RESEARCH PAPER

Corrosion Protection of Low Carbon Steel by Coating of Graphene Oxide Nanoparticles and Galvanization Process

Prantasi Harmi Tjahjanti *, Rachmat Firdaus, Iswanto, Ahmad Nova Irfian

Department of Mechanical Engineering, Faculty of Science and Technology, Universitas Muhammadiyah Sidoarjo, Sidoarjo, Indonesia

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ABSTRACT

The controlled formation of graphene oxide coatings in the form of the homogenous structure on stainless steel is demonstrated by scanning electron microscopy (SEM). The characterization of the material was assessed by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The carbon content in low carbon steel is ≤ 0.3% or, to be exact around 0.1%. Problem that commonly arises with low carbon steel is that the zinc coating, known as galvanization, can easily peel off or crack when moved or transported. The objective of this study is finding alternative coatings which are more adherent and can blend with the steel by testing a mixture of galvanized coating compound (type ER-809 Zinc Rich Cold) and graphene oxide (GO). The composition of the mixture is 15% graphene oxide (GO) and 85% galvanized coating compound. The immersion times were 30 seconds, 60 seconds, and 90 seconds. Dry corrosion test was conducted by heating in a furnace at 700 ^{0}C with variations in holding time for 30 minutes, 1 hour, and 1.5 hours. Weight Loss method was used to find out the Corrosion Penetration Rate (CPR). The lowest CPR result was obtained from 30 minutes heating time. The analysis of Scanning Electron Microscope (SEM) shows that the corrosion level on low carbon steel is low. Overall, low carbon steel coated with the mixture of galvanized (type ER-809 Zinc Rich Cold) and graphene oxide (GO) has lower CPR compared to low carbon steel without coating or coated with zinc alone.

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INTRODUCTION

Carbon steel is generally used as a construction material in industry and is considered a more economical option than corrosion-resistant and relatively more expensive alloys. Carbon steel contains less than 1.5% carbon and a mixture of other elements, such as Mn, Si, P, and S. Based on its carbon content, carbon steel can be classified into three types; low carbon steel (<0.25% C), medium carbon steel (0.25-0.70% C), and high carbon steel (0.70-1.05% C). Since carbon steel is generally susceptible to corrosion in industrial operating conditions, corrosion prevention is required for a safe operation [1].

Steel as a component of machining and construction is often damaged before the calculated time and is often used without adequate wear and corrosion protection. The

* *Corresponding Author Email: prantasiharmi@umsida.ac.id*

corrosion mechanism is characterized by the ion exchange process between the metal and its environment, which results in physical changes and decreases in the mechanical properties. Therefore, a method to prevent early wear and corrosion is implemented by carrying out a surface treatment process, namely coating a metal surface with other metals [2].

In its manufacture, steel is coated with anti-corrosion materials, such as Galvalume and galvanized coating. Galvalume coating is a coating composed of aluminum and zinc, while galvanized coating is a coating that is almost 100% made of zinc or with a little addition of silicon. The disadvantage of galvanized coating is its low resistance to acids and salt. When compared to Galvalume coating, galvanized coating has lower resistance to salt water [3].

Various protection methods for carbon steel have been developed to prevent carbon steel corrosion. Corrosion protection in carbon steel is generally carried out by means of coating, the use of inhibitors, and protection of the cathodic system [4,5,6,7]. The use of organic coatings is the method most frequently used in the corrosion protection of industrial materials. Epoxy resins are also widely used as a coating method to prevent corrosion because they have good chemical resistance, toughness, low shrinkage rate in the curing process, high corrosion resistance, and excellent adhesion to metal surfaces [8].

In general, organic coating process often uses inhibitor pigments as the main ingredients in inhibiting the corrosion process. Based on the inhibitory mechanism, inhibitor pigments can be classified into active pigments and barrier pigments [9]. Barrier pigments inhibit metal corrosion by extending the diffusion paths of water and ions to the metal surface so that metal corrosion resistance increases. Despite their excellent corrosion inhibition properties, active pigments, such as red lead and chromate, are toxic and thus have limited application due to environmental measure [10]. Therefore, it is necessary to develop pigments that are more environmental-friendly. Zinc phosphate is a coating pigment that is often used in metal coating due to its environmentally friendly nature [11].

