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Corrosion behavior of GA-TiO_2-Ag thin film in 3.5% NaCl solution

GA-TiO_2-Ag ince filminin %3,5 NaCl çözeltisindeki korozyon davranışı

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ABSTRACT

In this study, the photo-corrosion properties of undoped TiO_2, Ag/TiO_2, and graphene aerogel-doped Ag/TiO_2 thin films prepared by the dip coating method were investigated in a 3.5% NaCl environment. In a 3.5% NaCl solution, Ag-doped TiO_2 thin film showed better photo-corrosion behavior than the base and pure TiO_2 thin film. It was determined that the graphene aerogel layer coated on the Ag-TiO_2 thin film increased the photo corrosion resistance of the Ag-doped film and showed quite superior strength.

Keywords: TiO_2 thin film, sol-gel preparation, photo-corrosion, 3.5% NaCl solution, graphene aerogel.

ÖZ

Bu çalışmada, daldırma kaplama yöntemi ile hazırlanan saf, Ag ve grafen aerojel katkılı TiO_2 nanoyapılı ince filmlerin %3,5 NaCl ortamında foto-korozyon özellikleri incelenmiştir. %3,5 NaCl çözeltisinde, Ag katkılı TiO_2 ince filmi, esas ve saf TiO_2 ince filminden daha iyi foto-korozyon davranışı göstermiştir. Ag-TiO_2 ince filmi üzerine kaplanan grafen aerojel tabakasının, Ag katkılı filmin foto-korozyon direncini artırdığı ve oldukça üstün bir mukavemet gösterdiği belirlenmiştir.

Anahtar Kelimeler: TiO_2 ince film, sol-jel hazırlama, foto-korozyon, %3,5 NaCl çözeltisi, grafen aerojel.

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Introduction

In recent years, studies have been carried out on the formation of various solid-phase materials by using transition metal oxides with a wide variety of chemical and physical properties due to their use in more than one technological process (Sidelev et al., 2016; Lv et al., 2019). Today, there are many technologies for forming various thin films based on binary/ternary compounds, layered systems, and nanostructured films (Sagu et al., 2018; Zubar et al., 2018). The most important reason for using thin films is that they show promise in microelectronic applications for photocatalysis, protective coatings, magnetic sensors, and solar energy (Abbasi et al., 2018; Higgins et al., 2018). Titanium dioxide (TiO_2) is the most promising material to have the chemical resistance and excellent optical properties required for coatings and composite materials (Manurung et al., 2013; Yao et al., 2013). TiO_2 is a valuable raw material used in composite polymeric materials, the dye industry, production of dielectric ceramics, and ceramic films (Tian & Tatsuma, 2005; Kawakami et al., 2018). The TiO_2 layer has chemical stability, which provides corrosion protection even in very thin layers. The hardness of the oxide film improves temperature resistance and wear (Kania et al., 2020). In addition, TiO_2-based thin films are accepted as coating materials for structural materials exposed to irradiation by ions and electrons, for aggressive environments, and for stainless steel materials (Shi et al., 2010; Varnagiris et al., 2017). Therefore, TiO_2 thin films can be widely used in modern materials science due to their modification possibilities and superior properties (Zhao et al., 2011; Chauhan et al., 2012). Today, methods such as the hydrothermal method (Hosono et al., 2004), chemical deposition (CVD) (Al-Kandari et al., 2015), sol-gel (Sabzi & Anijdan, 2019), and micro-arc oxidation (MAO) (Wan et al., 2007) are used to produce TiO_2-based thin films. Sol-gel process enables the production of thin films with thermal/mechanical resistance, thickness/porosity control, high purity, chemical resistance (Reddy et al., 2001). The viscosity of the starting solution, the density, the number of dips, the concentration of oxides, and the drying temperature affect the sol-gel storage parameters, particle shape, particle size, and degree of oxidation affect the properties of the powder (Yu et al., 2000).

In many cases, when the material comes into contact with a solution or various electrolytes, corrosion processes occur, with combined electrochemical reactions occurring, resulting in oxidation and degradation of the structure (Curkovic et al., 2013). The use of thin nanostructured films with high dislocation defects causes a decrease in the oxygen rate transferred to the surface layers and reduces the corrosion rate (Liu et al., 2010). Fu et al. (2014) showed that the application of Ag-containing TiO_2 films on the TiNi alloy with surface roughness increased the surface hydrophilicity of the Ag additive by reducing the contact angle of the samples.

