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Magnetite thin film on mild steel formed by hydrothermal electrolysis for corrosion prevention

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HIGHLIGHTS

- Magnetite was formed dominantly on the surface of mild steel with black color.
- The growth rate of magnetite film increased with increasing temperature and reaction time.
- The magnetite films formed on the mild steel surface could prevent or minimize the corrosion on its surface.

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ABSTRACT

Magnetite film was successfully prepared on the mild steel surface in alkaline environment by hydrothermal electrolysis treatment. The principle of hydrothermal electrolysis is applying current directly to electrolyte solution at hydrothermal conditions. The anodizing of mild steel was conducted at temperatures of 100–200 °C and applied current densities of 0.1–0.4 A/cm^2 for 5–60 min reaction time with sodium hydroxide (NaOH) as an electrolyte solution (5–15%). Magnetite film on the mild steel surface was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and cyclic voltammetry. The patterns of XRD showed that magnetite was formed dominantly in the surface of mild steel with black color. Cyclic voltammetry analysis showed that the magnetite films produced on the mild steel surface could prevent or minimize the corrosion on its surface.

1. Introduction

Mild steel is the most common steel used. Many of the objects created from steel are made of mild steel, including automobile chassis, motorcycle frames, and most cookware. Mild steel is weldable, very hard, and very durable. However, it will be rust when exposed to neutral pH water, saltwater or high humidity air. In order to prevent rust from damaging it, there are numerous methods and many of them involve a barrier layer between the steel and the environment. This barrier layer can be a sacrificial coating, such as zinc or aluminum, or an organic coating, such as paints, waxes or oils, or a barrier oxide [1,2].

It is well known that magnetite (Fe_3O_4), a ferromagnetic ore compound, is one form of iron oxides like hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and wustite (FeO). Magnetite is also the oldest magnetic material known to mankind. It presents the most interesting properties because of the presence of iron cations in two valence states, Fe^{2+} and Fe^{3+}, in the inverse spinel structure [3]. Due to its interesting magnetic properties, Fe_3O_4 has important applications in pigment, recording materials [4], photocatalysis [5], ferrofluid technology [6] and magnetic refrigeration [7]. Recently, magnetite in thin film form has been attracting extensive research interest due to its application in modern magnetic devices [8–14]. Therefore, the preparation of Fe_3O_4 thin films has attracted much attention.

In this work, the blackening method will be carried out by hydrothermal electrolysis to form a passive oxide film, usually black magnetite, on the surface of carbon steel. This oxide coating has many advantages such as a strong adhesion between substrate and film, a good lubrication and a strong corrosion resistance. Farrell [15] reported that hot alkaline nitrate black oxide was originally developed in Germany as a two-bath system during the early 1900s. Next, the modern single bath oxidizing solutions became commercially prevalent during the later 1930s.

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Modern hot black oxidizing solutions are proprietary blends of sodium hydroxide, sodium nitrate, sodium nitrite, wetting agents, and unique rectifiers supplied as powdered compositions or ready-to-use liquid formulations. This process consists of five steps: (1) hot alkaline soak clean to remove grease and oils, (2) overflowing cold water rinse, (3) blackening, (4) overflowing cold water rinse, (5) final seal with a water displacing oil, a wax, an acrylic, or a soluble oil. This process is simple, however, the chemical agent such as nitrate is considered to be a hazardous substance that can cause cancer for human body [16,17]. Therefore, the development of environmental-friendly blackening processes is still of considerable attractive to industries.

At hydrothermal conditions, the oxidation of iron is accomplished by the reduction of hydrogen ions supplied by the hot water [18]. The magnetite film is thus formed directly.

$$Fe + H_2O \rightarrow Fe_3O_4 + H_2 \qquad (1)$$

The formation of a magnetite film, although highly desirable, is itself a form of corrosion. This view of the corrosion process is more complicated than above showed chemical reaction and include physico-chemical reactions which probably includes secondary reactions. Under adverse conditions, such as the pH is either too high or too low, the coarse magnetite film may form in the water as well as on steel surfaces. This magnetite film is less than ideal and tends not to be stable film. The use of sodium hydroxide as a solution will promote the soluble sodium hypoferrite. This reaction can remove the protective magnetite film by the following reactions:

$$NaOH + Fe_3O_4 \rightarrow NaFeO_2 + Na_2FeO_2 + H_2O \qquad (2)$$

Next, sodium hydroxide can then react with freshly exposed base metal to yield sodium ferroate and atomic hydrogen.