The use of zinc phosphate as an anti-corrosion pigment is a promising method to improve corrosion resistance in iron and steel [12]. Several studies have shown that the combination of micro- and nano-sized zinc phosphate can have an active and inhibition properties which is quite effective in reducing the corrosion rate of metals [13]. There have been several studies on the micro/nano-sheet synthesis of zinc phosphate using zinc ions and different amines which are used to improve the relationship between the properties, structures, and functions of these materials [14]. In addition, the synthesis of layered zinc phosphate is also developed by utilizing different zinc ions and alkaline hydroxide ions as substitutes for amines [15]. Meanwhile, nano-sized zinc phosphate is used as an anti-corrosion coating material on carbon steel in 3.5% NaCl electrolyte at room temperature. The results of the study indicate that carbon steel coated with zinc phosphate has better corrosion resistance than carbon steel coated with zinc oxide [12].

When low carbon steel with galvanized coating is moved or transported, it will experience peeling or tearing [16]. Research on finding alternative coating materials has been carried out. For instance, an A36 low carbon steel coating made of 20% graphene oxide and 80% waterborne paint is found to give protection against corrosion when immersed in sea water (0.1 M NaCl). The Corrosion Penetration Rate (CPR) value indicates that A36 steel coated with graphene oxide and waterborne paint has lower CPR value compared to A36 steel without coating or with a galvanized coating. The CPR value of graphene oxide coating and waterborne paint does not exceed the standard value of 0.5 mm / yr) [17]. Due to its success, this coating method has been registered for a copyright [18].

A study has also been carried out to make a graphene oxide coating with material obtained from the synthesis of the carbon materials of zinc batteries with liquid and surfactant exfoliation methods. The results of UV-Vis spectrophotometer test show that there are three typical absorption peaks at wavelengths between 300-345 nm. It has been found that the combination of battery + H_2SO_4 + water coating, immersed in 0.1M NaCl solution, succeeded in making carbon-based batteries that can protect low carbon steel from corrosion [19]. The objective of this study is to make a coating mixture consisting of graphene oxide and galvanized which is able to coat low carbon steel and to improve its resistance to corrosion.

MATERIALS AND METHODS

A mixture of 15% graphene oxide (GO) (Fig. 1 a) and 85% galvanized (type ER-809 Zinc Rich Cold) (Fig. 1 b) is made in the form of a 0.25liter solution. Subsequently, GO and galvanized are mixed and stirred with a blender at level 1 speed for 30 minutes. GO and galvanized mixture is shown in Fig. 1 c. The material used is an A36 low carbon steel plate with a length of 15 cm, width of 15 cm, and thickness of 0.8 cm. The specimen is weighed to determine the initial weight (mo).

In the next stage, the A36 steel plate sample is coated by immersing/dipping it in a mixture of graphene oxide and galvanized with different immersion periods;30 seconds, 60 seconds, and 90 seconds. The scheme is shown in Fig. 2.

After coating and drying the sample, the dry corrosion test is then performed. The plate is heated in a furnace at 700°C with different holding time periods; 30 minutes, 1 hour, and 1.5 hours. When the A36 steel sample is cold, weighing (m) is performed. The calculation of the Corrosion Penetration Rate (CPR) uses the weight loss equation (equation 1) as follow:

$$CPR = \frac{KW}{ADT} \quad (1)$$

CPR is Corrosion Penetration Rate with a measurement unit of mile per year (mpy) or millimeter per year (mm/yr). D is density (gr/cm^3), T is time (hours), W is weight loss = mo - m (mg), mo is weight before corrosion (mg), and m is weight after corrosion (mg). K is constant and the measurement unit with a condition K = 534 (mpy); K = 87.6 mm/yr. A is surface area (cm^2). The safety standard for CPR value is less than 20 mpy (0.5 mm/yr).

RESULTS AND DISCUSSIONS

Characterization

Fig. 2 shows the XRD pattern of graphene oxide (GO). A Philips diffractometer with Cu Kα radiation (λ = 1.54060 Å) was used. The XRD pattern of graphene oxide shows a sharp diffraction peak (001) at 2θ = 11.58° corresponding to an interlayer d-spacing of 7.7 Å and the (100) diffraction peak at 2θ = 42.0° according to a d-spacing of 2.13 Å, which confirms the characteristic peaks of GO. Crystallite size of GO was calculated by Scherrer equation. It was found that the grain size of the samples was 18 nm.