Although silver (Ag) has long been reported as antibacterial and antimicrobial material, its film integrity and structure, which are important for corrosion resistance and biomedical applications, have rarely been studied. Therefore, in this study, the effectiveness of graphene aerogel supported Ag-doped TiO_2 thin films on corrosion resistance was investigated.

Methods

Materials

Titanium (IV) isopropoxide (TTIP), Absolute ethanol (C_2H_5OH, 99.8%), Graphite powders, Sodium Nitrate ($NaNO_3$), Potassium Permanganate ($KMNO_4$), Hydrogen peroxide, (30%), silver nitrate $Ag(NO_3)$, nickel nitrate $Ni(NO_3)_2.6H_2O$, 3-Triethoxysilylpropylamine (APTES), Acetic acid (CH_3CO_2H), Nitric acid (HNO_3), Sodium chloride (NaCl) were provided from Sigma Aldrich. Sulfuric acid (H_2SO_4) was provided by Merck.

Synthesis of Graphene Oxide

Graphene oxide was synthesized according to the Hummers method. Graphite powders (3 g) and sodium nitrate (1.5 g) were mixed in sulfuric acid (69 mL). Potassium permanganate (9 g) was added slowly to the mixture. The mixture was heated at 35°C and stirred (30 min) by adding ionized water (138 mL). The mixture, kept at 98°C for 15 minutes, was cooled in a water bath (10 min). Then, ionized water (480 mL) was added, and GO was obtained by dropping H_2O_2 (30%). The solution was filtered and dried at 60°C.

Synthesis of Graphene Aerogel

1.25 g of GO was sonicated in a mixture of 100 ml of water and 100 ml of alcohol for approximately 1 hour. Then the mixture was transferred to the autoclave and kept at 180˚C for 24 hours. The solution was filtered and dried at 60˚C.

Synthesis of TiO_2 Thin Film

4.4 ml of TTIP was added to 50 ml of ethanol and magnetically stirred for 1.5 hours. On the other hand, 5 ml of the ionized water was added to 10 ml of acetic acid and stirred for 1.5 hours. Then, the acetic acid solution was added dropwise into titanium dioxide and stirred for 3 hours. The prepared solution was coated on Ti substrates by the dip-coating method. In the dip-coating method, the dipping process was carried out at speeds of 1-2 mm s^{-1}. Then, the obtained thin film was calcined at 500°C for 3 h in an air atmosphere.

Synthesis of Ag-TiO_2 Thin Film

4.4 ml of TTIP was added to 50 ml of ethanol and magnetically stirred for 1.5 hours. On the other hand, 1.78 gr $Ni(NO_3)_2.6H_2O$ was dissolved in 20 ml of ionized water. The Ni solution was added dropwise into the Ti solution. The pH of the solution was adjusted to 3-4 using nitric acid. The prepared solution was coated on Ti substrates by the dip-coating method. Then, the obtained thin film was calcined at 500°C for 3 h in an air atmosphere.

Synthesis of GA-Ag-TiO_2 Thin Film

3% APTES solution was used to prepare the GA-TiO_2-Ag thin film. 0.1 g of GA was added to the 3% APTES solution and stirred for 1 hour. Then the Ag-TiO_2 film was immersed in the GA solution, and the coating process was carried out. Finally, the sample was dried in an oven at 100°C for 30 minutes.

Photo-corrosion Tests

Photo-corrosion resistance of the synthesized TiO_2, Ag-TiO_2, and GA-Ag-TiO_2 thin films was investigated in a 3.5% NaCl solution. All experiments were carried out with a computer-controlled, 3 electrode connection potentiostat/galvanostat. In this system, Ag/AgCl was used as the reference electrode, a graphite rod was used as the counter electrode, and a Ti plate was used as the working electrode. After half an hour of equilibration, scanning was stopped when the samples started at a cathodic overpotential (open circuit potential) of −1 V to +1 V against E_{ocp} and reached a specified anodic potential (+1V). The synthesized thin films were corroded under UV light (with a wavelength of 254 nm, 44 W m^{-2}) and in a 3.5% NaCl aqueous solution, and the photo-corrosion activities of the coatings made by giving potential in the specified range were determined. The exposed area of the test specimens is approximately 1 cm^2, and all data are normalized to the surface area.

Results and Discussion

One of the most common methods of determining the corrosion rate is to use electrochemical methods such as polarization. Figure 1 shows the potentiodynamic polarization curves of TiO_2, Ag-TiO_2, and GA-TiO_2-Ag thin film coatings made in a 3.5% NaCl solution.

