for an area of 1cm². Galvanic corrosion current and potential were measured during 5 hours using a potentiostat (Gamry co. Interface 1000, DC105). The reference electrode was a saturated calomel electrode (SCE), and the working electrode was A516Gr.55 and the counter electrode was CFRP. Test solutions were no-deaerated 0.1% NaCl at 30 °C, 50 °C, and 75 °C, and 0.01% NaCl, 0.1% NaCl, 1% NaCl at 50 °C. Corrosion rate was calculated using a current-time graph. Galvanic corrosion test was performed using the combination of two flat cells.

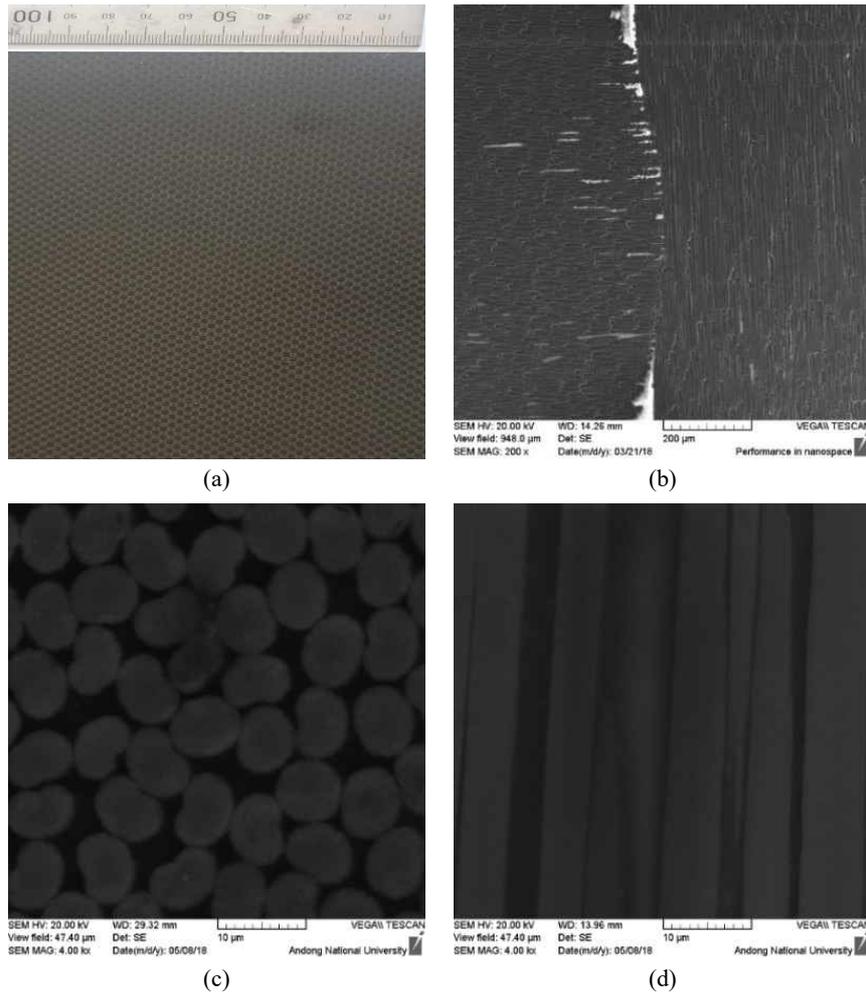


Fig. 1 Morphologies of CFRP: (a) digital camera image, (b) interface of crossed CFRP (SEM, x200), (c) cross section of cut-CFRP (SEM, x4000), and (d) cross section of longitudinal-CFRP (SEM, x4000).

3. Results and discussion

3.1 Effects of NaCl concentration and temperature on the properties of CFRP

Fig. 1 shows the morphologies of CFRP. Fig. 1a is for digital camera image, Fig. 1b is the interface of crossed CFRP, Fig. 1c is the cross section of cut-CFRP, and Fig. 1d is the cross section of longitudinal-CFRP. As shown in the figures, carbon fibers were cross-linked every 90 degree (Fig. 1a) and some epoxy was observed during the polishing (Fig. 1b). When the carbon fiber was cut, we can find out two kinds of the cross section (Fig. 1c and Fig. 1d). These carbon fibers would be connected from one point to another and because of their electrical conductivity, carbon fiber may affect corrosion behavior of other materials.

