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PANi/ZrO_2-composite coating for corrosion protection in 3.5 M NaCl solution

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Abstract. This study was designed to investigate PANi/ZrO_2 as an anti-corrosion coating material. An extraction of Zirconia (ZrO_2) from natural zircon sand of Kereng Pangi has been conducted by means hydrothermal process and alkali fusion. In this composite system consist of Polyaniline (PANi) as a matrix and ZrO_2 as a filler material for an anti-corrosion coating. PANi/ZrO_2 composites were synthesized by an in-situ polymerization method. The structure of synthesized ZrO_2 was characterized using X-Ray Diffraction (XRD). The samples for corrosion testing were original steel (SS), paint coated steel (PS), paint/ZrO_2 coated steel (ZS), paint/PANi/ZrO_2 coated steel (PZ) with dimensions of 2 cm x 2 cm. Corrosion rate was tested in 3.5M NaCl using polarization method. XRD result showed that the structure of obtained ZrO_2 was amorphous. The corrosion rates for the four samples SS, PS, ZS, and PZ were $2{,}36\times10^{-2}$, $1{,}3\times10^{-5}$, $1{,}35\times10^{-7}$, and $5{,}97\times10^{-7}$mpy, respectively. The result of corrosion rate showed that the lowest corrosion rate was steel coated with ZrO_2 (ZS). It was 1,35 x 10^{-7}mpy. The result indicated that the zirconia coating is a prospective material for anti-corrosion.

1. Introduction

Zirconia, ZrO_2 is refractory ceramic that has low heat conductivity, high hardness and density, and good polymorphs [1]. Zirconia is a mineral that is rarely found in nature in its form as a ZrO_2 crystal. It is found naturally as ZrO_2 crystal in baddeleyite minerals, and has a monoclinic crystal structure. It is rarely found with zircons because it forms on rocks with unsaturated silicates. If the silica in the rock is saturated or oversaturated, what is found in the rock is no longer a zirconia crystal but zircon crystals. Zircon ($ZrSiO_4$) crystal is the principal mineral for producing zirconia. Zircon is found everywhere in the earth's crust with a content of around 25 %. [2]. It is a common element of most sand so it usually found in sediment deposits. Many zircon minerals are found in nature as zircon sand. This sand mining, legally and illegally, mostly found in the Kereng Pangi area (Central Kalimantan).

Various techniques for zirconia extraction from zircon have been proposed in the literature [3], including extraction with basic oxides, chlorination reductive smelting and alkali digestion. The present work has processed zircon (Puya sand) by alkali fusion. The principle of the alkali fusion method is to disassemble chemical bonds in the material by using alkali compounds such as KOH, NaOH, and Na_2CO_3 [4,5].

Corrosion is a material degradation due to electrochemical reaction with the surrounding environment where electron transfer process occurs from metal to environment. Corrosion is one of the problems that often occur in everyday life, especially on materials made of metal. Corrosion cannot be eliminated at all but can only be slowed down the process.

There has been a lot of research that investigated the corrosion protection method, including with cathodic protection, the application of a thick coat of paint, and the application of anti-corrosion paint that can inhibit corrosion rate [1]. The application of this anti-corrosion paint usually contains pigments which can inhibit corrosion rate, one of them by using conductive polymer. Basically, polymer is an insulating material but can be used as conductive material if it is doped with a strong acid.

Polyaniline (PANi) is one of the most conductive polymers used as a protection against corrosion due to some advantages compared to other conductive polymers. The advantage of using PANi is that its chemical and electrochemical polymerization process is simple, easy to be doped and dedoped by treatment using strong acid [1,4]. But its melting point is low, so it needs to be combined with heat-resistant material and become a composite with that material so that the composite will not easily cracked.

In this research, zirconia was composited with polyaniline polymer by an in-situ polymerization method. The PANi/ZrO_2 composite was coated on stainless steel 304. This work focuses on the effect of the PANi/ZrO_2 composite coating for corrosion protection in the 3,5M sodium chloride solution.