It was observed that all thin film samples exhibited certain characteristics and passivation behaviors in NaCl aqueous solution. Thin film samples exhibit some fluctuations in the passivity regions. It is estimated that the reason for these fluctuations is the destruction of the passive layer formed on the thin films after a certain period of time. Corrosion potential (E_{corr}), corrosion properties, and corrosion current (I_{corr}) were obtained by the intersection of cathodic and anodic Tafel curve tangents using the Tafel extrapolation method.

Table 1.

Corrosion parameters for samples

Samples	E_{corr} (mV)	I_{corr} (x 10^{-9}A cm^{-2})	Corr Rate
TiO_2 substrate	-386.576	1638	28.448
TiO_2 thin film	-431.576	1538	19.2
Ag-TiO_2 thin film	-151.37	462.4	12.811
GA-TiO_2-Ag thin film	-107.382	212.914	5.428

Figure 1.
Corrosion current density graph

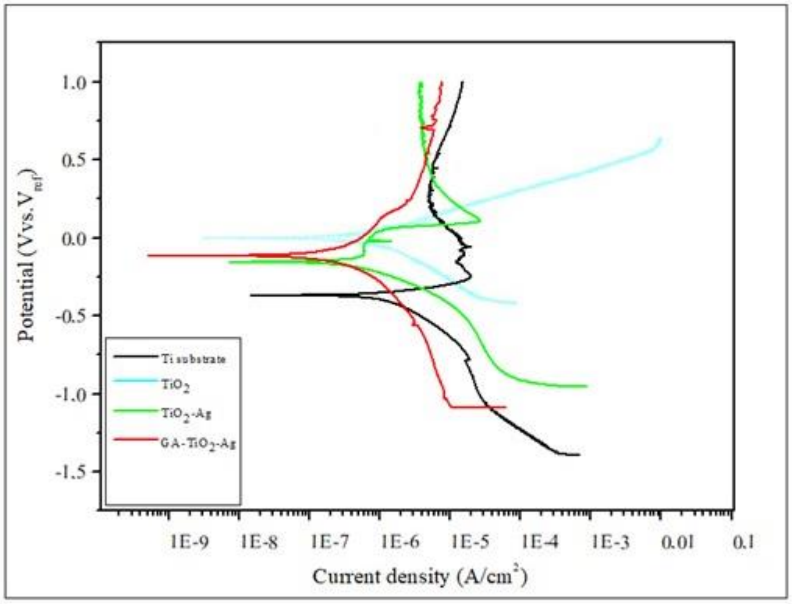

Table 1 shows the values obtained from the parameters corresponding to the corrosion, passivation, and passivation potentials of I_{corr}, I_{pit}, and E_{corr}.

As a result of the trials, it is seen that only the TiO_2 coating reduces the corrosion resistance. It is estimated that this situation may be due to non-adhesion (adhesion) or insufficient calcination between the TiO_2 coating and the base material. However, it is seen that the polarization resistance of the TiO_2 thin film increases with the addition of Ag.

The graphene aerogel layer coated on the Ag-TiO_2 thin film contributed positively to the polarization resistance. The reason for this is that multilayer graphene increases the corrosion resistance of the base material. The fact that Ag is a more noble metal in the galvanic series provides a positive effect on corrosion resistance. Therefore, the addition of Ag to the structure increased the polarization resistance of the thin films (Huang et al., 2022). It is understood that TiO_2 thin films prepared by the dip-coating method with a film thickness of 255 nm have good corrosion resistance.

Conclusions

In this study, TiO_2, Ag-doped TiO_2, and graphene aerogel (GA)-supported Ag-TiO_2 thin films were successfully synthesized by sol-gel and dip-coating methods. The photo-corrosion resistance of these films was evaluated using a 3.5% NaCl solution under UV light irradiation. Electrochemical measurement revealed that the undoped TiO_2 film exhibited lower corrosion resistance compared to Ag-TiO_2, which significantly improved the electrochemical stability of the coating. Furthermore, graphene aerogel coating on the Ag-TiO_2 surface resulted in a further increase in corrosion resistance. Among the samples under corrosion measurement, the GA-TiO_2-Ag thin film exhibited the lowest corrosion current density and the most positive corrosion potential, indicating superior protective performance. Ag, a noble metal, served as a cathodic protector and enhanced the corrosion resistance of the TiO_2 thin film. These findings suggest that GA-supported Ag-TiO_2 thin films are promising candidates for protective coatings in chloride-rich environments, especially in applications requiring both photocatalytic activity and corrosion resistance.

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