Carbon fiber in the CFRP was filled with an epoxy including the surface and between the fibers. When the coated

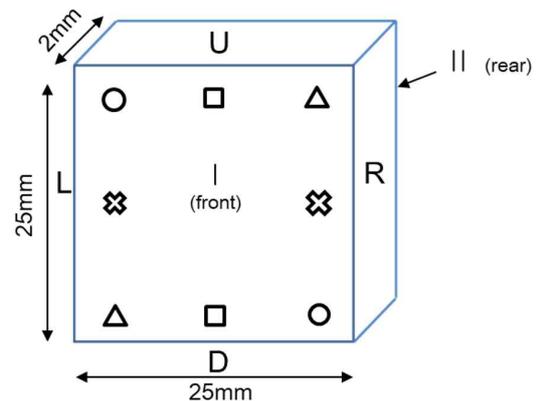


Fig. 2 Identification position to measure the electrical connection of CFRP.

Table 1 Electrical connection measurements on the CFRP in Fig. 2

Measured points	As-cut specimen	Polished specimen
○ - ○	No electrical connection	26 Ω
⊗ - ⊗	No electrical connection	26 Ω
△ - △	No electrical connection	37 Ω
□ - □	No electrical connection	33 Ω
U - L	12 Ω	20 Ω
U - R	40 Ω	24 Ω
U - D	40 Ω	20 Ω
L - R	30 Ω	30 Ω
L - D	50 Ω	28 Ω
D - R	22 Ω	29 Ω
I - II	No electrical connection	60 Ω

epoxy has a good performance in a corrosive environment including atmosphere, CFRP may not affect the corrosion behavior of galvanic coupled metals, but if the coated epoxy was damaged, the carbon fiber will induce the accelerating corrosion of metals. Fig. 2 shows the identification position to measure the electrical connection of CFRP; front surface (I) and rear surface (II), up (U) and down (D), left (L) and right (R), various positions on the surface.

Table 1 summarized the electrical connection measurements on the CFRP in Fig. 2. In the case of as-cut specimen, no electrical connection was measured on the surface, but it can be confirmed that the cut surface was electrically connected. If the surface was polished, every position was electrically connected each other. Therefore, if the coated surface of CFRP degrades or suffers the mechanical damage, carbon fiber in the CFRP may affect the corrosion behavior of galvanic coupled metals.

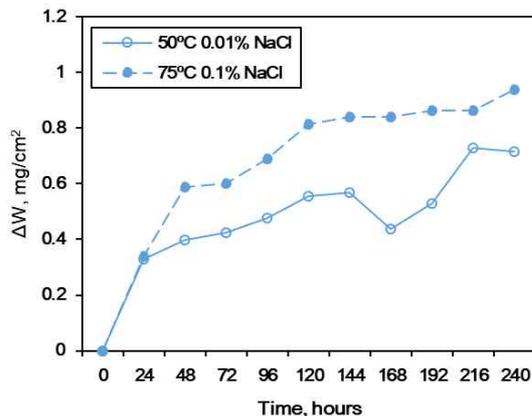


Fig. 3 Weight gain of CFRP immersed in 0.01% NaCl at 50 °C and 0.1% NaCl at 75 °C.

Fig. 3 reveals the weight gain of CFRP immersed in 0.01% NaCl at 50 °C and 0.1% NaCl at 75 °C. This weight gain implies the absorption of water and this water absorption accelerate the corrosion of metals because of increased electrically contacted area. Moreover, higher NaCl concentration and temperature increased the absorption of water and this behavior was coincident with the result of another research [23].

