Technical Report

Development of Steel Sheet Layered by Composite Material of Carbon Fiber Reinforced Thermoplastic

Yuka ANEGAWA*
Noriyuki NEGI
Kohei UEDA
Masumi KOORI
Ryosuke HARAKO
Masaharu IBARAGI
Masafumi USUI
Atsuo KOGA
Hiroyuki TAKAHASHI

Abstract

Carbon fiber reinforced plastic (CFRP) is expected as a new material to reduce the weight of automobiles; however, it is expensive. Composite steel sheet, in which CFRP is partially bonded to steel, is cost-effective, but it is essential to improve production efficiency, processability, and corrosion resistance. In this study, we found that productivity can be improved by integrated press forming CFRP and steel plates using phenoxy resin, which has excellent workability and adhesiveness to steel, and that corrosion at the interface can be suppressed by properly arranging the coating layer and insulation layer. These technologies enable the development of materials with higher mechanical properties than metals and resins, and with better productivity, processability, and corrosion resistance than conventional composite materials, and are expected to be applied not only to automobiles, but also to air mobility vehicles such as "flying taxis".

1. Introduction

In recent years, reducing the weight of components for automobiles and other transport equipment has been strongly demanded in order to reduce CO_2 emissions.[1)] Steel has traditionally been used for the structural components of vehicles; however, as one of the measures to meet this social need, the use of multi-materials in car bodies, where lightweight materials such as aluminum and fiber-reinforced plastics are used in the right places, is being considered in a number of cases. Among lightweight materials, carbon fiber-reinforced plastic (CFRP) is expected to be utilized by taking advantage of the high strength and the high rigidity of the carbon fiber. However, it is extremely expensive, and when it is used as it is for the structural members of automobiles, the cost will be very high. Furthermore, in the employment of multi-materials, the application of the traditionally proven mechanical fastening methods such as spot welding and riveting is difficult, and how dissimilar materials can be joined is an issue to be addressed. In addition, the development of the adhesion agent which enables such joining is under way. However, in the case of automobiles for instance, the investment of new equipment into the existing production line becomes necessary, and the process inclusive of the curing time cannot be justified in terms of cost as compared with the conventional method.

Therefore, we thought that we could improve performance, suppress cost, and use the conventional joining method which have been used conventionally for steel materials by gluing CFRP to wherever necessary on the steel material having long-term proven records and reliability. A hardening type resin like epoxy resin is used as the matrix resin of CFRP in a number of cases. However, brittle fracture occasionally occurs after hardening, and furthermore, a curing time is necessary, and the production tact time increases. In addition, once hardened, bending work cannot be applied. For these issues, the use of a thermoplastic resin for the matrix resin is effective, and by using a resin which has an excellent adhesive strength to a steel sheet,[2)] and by laminating CFRP on a steel sheet, and applying press forming accompanying heating and pressurization, the integrated press forming of simultaneously applying adhesion and forming is enabled, and the enhancement of productivity is expected.

* Composite Materials Research Dept., New Materials Research Lab., Advanced Technology Research Laboratories, Nippon Steel Corporation
20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511

However, the resins used for the general thermoplastic CFRP are polyamide, polycarbonate, and polypropylene, and they do not have high adhesive strength to a steel sheet or to other materials as realized by the thermocompression bonding, and they are not appropriate for multi-materials without the use of an adhesive agent. Nippon Steel Chemical & Material Co., Ltd. manufactures and sells the thermoplastic phenoxy resin which has a high adhesive strength equivalent to that of epoxy resin. This realizes a composite material with carbon fiber, and therefore, by using the phenoxy based thermoplastic CFRP, a suitable CFRP composite steel sheet is obtained. This paper describes the integrated press formability of the phenoxy resin based CFRP composite steel sheet under the heating and pressurization condition, its excellent mechanical properties, and the rust prevention technologies required when laminating CFRP to a steel sheet, all recognized in the development of the phenoxy resin based thermoplastic CFRP composite steel sheet conducted jointly with Nippon Steel Chemical & Material.

