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THE SYNTHESIS AND CHARACTERIZATION OF NANOMATERIAL ZNO-CUO PP AS AN ANTICORROSIVE MATERIAL ON THE SHIP HULL USING AN ELECTROCHEMICAL METHOD

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ABSTRACT

Corrosion on the hull of the ship which is an electrochemical process due to seawater which has very low resistivity. The mechanism of corrosion occurs because of the electrochemical process due to the flow of negative poles to the positive pole. Basically corrosion is the event of the release of electrons from metals (iron or steel) that are in an electrolyte solution such as sea water. Whereas positively charged atoms of metal (Fe+3) will react with hydroxyl (OH-) ions to form rust (ferric hydroxide [Fe(OH)3]). Similar studies in modifying Zn to have anti-corrosive properties have been carried out such as modifying Mn, Fe, Sn, and Ni metals. In this study modified Zn composite materials using Polypropylene waste material and CuO material. Polypropylene is an organic material, low conductivity, and cannot be ionized, ZnO as anti-corrosion particles, CuO as fouling, and PP as a matrix. The initial findings show that it can be made material that has a strong, durable, and environmentally friendly anti-corrosion properties.

Keywords: electrochemical method, ship hull, anti-corrosion, synthesis, characterization, nanomaterial

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1. INTRODUCTION

One of the problems with the ship is damage due to corrosion that occurs on the ship's plate (Arita, 1991). The resulting corrosion will produce a domino effect that results in damage to ship construction such as structural scaling, strength, flexibility, ship life, speed and even reduce the value of safety in goods and passengers (Garbatov, 1996; Melchers, 1999). Corrosion on the hull of the ship which is an electrochemical process due to seawater which has very low resistivity (Cui, 2017; Chrismianto et al., 2015). The mechanism of corrosion occurs because of the electrochemical process due to the flow of negative poles to the positive pole (Chen, 2017). Basically, corrosion is the event of the release of electrons from metals (iron or steel) that are in an electrolyte solution such as sea water. Whereas it is positively charged atoms of metal (Fe + 3), it will react with hydroxyl (OH-) ions to form rust (ferric hydroxide [Fe (OH) 3]). Based on the terms of construction on ships, the hull plate is the area that was first exposed to sea water. Some previous studies have extensively examined the hull area in being exposed with seawater environment and its strength and resistance behaviour. Zakki et al. (2018) evaluated the cone capsule as an alternative hull form for portable tsunami lifeboat to support evacuation system in the coastal regions and small islands. In examining the buckling strength behavior of submarine pressure hull, Windyandari et al. (2018) comparatively studied buckling strength between the swedge-stiffened and the ring-stiffened of the midget type submarine pressure hull, while Yudo et al. (2017) investigated ring stiffened submarine pressure hull. Prabowo et al. (2017) estimated damage behavior of double hull under ice-grounding scenario models.

In the ship hull, either the underwater or the upper area of the water is exposed to corrosion (Tanaka, 2014). The form of corrosion that occurs in the hull of the ship is evenly corrosion (Nan, 2008). Even corrosion is a type of corrosion where in this type of corrosion the corrosion rate that occurs on all metal surfaces or alloys exposed or exposed to the environment takes place at almost the same rate. Almost all metal surfaces reveal a corrosion process (Zhao, 2012; Nejad, 2016; Menan, 2010). The current solution to solving corrosion problems is to avoid the hull from corrosion, active methods (cathodic protection), and passively (painting on the ship). The cathodic protection method is a method that is often used for corrosion protection on the hull of the ship, but it is not taken very seriously so that the desired results are usually missed and inefficient. One method of cathodic protection is the sacrificial anodic protection method. The sacrificial anodic protection method (sacrificial anode) usually uses Cadmium (Cd) base material (Morrow, 2010). However, the use of this material is limited because this type of metal is classified as heavy metal and is not environmentally friendly. Therefore the need for an environmentally friendly material has good efficiency in dealing with corrosion. For example, previous studies in modifying Zn to have anti-corrosive properties have been carried out such as modifying Mn, Fe, Sn, and Ni metals. In this study modified Zn composite materials using Polypropylene waste material and CuO material. Polypropylene is an organic material, low conductivity, and cannot be ionized (El Jaouhari, 2017), ZnO as anti-corrosion particles, CuO as fouling, and PP as a matrix. The initial findings show that it can be made material that has a strong, durable, and environmentally friendly anti-corrosion properties. Accordingly, there is a need to make material that has strong anti-corrosion advantages, is durable, and is environmentally friendly.

