様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　４ 年　 ６ 月　 ６ 日現在

機関番号：１７１０２

研究種目：若手研究

研究期間：2019～2021

課題番号：１９Ｋ１５０７４

研究課題名（和文）Development of anti-corrosion technique of CFRP strengthened steel structures and durability prediction under atmospheric environment

研究課題名（英文）Development of anti-corrosion technique of CFRP strengthened steel structures and durability prediction under atmospheric environment

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交付決定額（研究期間全体）：（直接経費）　　3,300,000円

研究成果の概要（和文）：炭素繊維による既存構造物の腐食部位に補強する接合界面の環境耐久性が向上するために、学際的研究方法を用いてCFRP-鋼接合継手の接合挙動とガルバニック腐食メカニズムを解明した。力学試験および熱分析結果から複合継手の成型・養生の最適化条件を明確にした。また、浸漬および乾湿サイクル試験を実施することで、CFRP-鋼接合部の劣化に対する湿気と熱の影響を検討した。一方、従来の除錆方法を実施した腐食鋼表面の物理的・化学的特性を明らかにし、機械的性質との関係が解明された。最後に、大気環境をシミュレートするために電解液膜厚の測定装置を開発し、水膜と浸漬環境におけるCFRP－鋼のガルバニック腐食機構を推定した。

研究成果の学術的意義や社会的意義
The present experimental results provide new insights regarding the interfacial bond mechanism between corroded steel structures and adhesive or CFRP composites to enhance their capability for use in aging steel structures in various fields.

研究成果の概要（英文）：The study focused on the CFRP strengthening technique applied to the corroded steel structures, committed to improving the environmental durability of adhesion interface and composite joint. It was aimed to evaluate the bond behavior and galvanic corrosion mechanism of the CFRP-steel bonding system through comprehensive research methods. Firstly, mechanical and thermal analysis optimized the curing condition and other variables during fabrication. Secondly, the moisture and thermal effects on the deterioration of CFRP-steel adhesive joint were discussed by conducting aging tests. Meanwhile, the conventional rust removal methods were studied by clarifying the physical and chemical characteristics of steel surfaces. Finally, an electrolytic film thickness measuring device was developed to simulate the atmospheric environment. The test results show that the water film and immersion environments can cause different corrosion rates and anodic zone.

研究分野：工学

キーワード：galvanic corrosion　CFRP　adhesion　thermal analysis　durability　mechanics

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

In recent years, for the damaged steel structures, CFRP strengthening has been a hot topic and received a great concern for its unique advantages. However, metal-adherent interfaces pose a difficult set of problems in practice, and weak bonds may cause premature failure. Bonding failure is the most common problem of concern for steel structures strengthened by various types of externally bonded CFRPs. In the atmospheric environment, epoxy resin, as a common adhesive agent, is prone to hydrolysis and reduces the mechanical properties of the CFRP bonding system immediately, as it is susceptible to thermal cycling, ultraviolet radiation, and moisture. Unfortunately, many civil engineering structures are inevitably exposed to such environments. The available durability data of CFRP-steel composites from previous investigations directly applicable to the exposure conditions of steel structures are scarce. Particularly in the case of fabric-based wet layup systems, whose entire fabrication process is conducted in the field, the fundamental studies on the parameters related to the degradation mechanism of steel members reinforced by carbon fiber sheets are still limited. In addition, the possibility of galvanic corrosion between carbon and steel would be sharply increased along with the adhesive deterioration. The specific environmental factors and corresponding galvanic corrosion behavior can affect the durability of the adhesion interface and composite joint. However, the anti-corrosion method or durability measures have not been developed yet.

The re-deterioration cases of the corroded steel members after CFRP reinforcement (wet layup by carbon fiber fabric) have been reported that the adhesion site rusted again under the CFRP layer after several years in service. It was suggested that the poor surface conditions, low adhesion quality, and unstable curing conditions further accelerate deterioration owing to the multiple effects of environmental factors and loads. Corrosion damage optimization should reflect not only the change in surface geometry but also the surface cleanliness, chemical composition, and modification method, all of which are critical for repair efficiency. There is a critical need to develop a guideline or optimization measures to enhance the environmental durability to adapt to the actual exposure conditions.