Fig. 4 shows the effects of (a) NaCl concentration at 50 °C and (b) solution temperature in 0.1% NaCl on the polarization curves of CFRP in deaerated solution. Increasing NaCl concentration at constant temperature, open circuit potential increased and limiting current density increased (Fig. 4a). Increasing solution temperature in constant NaCl concentration, open circuit potential lowered and the limiting current density increased (Fig. 4b). This means that the interaction between CFRP and solution has occurred vigorously when NaCl concentration and solution temperature were higher [24].

3.2 Effects of NaCl concentration and temperature on the galvanic corrosion between CFRP and A516Gr.55

Fig. 5 shows the effect of NaCl concentration on the corrosion rate of A516Gr.55 by galvanic coupled CFRP and solution temperature was 50 °C. In the single specimen, corrosion rate was almost constant even higher concentration. However, when carbon steel was galvanically coupled with CFRP, corrosion rate of the steel greatly increased. That is, average corrosion rate of single specimen was increased 0.63% per 10 times concentration but its rate of galvanically coupled specimen was increased 46.9% per 10 times concentration. In other word, the corrosion rate of specimen coupled CFRP was 2.2 times higher than that of single specimen in 1% NaCl solution.

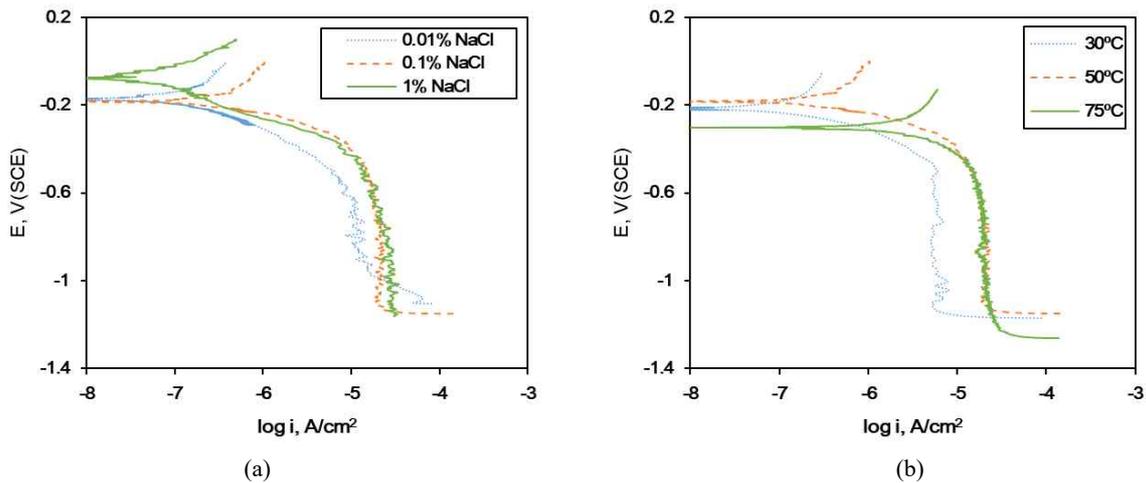


Fig. 4 Effects of (a) NaCl concentration and (b) solution temperature on the polarization curves of CFRP in deaerated solution: (a) 50 °C, (b) 0.1% NaCl.

Fig. 6 reveals the effect of NaCl concentration on the surface appearance of A516Gr.55 after the corrosion tests. Fig. 6a shows the corrosion morphologies of single specimen and Fig. 6b shows the corrosion morphologies of galvanic coupled specimen with CFRP. Solution temperature was 50 °C. Corrosion of carbon steel was general corrosion but not uniform on the whole corroded surface. Distinct difference of corrosion morphology was not observed in all cases of single or galvanic coupled specimen including different NaCl concentration.

Fig. 7 shows the combination between cathodic polarization curves of CFRP and anodic polarization curves of A516Gr.55. Solution temperature was 50 °C. As shown in the figures, cathodic polarization curves of CFRP met

the anodic polarization curves of carbon steel regardless of NaCl concentration. On the base of the mixed potential theory [25], corrosion cell divided into anode and cathode, and the summation of cathodic current is same to that of anodic current. Therefore, if two materials forms the galvanic cell, CFRP will be the cathode and carbon steel will be the anode, and carbon steel will corrode about the current density at cross point.