$$Fe + NaOH \rightarrow Na_2FeO_2 + H \qquad (3)$$

Several literatures have reported that hydrothermal method has been becoming one of the most important wet-chemical routes for synthesizing nanostructured materials [19–26]. Hydrothermal method is based on the use of water as solvent at temperatures between 100 and 374 °C and under pressure high enough to maintain the liquid state and lead to increase the solubility of a solid and to speed up reactions between solids. Zhu et al. [20] developed a hydrothermal method for growing magnetite coating on the surface of carbon steel in $N_2H_4{\cdot}H_2O$–$FeSO_4$–NaOH solution at 150 °C. They have successfully prepared Fe_3O_4 thin film on the surface of steel. But this method has a weakness. This method used hydrazine hydrate as the mineralizer which is toxic for human being and cause long-term harm to the environment as documented in MSDS (material safety data sheet). Chen et al. [21] has also developed a 'green' hydrothermal process for preparing Fe_3O_4 film on bare Fe foil. They used $FeSO_4.7H_2O$ as the iron source and H_2O_2 as the oxidant which is harmless and environmentally friendly. They have successfully formed the octadecahedron morphology that was rare but they still didn't study about the effect of temperature and pressure to the formation of the magnetite film. Recently, Whalen et al. [22] showed a simple practical approach for the formation of acmite ($NaFeSi_2O_6$) coatings with a uniform, passivating coverage on steel at substantially mild reaction conditions. Acmite films were formed on steel via solvothermal reaction of silica, sodium hydroxide, and 1,4-butanediol in an autoclave under autogenous pressure at 240 °C. However, the long reaction time was needed (72 h) to create coverage of the steel substrate with acmite. Freire et al. [25] conducted experiments for iron oxide thin layers formation on mild steel substrates in alkaline media by the application of different anodic potentials. Surface analysis revealed the existence of a duplex structure in the passive layer: an inner layer rich in Fe^{2+} oxides whose thickness depends on the potential, and an outer layer richer in Fe^{3+} hydroxides. They concluded that the cathodic prevention can be applied to modify the structure of the passive film and make cathodic protection more efficient. Ayman et al. [26] suggested that the magnetite films assembled on the iron surface can protect the iron from corrosion efficiently. Again, the long reaction time was needed.

In order to improve the rate of the blackening process, the electrochemical process was employed [1,2,27–32]. Bacsa et al. [29] introduced the hydrothermal–electrochemical technique to synthesis barium titanate ($BaTiO_3$) at temperatures 80–200 °C with titanium as an electrode and barium hydroxide ($Ba(OH)_2$) as an electrolyte solution. They reported that the films of cubic $BaTiO_3$ could be produced in the electrochemical process by the anodization of a titanium substrate in barium hydroxide solution. They explained that after the first layer of $BaTiO_3$ is formed, the growth continues because of the possibility of the dissolution of $BaTiO_3$ during the process. Then, the dissolution of $BaTiO_3$ may expose fresh metal surface to the electrolyte and the reaction may continue through the pores formed. Kajiyoshi et al. [30] also succeed to synthesis strontium titanate ($SrTiO_3$) by using hydrothermal–electrochemical technique. The thin films of strontium titanate could grow on titanium electrodes up to ca. 2 μm in thickness. Next, Burleigh et al. [1,2] demonstrated the possibility to electrochemically grow an adherent blue-black magnetite layer, a light brown oxide, or a semiadherent dichroic magnetite layer on many different types of steel in either KOH or NaOH solutions. The adherent, blue black magnetite layer that provide corrosion protection can be grown several micrometers thick on some carbon steels by selecting a narrow range of temperature, voltage and electrode spacing. Klimas et al. [28] reported the formation of anodic film on the surface of the same type of stainless steel by direct current anodizing in electrolyte that comprised glycerol and NH_4F with and without H_2O at elevated temperatures. The formation of anodic films are composed of both amorphous and crystalline species whose composition and contents depend on the anodizing conditions and the content of H_2O in solution. However, the long reaction time was needed to obtain the desirable products so that the energy consumption becomes high.

Here, as described above, hydrothermal electrolysis would be utilized to prepare magnetite film. In this system, water would be conditioned at temperatures ranging between 100 and 374 °C under high enough pressure to maintain water in the liquid state. At these conditions, dielectric constant, which can be changed by temperature, is the most important factor when using water as an reaction solvent; it decreases from 78 (at room temperature) to 34 (at 200 °C). Therefore, the reaction rate, equilibrium, and solubility of metal oxides were also could be controlled [33]. The effect of experimental parameters, such as current, NaOH concentration, reaction time, and temperature, on the formation of oxide film are investigated. The protective behavior against corrosion on carbon steel is evaluated using cyclic voltammetry, linear polarization and electrochemical impedance spectroscopy. This method is not often performed owing to the severe reaction conditions. Some interesting reaction behavior different to the general electrochemical reaction under ambient temperature and pressure has been confirmed for hydrothermal electrolysis [34,35]. The main advantages of this technique over the conventional hydrothermal method are improved purity of the products, lower reaction temperature and higher film growth rates [31,32]. This suggests that the method has some potential as a novel phenomenon and is different from the conventional reaction.