This study provides experimental details of an investigation of the bond behavior of a CFRP-strengthened steel system using a wet layup carbon fiber fabric, with emphasis on the improvement in the surface treatments of the steel substrate, thermal properties of the epoxy resin, and curing process of the composite. Multiscale characterization and mechanical tests were performed to determine the effect of clean and corroded surface conditions on the interfacial bond behavior of the steel-CFRP adhesion joint. Furthermore, part of the fundamental study on the galvanic corrosion behavior of CFRP/carbon steel coupling in the atmospheric environment was also investigated to determine the accelerated corrosion mechanism of the CFRP-steel contact system.

２．研究の目的

The applications of CFRP to steel structures continue to remain limited. The main technical barriers concerning this strengthening technique are the bond strength of the adhesion interface, environmental durability of the composite joint, as well as the possibility of galvanic corrosion between carbon and metals after the adhesion deteriorates. The research purpose and originality include:

① Improvement in bond behavior and durability of CFRP strengthened steel structures

② Bond behavior between CFRP and corroded steel plate associations with surface treatments

③ Galvanic corrosion mechanism of carbon fiber reinforced polymer/carbon steel coupling in an atmospheric environment

３．研究の方法

To evaluate the bond behavior and galvanic corrosion mechanism of CFRP-steel bonding system exposed to atmosphere environment, a more comprehensive research methods of observation and assessment were formed. The main experiments were all conducted indoors, including the electrochemical test, two kinds of the aging test (immersion and wet-dry cyclic conditions), mechanical test, thermal measurement, microstructure characterization, etc.

In addition to the above-mentioned conventional test methods, this study has done some innovative works in terms of corrosion surface analysis, in which the fractal dimension (D_f) was used to describe the surface complexity. In the electrochemical tests, a self-developed measuring setup of electrolytic film thickness was used to prepare water films accurately. These novel research methods mentioned above are the basis for the innovative results obtained in this study.

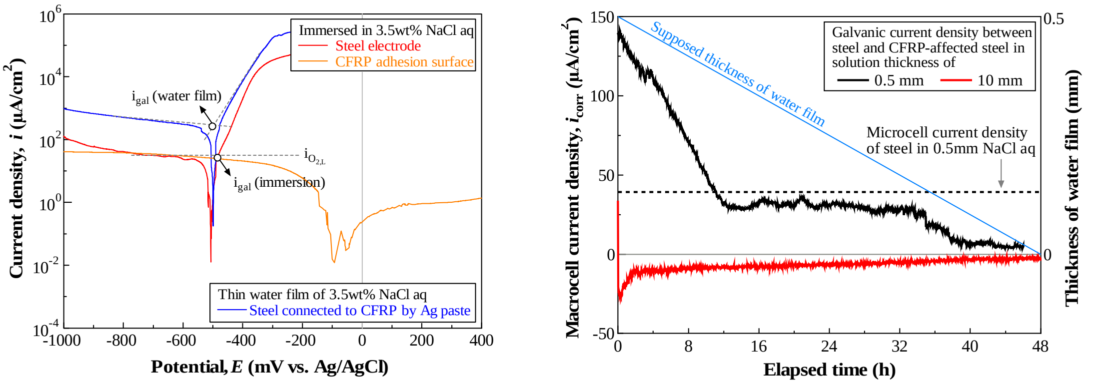
４．研究成果

In the 2019 year, the fundamental studies on the adhesion interface fracture between CFRP and cleaned steel substrate were simulated by parametric FE analysis, using a CZM (cohesive zone model) numerical simulation. Moreover, thermal characterization of the epoxy resin was conducted by DSC analysis. From 2020, it was focused on the electrochemical test and indoor corrosion/deterioration tests. In the 2021 year, the main study focused on the interfacial bond behavior of steel-CFRP adhesion joint associations with different steel surface treatments. Based on the three years of detailed research work, the main findings of this study were summarized in the following (1~5) parts.

(1) Galvanic corrosion mechanism under the water film condition

The electrochemical tests were measured using a conventional three-electrode cell, carried out in the naturally aerated 3.5 wt% NaCl solution. **Fig.1(a)** shows the galvanic potential of the immersion and water film environments are approximated, whereas there is a tenfold difference in current density. For the polarization curves of steel electrodes affected by CFRP in an 0.5 mm water film, the full contact state between CFRP and steel leads to a significant increase in the corrosion rate of steel electrodes. The short-connected fiber surface can serve as the cathode reaction area of the total system. Also, as the CFRP was partially exposed to the atmosphere above the water film, that improved the oxygen diffusion control of corrosion reactions, which further promotes the active dissolution of steel.