Fig. 8 shows the effect of solution temperature on the corrosion rate of A516Gr.55 by galvanic coupled CFRP in 0.1% NaCl solution. Corrosion rate of carbon steel increased greatly with increasing temperature, regardless of single or galvanic coupled specimen. Whenever the temperature increases by 10 °C, corrosion rate of single specimen increased by 22.2% and the rate of galvanic coupled specimen increased by 21.7%. However, the rate of galvanic coupled specimen was 1.4 times faster than that of single specimen, in the case of 75 °C.

Fig. 9 shows the effect of solution temperature in 0.1% NaCl on the surface appearance of A516Gr.55 after the corrosion tests. Fig. 9a shows the corrosion morphologies of single specimen and Fig. 9b shows the corrosion morphologies of galvanic coupled specimen with CFRP. NaCl concentration was 0.1% NaCl. Corrosion of carbon steel was general corrosion but not uniform on the whole corroded surface. Distinct difference of corrosion morphology was not observed in all case of single or galvanic coupled specimen including different solution temperature.

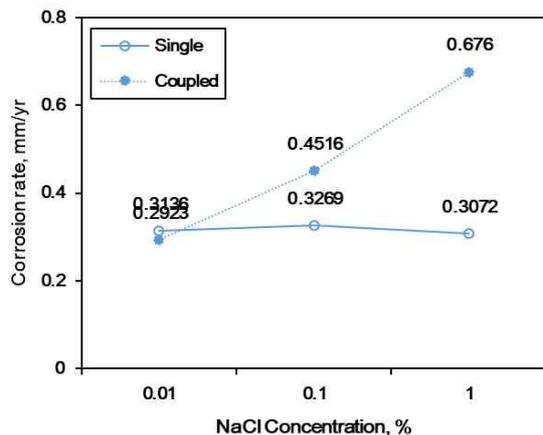


Fig. 5 Effect of NaCl concentration on the corrosion rate of A516Gr.55 by galvanic coupled CFRP (Solution temperature: 50 °C).