2. RESEARCH PURPOSE

This research is expected to be an illustration and preliminary research of the solution to the problem of corrosion in the hull of the ship which results in a decrease in the age of the ship. The specific objectives of this study are

1. Modify the Zn-PP-CuO nanoparticle material and test the corrosive resistance of the material
2. Study of the composition of Zn-PP-CuO material to be an anti-corrosion material
3. Development of research and technology in overcoming anti-corrosion in the hull of the ship.

3. URGENCY OF RESEARCH

The structural age of the ship depends on the hull of the ship. The resulting corrosion will produce a domino effect that results in damage to ship construction such as structural scaling, strength, flexibility, ship life, speed and even reduce the value of safety in goods and passengers (Garbatov, 1996; Xu, 2000; Melchers, 1999). This study conducted a study of CuO, ZnO and PP nanocomposite materials from previous studies which are material that have anti-corrosive properties, are environmentally friendly, and have a longer durability.

4. WORK PROCEDURES

The synthesis of ZnO nanoparticles was carried out by the sol gel method with precursor Zn (CH3COO2) 2.2H2O as a source of Zn and isopropanol (IPA: (CH3) 2CHOH), monoethanolamine (MEA: HOCH2CH2NH2). Making ZnO nanoparticles by dissolving Zn Acetate into propanol and monoethanolamine solutions at room temperature with a concentration of 0.3M Zn Acetate with a 1: 1 molar ratio and then sterile for 1 hour. The result is a clear white solution. The next process is coating on CuO and PP substrates with a temperature of 500^{o}C.

5. TESTING AND CHARACTERIZATION

In making this prototype several tests were carried out including:

1. X-Ray Diffractometer (XRD) Testing
1. The crystal structure of ZnO was analyzed by XRD.
2. Scanning Electron Microscopy (SEM)
   SEM is used to analyze the morphology of ZnO thin films
3. Test the Voltmeter

The voltmeter is used to determine the percentage degradation of the corrosion rate.

5.1. Variables

The variables in this study refer to the research of El Jaouhari (2017), and Zhao (2016) which uses mass comparison composition, the next stage is anticorrosive testing by taking the resistance value which is then included in the reduction of the voltaic equation below, and the weight calculation method.

Corrosion Penetration Rate (CPR)

$$CPR = \frac{KW}{\rho At} \qquad \text{Eqn. 17.23}$$

CPR – corrosion penetration rate
(mils per year mpy where 1 mil = 0.0001 in, or mm/yr)
W – weight loss
t – time exposure
K – constant
A - exposed specimen area
ρ - density

Source: https://slideplayer.com/slide/9782215/

Equation 1. Corrosion Penetration Rate

5.2. Nanocomposite

Composite is a combination of 1 or 2 materials combined into one without producing new properties. In other words each material has its own properties (Subagio, 2015). Composite consists of filler as a base material and matrix as an adhesive. One example of composite material is a board which is the result of a blend of wood powder and glue. The purpose of making composites is to increase the quality of a material. Composites currently using nano-based materials called nanokompoit.

Nano materials when made as composites have the advantage of being more easily mixed, and improving the properties of the material. This technology is called nanocomposite. Nanocomposite is currently commonly used in manufacturing technology in industries such as materials on airbus A320 aircraft, and mild steel materials for weapons, energy storage (Darari, 2015), anti-radar materials, and other fields of application, so this nanokomposite research continues to be developed.

5.3. Zinc Oxide (ZnO)

ZnO is one of the interesting ingredients to be used as photocatalyst material. ZnO has high conductivity and transparency and its emission properties are close to UV light (Guanglong, 2007). ZnO is a group II-IV n-type semiconductor material with a band gap width of 3.2 eV at room temperature (Yaoming, 2010).

ZnO is a solid hexagon / amorphous powder that is white when cold, yellow when hot, bitter and does not smell. This amphoteric oxide is difficult to dissolve in alcohol / water, but dissolves in ammonium, acid or alkaline and non-toxic salts. ZnO is used as a reagent, neutralizing agent, skin protective agent and photocatalyst (Arsyad, 2001).