The ZRA test of 24 hours, as shown in **Fig.1(b)**, it is a system to measure the galvanic current density between steel and CFRP-affected steel in electrolyte thicknesses of 0.5 mm and 10 mm. The anode/cathode electrode can be determined from the current direction. Obviously, the CFRP-affected steel was the cathode in the 0.5 mm water film environment, while it acted as an anode in the immersion environment. The phenomenon of opposite current direction should cause by the different dominant inducing factors. For the water film case, the steel electrode of noble potential, i.e., the one polarized by CFRP, was determined to be the cathode. For the immersion case, both steel electrodes and CFRP were under the waterline. Thus, the oxygen diffusion limitation would restrict the cathodic reaction of the whole system. Macrocell corrosion occurred by differential oxygen concentration, leading to the current flows between two steel electrodes while the oxygen-rich zone became the cathode, i.e., the electrode without CFRP cover.



(a) Polarization curves (b) ZRA test during 24h

Fig.1. Galvanic corrosion behavior in water film and immersion environments.

The current experimental results show that the water film and immersion environments can cause a significant difference in the corrosion rate of steel and might lead to a reversal of the surrounding cathodic and anodic zones. These results will have a significant impact on the assessment of galvanic corrosion rate in a specific environment.

(2) Surface treatment on steel substrate and rust removal efficiency

For the milled specimens after different surface treatments, the most utilized roughness profile parameters were obtained by LSCM. The results showed that the roughness parameters were similar for the steel substrates polished by the electric power tools. The Wenzel roughness factor of Blast shows that its true surface is approximately 1.266 times the nominal area. An increase in the actual surface area may lead to a proportional increase in adhesion, which was verified by pull-off test results. Among four surface treatment methods, the Pearson correlation coefficient shows the Wenzel roughness factor strongly correlated to the bond strength. The roughness parameters Ra, Rzjis, Sa, Sq, and Sz corresponding to the height direction of the surface undulation, conform to the relation that BS ＜DS＜Brush＜Blast, and they all own a high correlation to bond strength.

For the corroded specimens, the rust residues are unavoidable in corrosion when treated with power tools. The elemental analysis results by SEM-EDX are shown in **Fig.2**, it showed that the steel base and corrosion pits on the BNA (an abrasive disk made of a bevel non-woven pad was installed on an electric rotating disc grinder and manually processed evenly on the rusted surface) were clearly demarcated with a high concentration of oxides and salts in the pits. For the brush surface, more chloride residues were discretely observed. Chloride ions and oxide residues are also distributed on the entire treated surface. The top view of the blast specimen reveals that there are few Cl and O residues on the surface. The related SEM image of the cross-sectional view of the blast case is shown in **Fig.4(d)**, which indicates that the blasted steel substrate has an irregular rough surface with fissures. This case not only increases the real adhesion surface but also forms an anchor effect for adhesive-penetrated fissures and further enhances the necessary fracture energy. Moreover, it was confirmed that a small number of abrasive remains on the blast steel surface, which might cause salt and rust to be embedded into the substrate.

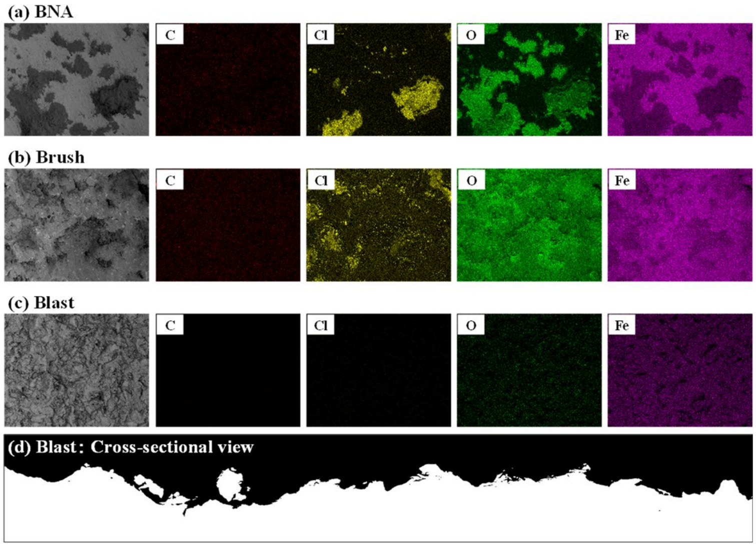


Fig.2. SEM-EDX analysis on the de-rusting surfaces (×50 magnification).