2. Integrated Forming of CFRP Composite Steel Sheet by Warm Working

As abovementioned, when using a CFRP composite steel sheet for automotive members, the phenoxy resin is suitable as the matrix resin, and from the viewpoint of the process of manufacturing members, the preferred process is laminating the prepreg, the precursor of CFRP, on the flat steel sheet, and the integrated press forming for thermocompression bonding and for forming to the configuration of the dies by a heating and pressurization press machine with one action. The CFRP prepreg using phenoxy resin as the matrix was laminated on a steel sheet, and heating and pressurization press forming by a die was applied with one action. In this section, the result of the integrated press forming is described.

2.1 Confirmation of basic processability by L-letter-bending

The integrated press forming was conducted as follows. As the test sample, a carbon fiber sheet of a cloth textile composed of a carbon fiber of the PAN system having an elastic modulus of 280 GPa and a tensile strength of 5500 MPa was prepared, and the phenoxy resin YP-50 produced by Nippon Steel Chemical & Material was impregnated into the carbon fiber sheet at the weight ratio of 6:4 to form a prepreg, and the prepreg of a weight of 8.6 kg/m^2 was laminated on the galvanized steel sheet (GA) 1.6 mm thick. The size of the test piece was 5 cm × 15 cm. Next, the whole of the laminated body was heated sufficiently to 240°C in a furnace, and it was taken out of the furnace, and was immediately placed on the die which executes L-letter-shape bending (punch tip R=10) as shown in **Fig. 1**, and the bending work was executed. For this operation, the mold was sufficiently coated with a mold lubricant. The observation of the sample after the bending work revealed that there was no separation of the CFRP from the steel sheet, and the CFRP adhered to the steel sheet firmly. The CFRP composite steel sheet could be processed to the L-letter-shape as shown in **Fig. 2**. According to the measurement of the thickness of the CFRP, it was about 5 mm regardless of the position, and Vf, the volume ratio of fiber in the CFRP, was about 55%. The CFRP of about 55% of Vf has a carbon fiber content percentage high enough to exert sufficient mechanical properties, and from this, it was confirmed that, by applying heating and pressurization press forming using dies to a steel sheet laminated with a prepreg, the CFRP is properly glued, and exhibits the potentiality of realizing integrated press forming of a composite steel sheet to a desired configuration.

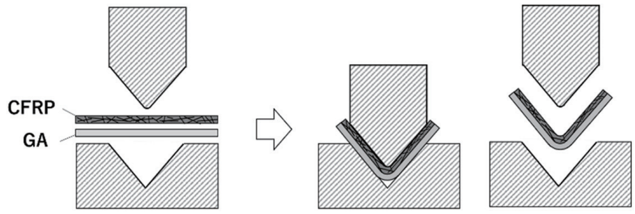

Fig. 1 Process of integrated press forming


Fig. 2 Appearance of CFRP and steel composite after press forming

3. Mechanical Properties of Phenoxy CFRP Composite Steel Sheet

Next, the mechanical properties and the peculiarities of the CFRP composite steel sheet laminated with phenoxy resin base CFRP glued by heating and pressurization are described.

3.1 Mechanical property evaluation method and result

The mechanical properties were evaluated as follows. As a sample, the prepreg with the same CFRP as that used in Section 2 above was used. A prepreg with a weight of 1.72 kg per 1 m^2 was laminated on the galvanized steel sheet 0.42 mm thick. A sample 2.5 cm in width and 20 cm in length was prepared, and a tensile strength test was conducted (conforming to JIS K 7164:2005), and the load was measured. Furthermore, tensile strength tests under the same condition were applied and the load and strain were measured. The samples were: the same weight sample CFRP made from the same CFRP prepreg by heating and pressurization, and the same steel sheet as that used for the CFRP composite steel sheet. The results are shown in **Fig. 3** (the graph of the average value of N=3). The highest load of the CFRP composite steel sheet is 27400 N, which is equivalent to the strength of about 770 MPa. To this, the highest load of the CFRP alone is 19000 N, and the load of the steel sheet alone in the neighborhood of CFRP rupture is about 4500 N. Worthy of attention is the fact that, as opposed to the sum of the loads of the CFRP alone and the steel sheet alone being about 23500 N, the load of the composite steel sheet is 27400 N, which is higher in load by 16% to 17%. Furthermore, in terms of CFRP fracture strain, the CFRP composite steel sheet exhibits a slight increase from about 1.2% of CFRP alone to about 1.5%.