FTIR of HGO confirmed the oxygen functional groups. A section of the IR spectrum confirmed the carbonyl functional group C=O at 1720 cm^{-1}, C=C 1620 cm^{-1} and epoxy functional group C-O 1060 cm^{-1}. The script on Fig. 3 deviated considering the high water content or O-H and H-O-H groups, which presented a peak at 3500–3300 cm^{-1}. The sample was difficult to fully dehydrate. Each synthesis created the distinguished GO which is why the results are slightly different Based on the literature, the FTIR signals are initiated to hydroxyl group (OH) 3400 cm^{-1}, epoxy (C-O) 1090 cm^{-1} and ketone (C=O) 1700 cm^{-1} [20]. Another group of scientists obtained the following vibration frequencies: hydroxyl group 3050–3800 cm^{-1}, carbonyl 1750–1850 cm^{-1}, carboxyl 1650–1750 cm^{-1}, C=C 1500–1600 cm^{-1} and ethers/epoxy 1000–1280 cm^{-1} [21,22]. Authors argue that peaks (~1730 cm^{-1} and ~1620 cm^{-1}) are not different

Fig.1 a) Graphene oxide, b) Galvanized and c) Mixture of GO and Galvanized sample.

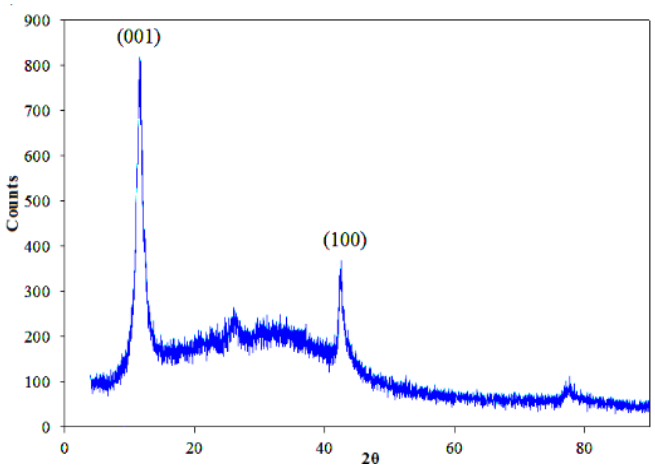


Fig. 2. XRD pattern of Graphene Oxide nanoparticle.

carbonyl/carboxyl groups but the doublet of keto-enol tautomers [23].

Spectrometer Test Results

The spectrometer test shows that A36 steel plate sample is classified as a low carbon steel. Low carbon steels are steels with a carbon (C) content less than 0.3%. An A36 steel plate has the average carbon content of 0.10609%.

CPR Calculation Results

CPR calculation results for A36 steel sample without coating are shown in Table 1. The CPR calculation results of A36 steel plate sample with galvanized coating are shown Table 2. Table 3 shows of the CPR calculation results for A36 steel sample with graphene oxide and galvanized coating.

The table shows that the lowest CPR value is obtained from the A36 steel sample which is tested for dry corrosion at a temperature of 700°C for 30 minutes, with a value of 0.0069 mm year. Even with the addition of heating time of up to 1.5 hours, despite the increase, the CPR value is still lower than the CPR value of the A36 steel sample which is coated with galvanized and even lower than the A36 steel sample which is not coated. Furthermore, the CPR value of the A36 steel sample without coating is soaring, exceeding the permitted standards. This indicates that A36 steel plates must be coated in order to prevent corrosion, especially in high temperature conditions. As a comparison, the ASTM steel coated with a composition of 20% graphene oxide

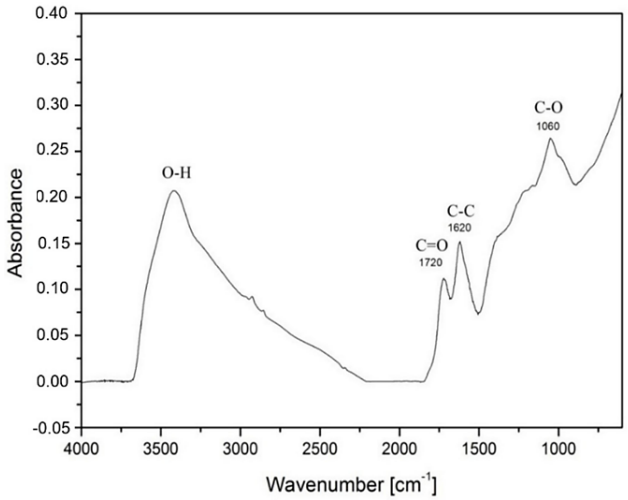


Fig. 3. FTIR spectrum of GO.