(3) Thermal properties of epoxy matric associated with curing temperatures

The curing temperature has an influence on the curing kinetics and final strength of the composite. The curing kinetics and thermal properties of the epoxy resin were investigated by DSC analysis. The curing reaction parameters were calculated by the phenomenological kinetic model, and the isothermal curing degree curves of the system were drawn as shown in **Fig.3**. It shows a required time at a certain temperature corresponding to a certain percentage of conversion, that longer curing time is necessary to reach the same conversion degree at low temperatures. The growth rate is basically linear when the conversion degree below 50%, while the curing process was significantly decelerated owing to the effects of material vitrification and diffusion control in the late curing stages.

The isothermal curing degree curves also indicate that specimens curing at 15°C (14 days) and 35°C (5 days) is approaching complete reaction (＞99%). The non-isothermal DSC curves of the fully cured epoxy matrix in composite joints are shown in **Fig.4**. According to the twice heat raising on the just mixed A/B epoxy resin, the DSC thermogram of the second run can be used to obtain the glass transition temperature $T_{g\infty}$=60°C. However, the glass transition temperature of both samples under 15°C and 35°C cure remain much lower than $T_{g\infty}$, because the polymer network was not crosslinked, and the polymerization does not achieve completion. For the glass transition temperature (T_g) of polymer adhesive applied to the steel structure reinforcement, the ambient temperature close to T_g leads to the thermal deterioration of epoxy. The local temperature of the steel structure has risks over 50°C in summer. However, a low T_g value in the range of about 45~48°C was obtained after curing at normal atmospheric temperature. Thus, the thermal properties of CFRP strengthened structure related to environmental durability should be paid attention.

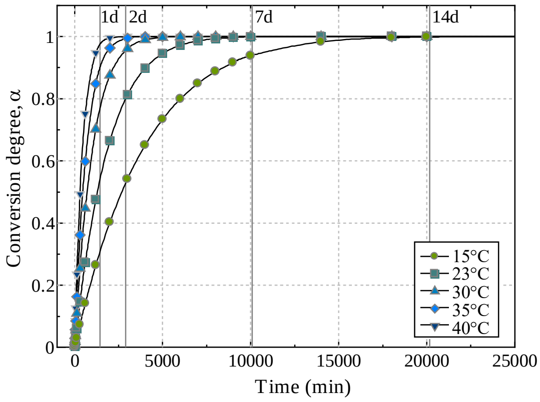


Fig.3. Degree of conversion as a function of the temperature in the isothermal curing.

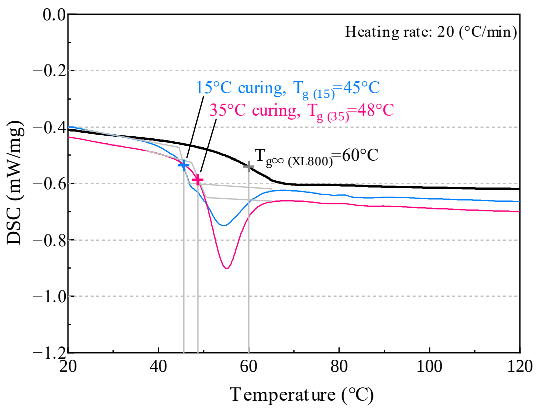


Fig.4. DSC thermograms for XL800 epoxy matrix, after cure at 15°C and 35°C.

(4) Deterioration behavior of adhesion interface of CFRP-steel joint

The moisture and thermal effects on the deterioration of the adhesive joint were examined by conducting short-period aging tests in immersion (W) and wet-dry cyclic (WD) environments, during which delamination strength reduction and failure mode transformation were observed. **Fig.5** shows the pull-off tensile strength of WD and W specimens after 30 cycles of deterioration tests. The bond strength reduction of WD specimens was more evident than that of the immersion group. The wet-dry cyclic exposure would lead to higher risks of the steel/adhesive interfacial debonding, especially for the relatively smooth steel surface. The debonding was mainly caused by the thermal deformation difference at the interface that occurred among all WD specimens except the Blast specimen. The grit-blast roughened surface provides an anchor effect that ensures the synchronous deformation of composite material under the 23°C~60°C temperature cycling.