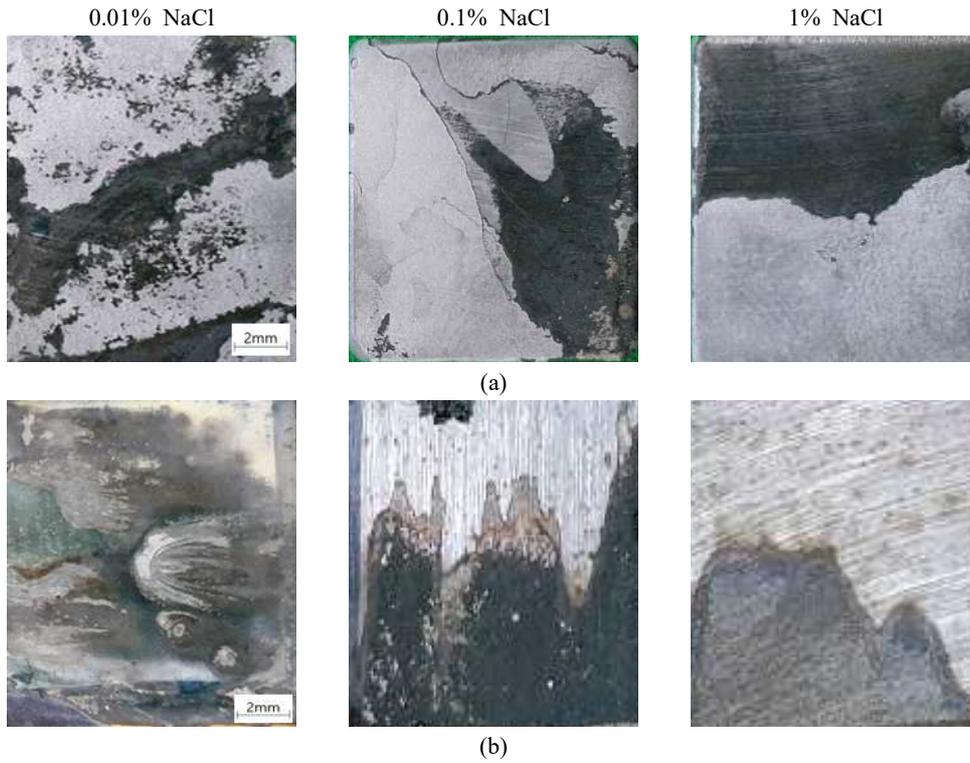


Fig. 6 Effect of NaCl concentration on the surface appearance of A516Gr.55 after the corrosion tests: (a) single specimen and (b) galvanic coupled specimen with CFRP (Solution temperature: 50 °C).

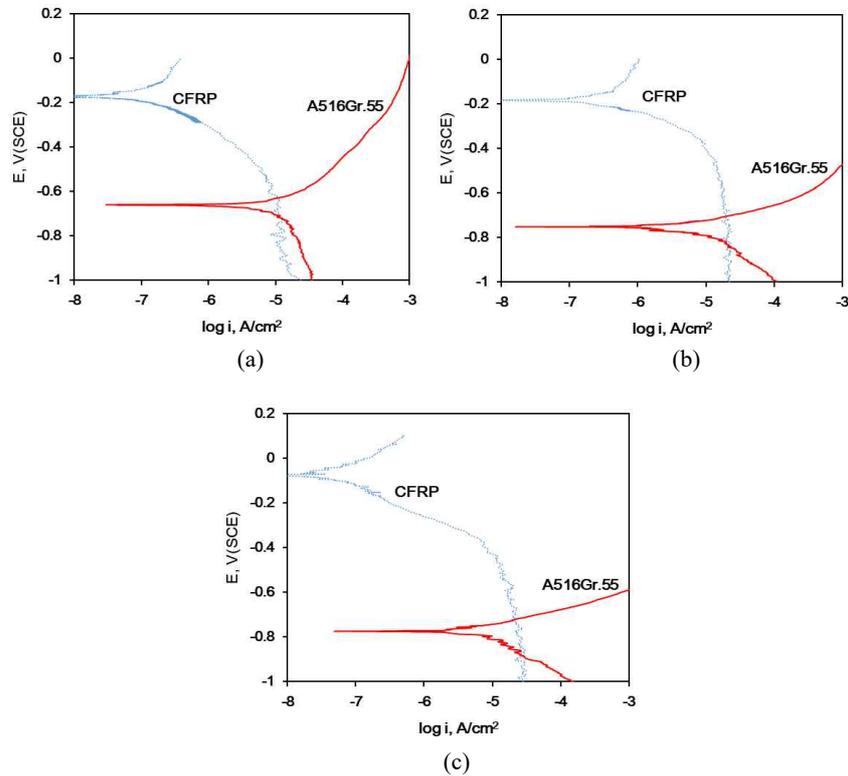


Fig. 7 Combination between cathodic polarization curves of CFRP and anodic polarization curves of A516Gr.55 (Solution temperature: 50 °C): (a) 0.01% NaCl, (b) 0.1% NaCl, (c) 1% NaCl.

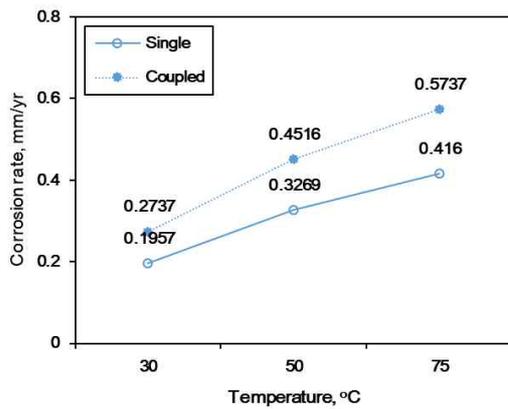


Fig. 8 Effect of solution temperature on the corrosion rate of A516Gr.55 by galvanic coupled CFRP in 0.1% NaCl solution.