Table 1. CPR results of A36 steel sample without coating

No	Sample Name	Initial thickness without coating (t_o) (cm)	Thickness without coating + heating (t_{op}) (cm)	Initial mass without coating (m_o)(kg)	No coating mass + heating (t_{gp}) (m_{op})(kg)	CPR (mm/yr)		
						30 min	1 h	1.5 h
1.	A36O1	0.81	0.75	1.5	1.45	0.52	0.66	0.83
2.	A36O2	0.80	0.76	1.5	1.46	0.53	0.68	0.82
3.	A36O3	0.81	0.75	1.5	1.45	0.52	0.68	0.83
Average						0.523	0.67	0.827

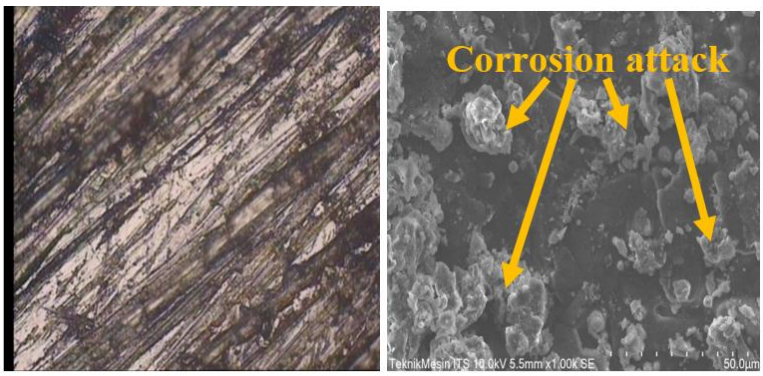
Table 2. CPR results of A36 steel sample with galvanized coating

No	Sample Name	Thickness after galvanized coating (t_g) (cm)	Thickness after galvanized coating + heating (t_{gp}) (cm)	Mass after galvanized coating (m_g) (kg)	Mass after galvanized coating + heating (m_{gp}) (kg)	CPR (mm/yr)		
						30 min	1 h	1.5 h
1.	G1A36	0.82	0.79	1.51	1.50	0.15	0.21	0.26
2.	G2A36	0.81	0.80	1.52	1.50	0.16	0.20	0.25
3.	G3A36	0.82	0.80	1.51	1.50	0.15	0.20	0.26
Average						0.153	0.203	0.257

Table 3. CPR results of A36 steel sample with graphene oxide and galvanized coating

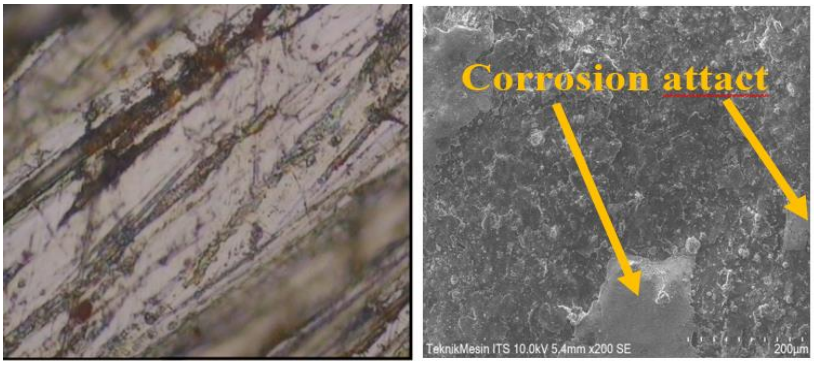
No	Sample Name	Thickness after galvanized +Graphene Oxide Coating (t_{go}) (cm)	Thickness after galvanized +Graphene Oxide Coating + heating (t_{gop}) (cm)	Mass after galvanized +Graphene Oxide Coating (m_{go}) (kg)	Mass after galvanized +Graphene Oxide Coating + heating (m_{gop}) (kg)	CPR (mm/yr)		
						30 min	1 h	1.5 h
1.	GO1A36	0.90	0.88	1.55	1.53	0.0070	0.060	0.057
2.	GO2A36	0.89	0.88	1.56	1.52	0.0069	0.058	0.057
3.	GO3A36	0.89	0.87	1.55	1.52	0.0069	0.061	0.056
Average						0.0069	0.00597	0.057