3.2 Consideration on mechanical property emergence mechanism

As abovementioned, the highest load of the CFRP composite steel sheet is higher than those of the CFRP and the steel sheet measured alone, and furthermore, the fracture strain of the CFRP composite steel sheet is larger than that of CFRP alone. The mechanism

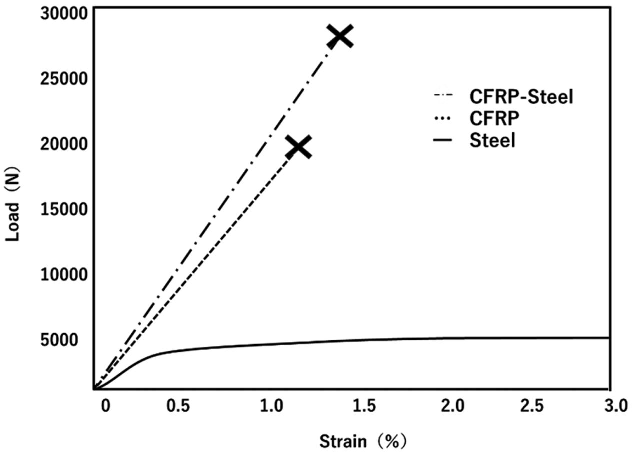

Fig. 3 Results of JIS K 7164:2005 tensile test

of these increases is considered.

The CFRP composite steel sheet employing phenoxy resin was manufactured by a heating and pressurization press machine, and the temperature at the time was 240°C. The materials bonded at the temperature at which thermal contraction develops as a matter of course when the temperature drops to an ordinary temperature. As opposed to the coefficient of linear expansion of the CFRP employing carbon fiber of the PAN system of cloth textile of about 0 to 5.0 (10^{-6}/°C), that of the steel material is about 12 (10^{-6}/°C).[3, 4] Namely, when the CFRP is bonded to the steel sheet at a high temperature, and when the temperature goes down to an ordinary temperature, the CFRP is subject to a force of the steel material which tends to contract more, and an additional compressive stress is applied. When a tensile strength test is applied to the sample, although a tensile load is exerted by the test machine, the tensile load is not substantially exerted to the CFRP until the load becomes balanced with the compressive load exerted by the steel material. Then tension starts to work at the balancing point, the equal amount of load is added, and therefore it is considered that the highest load increases. Similarly, as the reason for the increase in breaking elongation, the increase in strain at the tensile breakage from that of the single piece CFRP which is not exerted by the compressive load is considered because the strain measurement is started where the compressive load is exerted to CFRP.

This mechanism is similar to that of the pre-stressed concrete technology in steel bar reinforced concrete. This technology is highly reliable, and used widely in the present civil engineering construction[5] because more rigid steel bar reinforced concrete is obtained due to a compressive stress acting on the concrete when the pre-stressed concrete is compatibly used with concrete and when the pre-stress is removed.

In addition, the CFRP composite steel sheet used in the test consists of a CFRP of a specific weight of about 1.7, and of a thickness of about 1 mm and a steel sheet of a specific weight of about 7.9, and of a thickness of 0.42 mm. Considering that the apparent specific weight of the composite material is about 3.5, and seeing that the strength is 770 MPa, the material is considered to have lightness not inferior to aluminum and high strength compatibility.

4. Rust Prevention Technology required for Laminating CFRP to Steel Sheet

A carbon fiber is a good electric conductor. Accordingly, in the composite body of a steel material and a CFRP, when the carbon fiber in the CFRP comes in contact with, or comes into close proximity with the steel material, they conduct electricity, and due to its electric potential difference, metals are corroded, and the contact corrosion between dissimilar metals (also termed as electrolytic corrosion) occurs.[6–8] In order to prevent such contact corrosion between dissimilar metals, a technology that prevents the electrolytic corrosion by inserting an insulation layer between the steel material and the CFRP has been proposed.[9, 10] However, when the thermocompression bonding by means of the thermoplastic resin as referred to in this report is used as a means to form a composite material using a conductive fiber like CFRP, even if an insulation layer is installed between the steel material and the CFRP, there are cases of occurrence of electrolytic corrosion, particularly more readily in the neighborhood of the edges of the insulation layer.[11] The vigorous study on this issue and the results thereof are described hereunder.