2. Experimental

2.1. Material preparation

In the present work, zirconia was obtained from the natural zircon sand from Kereng Pangi, Central Kalimantan. Before being processed, magnetic elements are separated from zircon sand using a magnet. The sand is then milled using wet milling in alcohol, after that leached with chloride acid (HCl). After the leaching process, the sand is extracted by hydrothermal method using 7M NaOH solutions at 250 °C. The extracted zircon powder was then processed into amorphous zirconia (*a*-ZrO_2) powder using NaOH solution with alkali fusion method and then continued with co-precipitation method using NH_4OH solution. The zirconia powder and polyaniline (PANi) are then processed into composites. Polyaniline solution was prepared for the process using ammonium peroxy disulfate, aniline and dodecyl benzene sulfonic acid. Then the in-situ polymerization of the composite process was carried out for 8 hours.

Stainless steel used in this research is SS 304. Before coated, it smoothed first by using sandpaper numbered mesh 80 - 1000. The paint used in this research is Agatha Paint Ship. The paint is then mixed with ZrO_2 and the composite PANi/ZrO_2 separately. The steel coating process is carried out using spraying techniques on all steel surfaces but previously the steel is coated with epoxy to improve the quality of coating adhesion.

2.2. Characterization

Characterization of samples in this study were carried out using *X-Ray Diffractometer* (XRD) to determine the phase in the sample, *Fourier Transform Infrared* (FTIR) to find out the bond or functional group formed through the process of synthesis PANi/ZrO_2 composite, and polarization test to measure the corrosion rate.

3. Results and discussion

3.1. X-Ray Diffraction spectroscopy

Natural zircon sand was extracted by several processing stages: wet milling, leaching, and hydrothermal processes. Each process generates a material with a different phase. From these processes, we obtained zircon ($ZrSiO_4$) with tetrahedral structure [6]. The process of producing amorphous zirconia (ZrO_2) powder from the extracted zircon powder involves the alkaline fusion and co-precipitation methods.

The chemical reaction to the alkaline fusion process with NaOH as a fluxing agent with various molar variations is: [7]

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O$$

$$ZrSiO_4 + 6NaOH \rightarrow Na_2ZrO_3 + Na_4SiO_4 + 3H_2O$$

$$ZrSiO_4 + 2NaOH \rightarrow Na_2ZrSiO_5 + H_2O$$

The X-Ray diffraction pattern of the zirconia powder shows that it has an amorphous structure as shown in figure 1.

3.2. FTIR spectroscopy

The purpose of Fourier Transform Infrared (FTIR) spectroscopy characterization is to find out the functional groups of zirconia (ZrO_2), polyaniline (PANi), and PANi/ZrO_2 composites. The result of FTIR spectroscopy characterization is shown by figure 2.

Table 1. Functional group absorption of the sampels

Wavenumber (cm^{-1})	Functionality	ZrO_2	PANi	PANi/ZrO_2
400-500	Zr-O Bending Vibration [8]	420.5	-	443.64
600-900	C-H Bending	-	665.08	663.53
1250-1360	Aromatic C-N Stretching	-	1284.46	1338.64
1400-1500	N-H Stretching	-	1442.81	1485.24
1430-1600	C=C Aromatic rings	-	1557.23	1535.39