Fig. 10 shows the combination between cathodic polarization curves of CFRP and anodic polarization curves of A516Gr.55. NaCl concentration was 0.1% NaCl. As shown in the figures, cathodic polarization curves of CFRP met the anodic polarization curves of carbon steel regardless of solution temperature. Therefore, if two materials forms the galvanic cell, CFRP will be the cathode and carbon steel will be the anode, and carbon steel will corrode about the current density at cross point.

Fig. 11 reveals the relationship between galvanic current density derived from the mixed potential theory using polarization curves and the corrosion rate of A516Gr.55 by galvanic coupled CFRP. With NaCl concentration and sol-

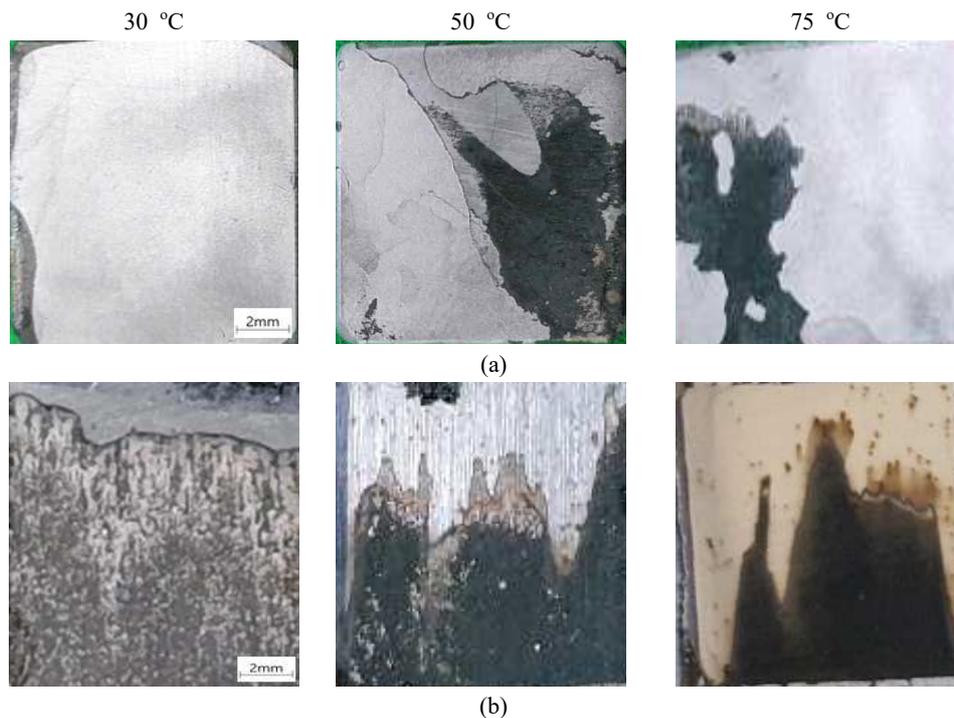


Fig. 9 Effect of solution temperature in 0.1% NaCl on the surface appearance of A516Gr.55 after the corrosion tests: (a) single specimen and (b) galvanic coupled specimen with CFRP.