4.1 Cause of electrolytic corrosion

A study on the cause of the electrolytic corrosion that occurs in the lamination of CFRP and a steel material was conducted. Conventionally, in the case of laminating a CFRP on a steel sheet by the thermocompression bonding with an insulation layer placed on the steel material, the laminated areas of the insulation layer and the CFRP are made the same in many cases. When the steel material and the CFRP is laminated by thermocompression bonding under such condition, the matrix resin of a thermoplastic resin is liquefied and flows out, and on which the carbon fiber resin will also flow out (**Fig. 4**). Electrolytic corrosion is considered to occur by the contact of the flowing-out carbon fiber with the steel material. Furthermore, if the insulation layer is completely liquefied during thermocompression bonding, almost all of the insulation layer will flow out by pressurization, the effect of the inserted insulation layer will cease to exist, and electrolytic corrosion will occur.

Furthermore, since the electrodeposition coating is applied in many cases to various steel merchandise represented by automotive steel sheets, the applicability of the electrodeposition coating is essentially needed for the actual usage. Corrosion in the neighborhood of the edge of the insulation layer was observed when the electrodeposition coating was applied to the composite steel sheet. In the neighborhood of the edge of the insulation layer on the steel material, namely, in the neighborhood of the borderline on the steel material between the area covered by the insulation layer and the area not covered by the insulation layer, the electrodeposition coating is not sufficiently formed, or lacks adhesiveness even if a coating is formed, a crevice where the steel material is exposed is developed, and the water penetrating the crevice is considered to cause the substrate steel corrosion (hereinafter referred to as crevice corrosion).

4.2 Rust preventing technology to suppress electrolytic corrosion

In the first place, in order to prevent the contact of the carbon fiber with the steel material due to the flow-out of the matrix resin in the width direction in the thermocompression bonding, use of the insulation layer larger in area size than the laminated CFRP was studied. (**Fig. 5**). As a result, it was confirmed that if the insulation layer width is larger by a CFRP thickness of about +0.2 mm at the CFRP edge, the contact of the carbon fiber with the steel material is prevented, and the electrolytic corrosion can be suppressed. Furthermore, by incorporating a non-conductive fiber like a glass fiber into the insulation layer, as the insulation and a certain thickness can be secured, the flow-out of the insulation layer due to liquidation is prevented, and the effect of preventing the electrolytic corrosion is enhanced.

Secondly, as a means of preventing the crevice corrosion, even if a crevice is developed between the insulation layer and the electrodeposition coating, water does not contact with the steel material and the crevice corrosion can be suppressed by coating a conductive cortical layer containing conductive particles on the steel material, and forming an insulation layer on this cortical layer.

In summary, by supplying the abovementioned cortical layer on the steel material, forming an insulation layer on this cortical layer, and by laminating a CFRP narrower than the insulation layer on the insulation layer, electrodeposition coating is enabled and both the electrolytic corrosion (contact corrosion between dissimilar metals) and the crevice corrosion can be suppressed. **Figure 6** shows the photographs of the results of the corrosion cycle tests (JASO M609-91) of the following samples consisting of a galvanized steel sheet (GA) and the laminations of CFRP laminated and electrodeposition coated, glass-fiber-reinforced resin (GFRP) as the insulation layer laminated under CFRP and electrodeposition coated, conductive cortical layer coated under CFRP and electrodeposition coated, GFRP as the insulation layer laminated under CFRP, and the conductive cortical layer coated under the GFRP and electrodeposition coated. In the sample without the insulation layer and conductive cortical layer, a large amount of rust is generated, and even in the sample having an insulation layer, rust is generated; furthermore, rust is generated similarly in the sample having only a conductive cortical layer. On the other hand, in the sample having an insulation layer and a conductive cortical layer, rust is not generated, and good corrosion resistance characteristics are obtained and confirmed.