and 80% waterborne paint which is wet corroded by immersion in 0.1 M NaCl solution for 6 hours has a CPR value of 0.02 mm/year. Meanwhile, when dry corroded at a temperature of 500^0C for 72 hours, the sample reaches a CPR value of up to 0.07 mm/year [18]. Another study has shown that low carbon steel coating with graphite bars obtained from batteries which are processed into graphene oxide and added with 25ml H_2SO4 and 25 ml distilled water, followed with a wet corrosion procedure by immersion in 0.1 M NaCl solution for 6 hours, results in a CPR value of 3.9 10^{-4} mm / year [19]. It can be seen that graphene oxide solution protects low carbon steel from corrosion due to the functional groups of the oxides in graphene, namely hydroxyl, carbonyl, and epoxy



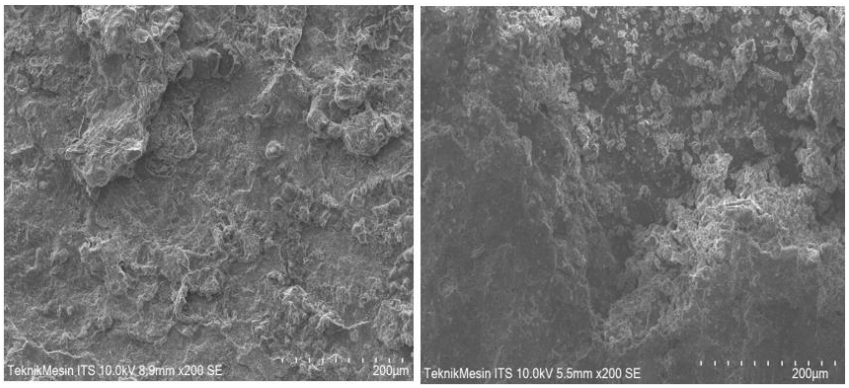
(a) (b)

Fig. 4. FESEM images of the micro-structure of A36 steel samples without coating; (a), before corrosion (using MO), and (b) after corrosion.



(a) (b)

Fig. 5. FESEM images of the micro-structure of A36 steel samples (galvanized coating); (a) before corrosion (using MO), and (b) after corrosion.



(a) (b)

Fig. 6. FESEM images of the micro-structure of A36 steel samples (galvanized and graphene oxide coating) (a) before corrosion (using SEM), and (b) after corrosion in a temperature of 700^{o}C for 1.5 hours.

groups, which are resistant to corrosion [24].

Analysis Results from Optical Microscope (OM) and Scanning Electron Microscope (SEM)

Micro-structure observations before and after the corrosion of A36 steel samples without coating, galvanized coating, and mixture of galvanized and graphene oxide coating are shown in Figs. 4, 5, and 6, respectively. It can be seen that the most significant corrosion occurs on A36 steel samples without coating. Meanwhile, the corrosion on A36 steel samples with galvanized and graphene oxide coating is relatively small.

CONCLUSIONS

There are several conclusions that can be drawn from this study. First, the mixture of 15% graphene oxide and 85% galvanized (type ER-809 Zinc Rich Cold) used as low carbon steel (A36 steel) coating with 60 second immersion period has the lowest CPR value. Furthermore, after dry corrosion test, which is done by heating in a furnace at 700°C with 30 minutes, 1 hour, and 1.5 hour holding periods, the CPR value of the A36 steel sample heated for 30 minutes is lower than the CPR value of the A36 steel sample without coating or with only galvanized coating. The CPR value of A36 steel sample with 5% graphene oxide and 85% galvanized (type ER-809 Zinc Rich Cold) coating does not exceed the standard value of 0.5 mm/yr.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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