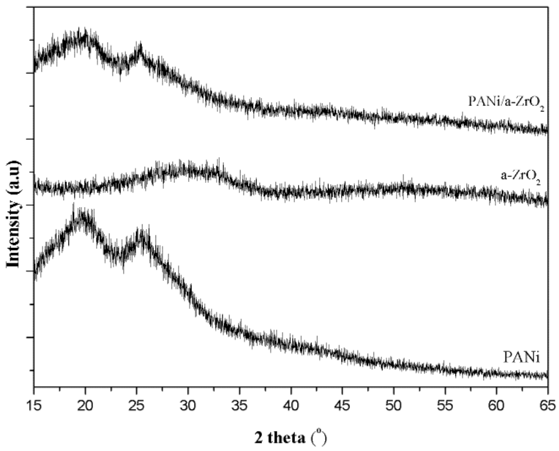

Figure 1. X-ray diffraction patterns of the composites

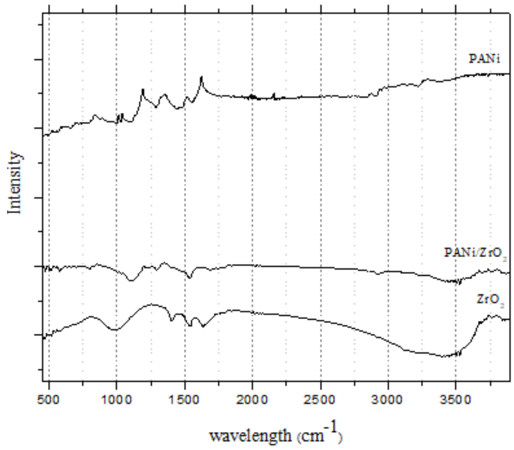

Figure 2. FTIR spectra of the samples

There are several wave absorption points, which represent the type of bond or a functional group formed. The results are then analyzed by using reference wave numbers to find out what functional groups are present in the material under test. Table 1 discusses the type of bond or functional group read from figure 2.

The absorption pattern of the PANi-ZrO_2 composites in figure 2 generally tends to resemble the PANi absorption pattern. It shows that the addition of ZrO_2 in the composite PANI-ZrO_2 synthesis process does not alter the matrix structure of polyaniline but will bring up a new functional group. The existence of absorption pattern in the wavelength range of 400-450 cm^{-1} shows the absorption pattern of functional group Zr-O that is characteristic of ZrO_2.

3.3. Corrosion performance test

In this work corrosion rate was tested by the polarization technique with a NaCl 3,5M electrolyte solution was used. The result of the polarization test is a Tafel diagram, which can be explained in figure 3. The Tafel diagrams give the value of corrosion current (I_{Corr}) and corrosion potential (V_{corr}) of the tested materials. The value of the corrosion rate is obtained from the meeting point between the slope I_{Corr} and V_{corr} in the Tafel diagrams.

The polarization test gives the corrosion rate of the stainless steels in mpy as shown in table 2. The highest corrosion rate is steel without coating (SS). The steel is exposed directly to the electrolyte solution so that nothing is resistant to negative ions in the 3.5 M NaCl solution resulting in an easily corroded steel. The PS sample shows protection against negative ions. The corrosion rate in this PS sample is as small as 1.3×10^{-5} mpy since the paint is a high-performance anti-corrosion paint for ships. The steel coated with PANi/ZrO_2 composite has a corrosion rate value in-between, i.e. lower than the the paint-coated steel but higher than the ZrO_2 coated steel.

4. Summary

In this work, the extraction of zirconia from the natural zircon sand using alkali fusion method has been performed and the extracted zirconia was used as corrosion inhibitor component with stainless

Table 2. Corrosion rate of the samples

Samples	Corrosion rate (mpy)
Stainless steel (SS)	2.36×10^{-2}
Stainless Steel +paint (PS)	1.30×10^{-5}
Stainless Steel+paint+ZrO_2(ZS)	1.35×10^{-7}
Stainless Steel+paint+PANi/ZrO_2 (PZ)	5.97×10^{-7}

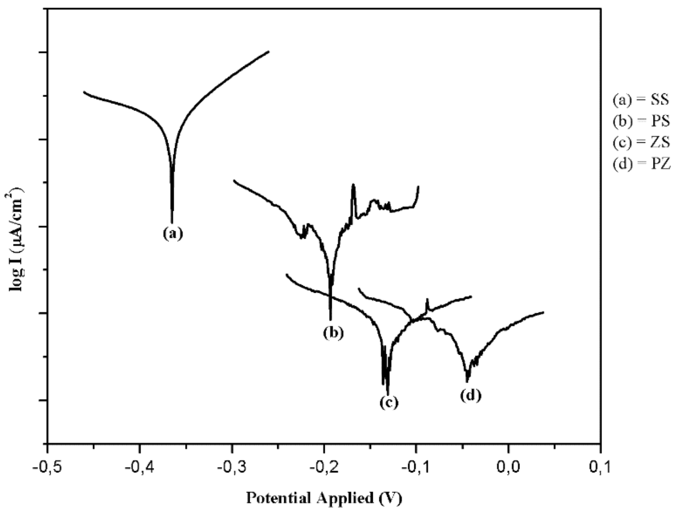

Figure 3. Tafel diagram of the samples

steel as the tested metal. The corrosion testing showed that the lowest corrosion rate was steel coated with ZrO_2 (ZS), i.e., as low as 1.35×10^{-7} mpy. The result indicated that zirconia coating is a prospective material for anti-corrosion.

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