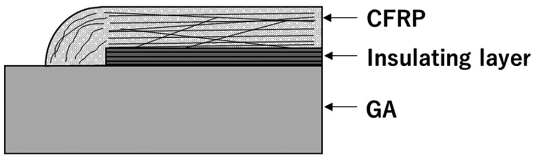

Fig. 4 Image of electrolytic corrosion caused by CFRP flow out

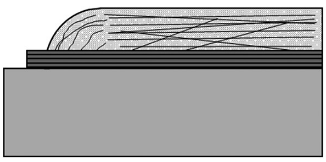

Fig. 5 Image of a structure to prevent electrolytic corrosion due to overhang of insulation layer

5. Conclusion

The excellent integrated forming workability and the mechanical properties of the phenoxy resin based thermoplastic CFRP composite steel sheet clarified in the development, and the rust preventing technologies required for the composite steel sheet were described. The composite steel sheet introduced in this paper has mechanical properties superior to those of the conventional steel materials and resin system materials when they are solely used, and furthermore, it has become clear that the composite steel sheet has higher productivity and workability than the steel sheet with CFRP simply glued together by an adhesion agent. We consider that these excellent properties can comply with the high demand from the transportation equipment field represented by the automobile sector where technologies are rapidly advancing and new models are being successively introduced, as well as the high demand from air-mobility vehicles like “flying taxis” which will soon be well underway.

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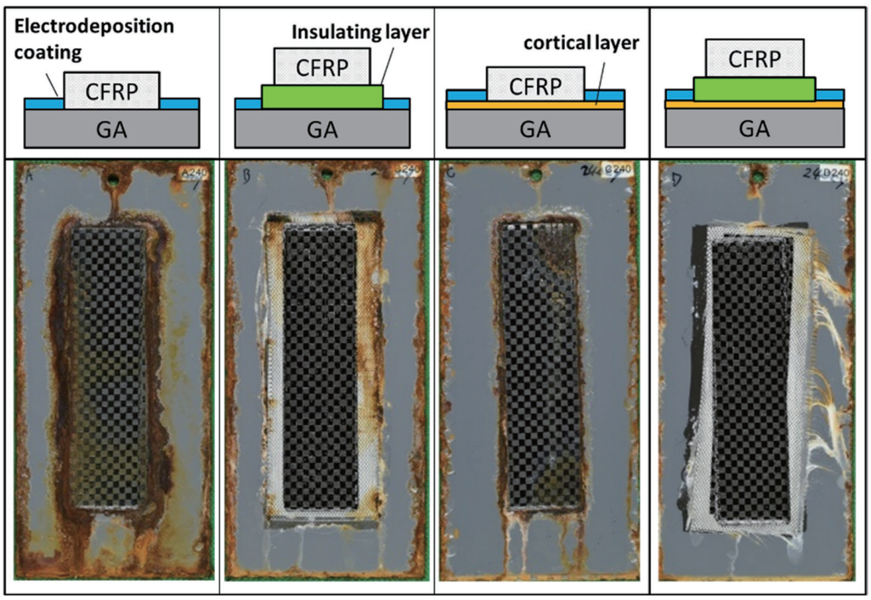

Fig. 6 Results of corrosion cycle test (After CCT/JASO 180 cycle)

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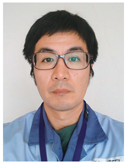
Yuka ANEGAWA
Composite Materials Research Dept.
New Materials Research Lab.
Advanced Technology Research Laboratories
Nippon Steel Corporation
20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511

Masaharu IBARAGI
Ph.D, General Manager, Head of Dept.
Composite Materials Research Dept.
New Materials Research Lab.
Advanced Technology Research Laboratories
Nippon Steel Corporation

Noriyuki NEGI
Principal Researcher
Composite Materials Research Dept.
New Materials Research Lab.
Advanced Technology Research Laboratories
Nippon Steel Corporation

Masafumi USUI
Senior Researcher
Composite Materials Research Dept.
New Materials Research Lab.
Advanced Technology Research Laboratories
Nippon Steel Corporation

Kohei UEDA
General Manager, Head of Lab.
Surface Treatment Research Lab.
Steel Research Laboratories
Nippon Steel Corporation



Atsuo KOGA
Senior Researcher
Functional Coating Research Dept.
Surface Treatment Research Lab.
Steel Research Laboratories
Nippon Steel Corporation

Masumi KOORI
Senior Researcher
Functional Coating Research Dept.
Surface Treatment Research Lab.
Steel Research Laboratories
Nippon Steel Corporation

Hiroyuki TAKAHASHI
Technology Planning Gr.
Functional Materials Business Management Dept.
Nippon Steel Chemical & Material Co., Ltd.

Ryosuke HARAKO
Researcher
Functional Resin Materials Development Center
Research & Development Div.
Nippon Steel Chemical & Material Co., Ltd.