ZnO is a crystalline ionic compound consisting of cations and anions which are arranged periodically and periodically. Regular and repetitive arrangement patterns of crystal lattice ions with certain structural shapes. ZnO has a crystal lattice with a wurtzit structure (Effendy, 2004).

5.4. Corrosion

Corrosion is a chemical reaction or an electrochemical reaction of an environment with a material, usually metal, and can lead to deterioration of metals (Effendy, 2004). The purpose of the environment in this context is anything that experiences direct contact with a material. Corrosion can be classified into various types according to their causes and processes (Garbatov, 1996; Xu, 2000; Melchers, 1999). such as uniform corrosion: corrosion that occurs due to chemical reactions and humid air (citation), Galvanized Corrosion is the contact of two different types of metals in the electrolyte system so that metals are more anodic or more reactive will corrode (Chen, 2017).

At present one of the ways to overcome corrosion problems is by selecting materials that do not have corrosive properties such as Au, Pt, Zn and other materials that have low voltaic number values (Melchers, 1999). That is usually matched on the corrosion rate table indicator (Table 1).

Table 1. Indicator of the compatibility of corrosion of metal alloys based on the corrosion rate

Relative Corrosion Resistance	mils/yr	millimeters/yr	micron/yr	nanometers/h	picometer/s
Outstanding	< 1	< 0,02	< 25	< 2	< 1
Excellent	1-5	0,02-0,1	25-100	2-10	1-5
Good	5-20	0,1-0,5	100-500	10-50	20-50
Fair	20-50	0,5-1	500-1000	50-150	20-50
Poor	50-200	1-5	1000-5000	150-500	50-200
Unacceptable	200+	5+	5000+	500+	200+

Source : William (2010)

The second method, which is cathodic protection, is utilizing the principle of galvanized corrosion where if there are two metals in contact, the more reactive metals will experience corrosion, while the less reactive metals will be protected (Nejad, 2016). The third method is by coating / coating which is classified as a protective function preventing the material from being oxidized (Nan, 2008)

5.5. Mechanism of Corrosion

Electrochemical corrosion phenomenon can be illustrated by the reaction between metal ions and water molecules. At first there will be hydrolysis which will result in increased acidity (Trethewey & Chamberlain, 1991). This can be explained by the following equation:

$$M^{+} + H_2O \rightarrow MOH + H^{+}$$

This equation illustrates the general hydrolysis reaction, where in actual electrolytes there will be an important role for chloride but it will be complicated to decipher. The low tendency of chloride to combine with hydrogen ions in water pushes down the pH of electrolyte solutions (Trethewey & Chamberlain, 1991).

The reaction equation above is iron ions and water molecules, as follows

$$Fe^{2+} + H_2O \rightarrow Fe(OH)^{+} + H+$$

Then this reaction can continue with the oxidation reaction by the presence of oxygen to iron (II), so that it will form iron ions. It was written in the reaction as follows

$$Fe(OH)^{+} + 1/2O + 2H \rightarrow 2\ Fe(OH)_2+ + H_2O$$

Henceforth it can be described the reaction of complex ions so that the main corrosion results are formed namely magnetite and rust, successively expressed the formula Fe2O4 and Fe (OH), with the reaction equation

$$2Fe(OH)_2+ + Fe_2+ + 2H_2O \rightarrow Fe_3O_4 + 6H^{+}$$

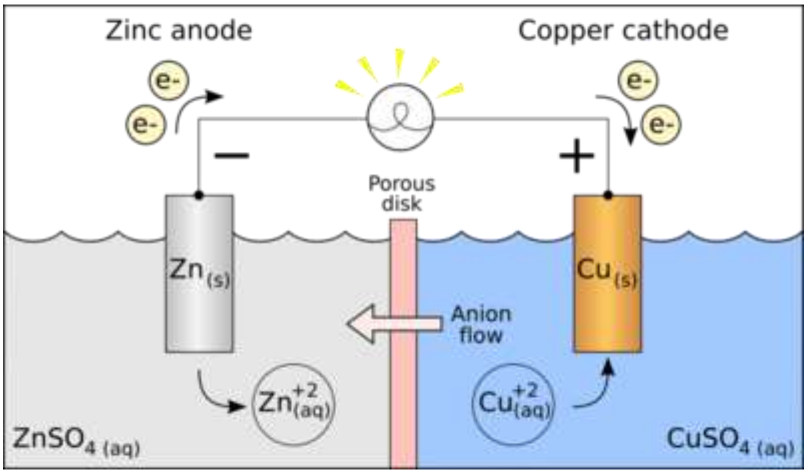
$$Fe(OH)_2 + OH^{-} \rightarrow FeO(OH) + H_2O$$