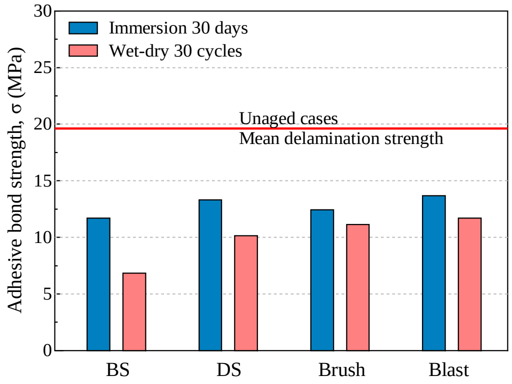


Fig.5. Pull-off test results of specimens of the composite joint after aging test.

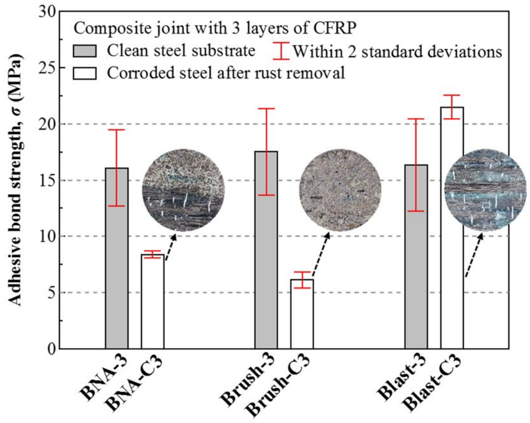


Fig.6. Adhesive bond strengths of milled/ corroded specimens.

(5) Bond behavior of clean/corroded steel-CFRP adhesion joint

This study evaluated the topography, microstructure, and surface composition of clean and corroded steel specimens, and qualitatively established their relation to bonding behaviors and failure modes. The pull-off test results for the composite joint specimen with three layers of CFRP are shown in **Fig.6**. For the clean steel substrate, all test failure modes were CFRP delamination, regardless of the surface treatments. For the corroded specimens, the failure mode of the Brush-C3 is a complete interfacial failure, which is a combination of interfacial failure and CFRP delamination, while Blast-C3 shows a typical delamination fracture. Accordingly, the tensile strength of the BNA-C3 and Brush-C3 dropped to more than half of the corresponding value of the milled specimens. In contrast, blast treatment resulted in increased bond strength of 31.7% for the corroded specimens.

It was speculated that the effective adhesion area was changed by residual rust or roughness. The corroded steel was then treated using power tools. Residual rust leads to cavities occurring between the adhesive and substrate, which significantly reduces the effective adhesion area and interfacial bond strength. Nevertheless, the blast specimen showed the opposite tendency. As shown in **Fig.4(c)**, there were rare–residual rust or oxide residues on the blast-treated surface. According to the calculated Wenzel roughness factor, there was a difference of 1.58 times in the actual adhesion area of the milled/corroded specimens after the same blast treatment. Therefore, the following two aspects are speculated to contribute to the increase in bond strength in Blast-C3： 1) When adhesive failure occurs at the interface, G_0 equals the work of adhesion W_a, which is strongly associated with the true surface area (in the case of a cohesive failure occurs, G_0 equals W_c, which is strongly associated with the true fracture area). Thus, a larger Wenzel roughness factor is the dominant factor that causes an increase in the surface energy term G_0, leading to a larger fracture strength. 2) When the bonding surface is more irregular (or rougher), a larger volume of epoxy resin is required to occur plastic deformation during the fracture process, which results in a significant increase in ψ (a term for other energy-absorbing processes occurring during fracture).

In addition to the above work, this study also found a strong correlation existed between the surface geometry properties and the tensile/shear strength. However, for clean and corroded steel surfaces their fracture mechanisms differ. Various physical property parameters of the corroded surface related to surface treatment will further affect the bond performance. The corresponding adhesion mechanisms were mathematically demonstrated based on the surface energy principle. The present experimental results provide new insights into the interfacial bond mechanism between corroded steel structures and adhesive or CFRP composites.

５．主な発表論文等

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２．発表標題 Deterioration Characteristics of Overlapping Layers between Al-5Mg Thermal Spray Coating and Heavy-Duty Paint Coating
３．学会等名 2nd International Conference on Materials Design and Applications, Tokyo, Japan, 2019（国際学会）
４．発表年 2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関