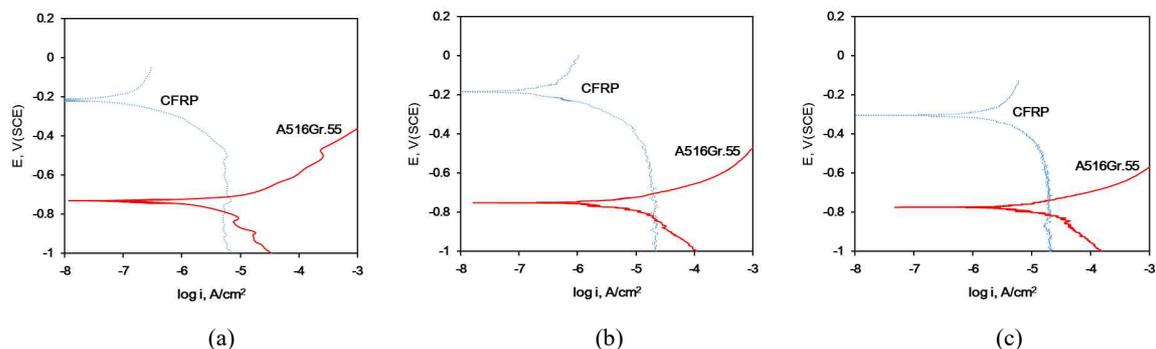


Fig. 10 Combination between cathodic polarization curve of CFRP and anodic polarization curve of A516Gr.55 in deaerated 0.1% NaCl solution: (a) 30 °C, (b) 50 °C, (c) 75 °C.

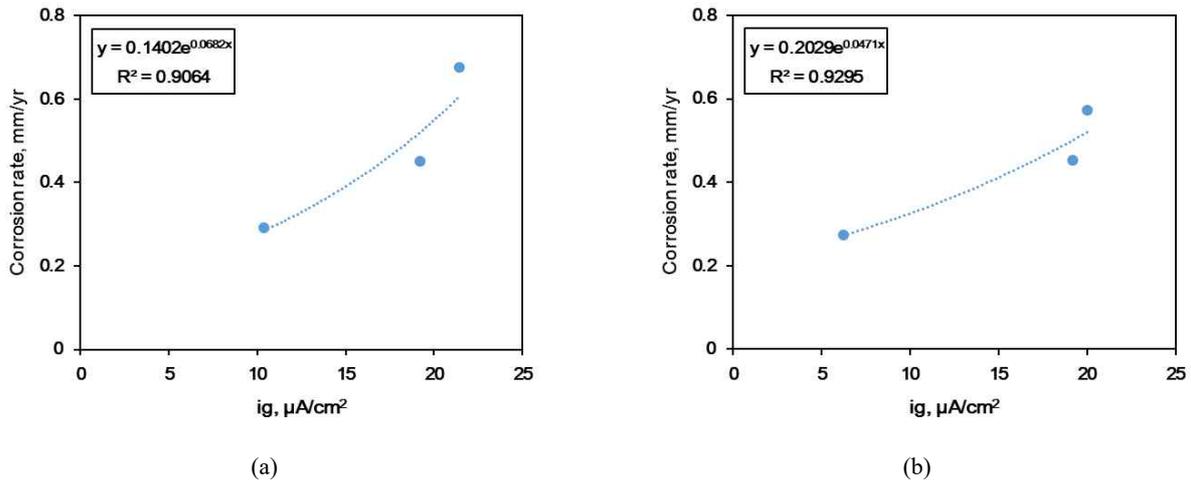


Fig. 11 Relationship between galvanic current density derived from the mixed potential theory using polarization curves and the corrosion rate of A516Gr.55 by galvanic coupled CFRP: (a) The effect of NaCl concentration, (b) The effect of solution temperature.

ution temperature, the relationship between two factors was the exponential relation.

4. Conclusions

This work focused on the effects of NaCl concentration (0.01 ~ 1% NaCl) and solution temperature (30 ~ 75 °C) on the galvanic corrosion between CFRP and A516Gr.55 carbon steel, and the followings can be concluded:

- 1) Since CFRP showed the water absorption and the high open circuit potential, most of metallic materials may be galvanically corroded if the materials contact with CFRP.
- 2) Average corrosion rate of single carbon steel increased 0.63% per 10 times concentration, but its rate of the steel coupled with CFRP increased 46.9% per 10 times concentration. However, when the temperature increases by 10 °C, corrosion rates of single specimen or coupled specimen with CFRP revealed a similar effect, even though the rate of coupled specimen was higher than that of single specimen.
- 3) The relationship between galvanic current density derived from the mixed potential theory using polarization curves and the corrosion rate of A516Gr.55 by galvanic coupled CFRP can be formulated with exponential functions.

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