The electrochemical corrosion rate is the average speed of change in thickness or weight of the metal that is corrosion against the watu through an electrochemical process (Trethewey & Chamberlain, 1991).

5.6. Anti-Corrosion Mechanism with Sacrificial Anode

There are two types of cathodic protection, namely the sacrificial anode method and the impressed current method. Sacrificial anodes are relatively inexpensive, easy to install when compared to the current method of competition. Another advantage is that there is no need for expensive electrical equipment and there is no possibility of misdirection in the flow of current (Trethewey & Chamberlain, 1991).

The workings of cathodic protection with sacrificial anodes are using the concept of wet corrosion cells such as Figure 1. The general rule of wet corrosion cells is that in a cell, anodize is corroded, while the one that is not corroded is the cathode. The anodes connected to the structure with the aim of effective protection against corrosion in this way are called sacrificial anodes. We can use knowledge about galvanic series to select a material that will become an anode. Sacrificial anodes commonly used in coastal environments include zinc and aluminum (Trethewey & Chamberlain, 1991; Sulaiman et al., 2018).



Source: https://en.wikipedia.org/wiki/Galvanic_cell

Figure 1 Simple corrosion cell

The protection that zinc will provide will be extraordinary if the metal can be dissolved at a more or less constant rate. Pure zinc available on the market, corroded in seawater while forming a layer of water-resistant skin which greatly limits the output of its current. Among impurities are iron, copper and lead with the most damaging effect on the anode being iron, and its solubility in zinc is so low (Ciu, 2017).

5.7. ZnO As Anti-Corrosion Particles

Nanotechnology research is currently growing rapidly, one of which is nanocomposite. Nanocomposite is a combination of two or more types of material, without changing the properties and characteristics of the material. One of the nanocomposite studies (Subagio, 2013). Various nanocomposite studies for corrosion such as those conducted by Ciu (2017) carried out nanocomposite tests for the 3100 TEU Container can add up to 0.25 years of age. Corrosion test of TiO / CaCO3 (Andi, 2013), and polyetylen composites (El Jaouhari, 2017). Chunyan Meng (2014) reported that Zn material modified with AL-Mg could extend the life of the metal so it would not be corroded and increase the mechanical value of the material. Similar studies in modifying Zn to have anti-corrosive properties have been carried out such as modifying Mn, Fe, Sn, and Ni metals. Modifying Zn composite materials is by using polypropylene waste material and CuO material. Polypropylene is an organic material, low conductivity, and cannot be ionized (El Jaouhari, 2017), ZnO as anti-corrosion particles, CuO as fouling, and PP as a matrix. The method used is the electrochemical method, the corrosion rate can be known through current changes per unit cross-sectional area of the specimen so that the current density value is obtained. The current density value is substituted through the corrosion rate equation, then the value of the corrosion rate can be obtained then the time unity.

6. CONCLUSION

Corrosion on the hull of the ship which is an electrochemical process due to seawater which has very low resistivity. The mechanism of corrosion occurs because of the electrochemical process due to the flow of negative poles to the positive pole. Basically corrosion is the event of the release of electrons from metals (iron or steel) that are in an electrolyte solution such as sea water. Whereas positively charged atoms of metal (Fe+3) will react with hydroxyl (OH-) ions to form rust (ferric hydroxide [Fe(OH)3]). Similar studies in modifying Zn to have anti-corrosive properties have been carried out such as modifying Mn, Fe, Sn, and Ni metals. In this study modified Zn composite materials using Polypropylene waste material and CuO material. Polypropylene is an organic material, low conductivity, and cannot be ionized, ZnO as anti-corrosion particles, CuO as fouling, and PP as a matrix. The initial findings show that it can be made material that has a strong, durable, and environmentally friendly anti-corrosion properties.

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