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Corrosion behavior of TiO_2–NiO nanocomposite thin films on AISI 316L stainless steel prepared by sol–gel method

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ABSTRACT

TiO_2–NiO nanocomposite thin films were deposited on the 316L stainless steel using sol–gel method by a dip coating technique. Different techniques such as differential thermal analysis, thermogravimetric analysis, X-ray diffraction, Fourier transform infrared spectrometry, scanning electron microscopy and scanning probe microscopy were carried out in order to characterize the structure of the coatings. The corrosion resistance of the coatings was evaluated by using Tafel polarization and electrochemical impedance spectroscopy tests of uncoated and coated specimens in a 3.5% NaCl solution at room temperature. It was found that to obtain desirable structure in coatings, the coatings should be calcined at 600 °C for one and half hour. $NiTiO_3$, anatase and rutile were the phases obtained in different calcination conditions in air atmosphere. The results of corrosion tests indicated that with increasing the dipping times from 2 to 4, the corrosion current density first decreases but when increasing the dipping times to 6, it increases. Also the corrosion current density decreased from 186.7 $nA.cm^{-2}$ (uncoated steel) to 34.21 $nA.cm^{-2}$ (80%TiO_2–20%NiO) and corrosion potential increased from −150.2 mV (uncoated steel) to −107.3 mV (67%TiO_2–33%NiO).

1. Introduction

Metals, such as iron, aluminum, copper, magnesium and their alloys are used in a myriad of structural, marine, aircraft applications and cultural heritage, etc. [1]. While these metals are useful because of their physical characteristics, such as stiffness and high strength to weight ratios, they are highly susceptible to corrosion in aggressive environments [2]. For example although one of the major reasons of using stainless steels is their corrosion resistance, these materials are susceptible to localized corrosion in some environments like chloride containing solutions [3]. In order to protect metals from corrosion, organic coatings have been widely used in the industry [4]. Ceramic coatings are also very attractive as coating materials because they possess good thermal and electrical properties and they are more resistant to oxidation, corrosion, erosion and wear than metals in environments having high temperature [5]. TiO_2, SiO_2, ZrO_2, Al_2O_3, etc. have been studied as corrosion resistant coatings on metallic substrates [6]. In an investigation in 1999, Taylor et al. deposited TiO_2–NiO nanocomposite thin films on Hastalloy by sol–gel method [7]. Also they used other two and three oxide systems to compare the results. The results showed that the TiO_2–NiO films had the lowest friction coefficient and the best wear behavior among all the coatings. These were the only coatings in which the pin did not wear through the substrate during the 3600 cycle test. They concluded that this improved friction/wear properties provided by the TiO_2–NiO coatings may be due to the formation of a mixed metal oxide phase, $NiTiO_3$. This phase, while it does not have a mineral name, has an ilmenite structure where nickel atoms sit on the iron sites.

So far different nanocomposite thin films have been studied in respect of corrosion resistance, but the corrosion resistance properties of the TiO_2–NiO thin films have not been investigated and these films have been only studied in respect of other properties like photocatalytic activity [8]. In this study we deposited these films on the 316L stainless steel substrates by sol–gel method using a dip coating technique and investigated the corrosion resistance properties of the obtained coatings.

2. Experimental details

2.1. Sample preparation

Titania and nickel oxide sols were prepared using tetra-n-butyl titanate (TBT) as precursor, ethanol as solvent, 65% nitric acid, ethyl acetoacetate (EAcAc) and distilled water, all from Merck Company and Nickel(II) acetate Tetrahydrate from Fluka chemicals.

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TiO_2 sols were prepared using TBT according to the following procedure: 20 ml ethanol and 1 ml EAcAc were mixed at room temperature. Then 4 ml TBT was added and the solution was stirred continuously for 2 h. In order to ensure sufficient degree of hydrolysis and to acquire homogeneity in the sol, 0.2 ml distilled water was carefully added to the solution within 30 min and kept stirring for a sufficient time. According to the composition of the nanocomposite, an appropriate amount of nitric acid was added to the sol in order to reach the required pH for a stable sol.

Nickel oxide sols were prepared by mixing Nickel acetate tetrahydrate and ethanol, followed by adding a sufficient amount of nitric acid to completely dissolve the nickel salt. The quantity of nitric acid was different for each composition. Then the sol was kept stirring for an appropriate amount of time. Eventually the nickel oxide sol was added carefully to the titania sol, while being stirred. The quantity of ethanol was chosen in a way that all the final sols with different compositions had molarities of 0.5. In order to obtain sols with different weight percent compositions of 50%TiO_2–50%NiO, 67%TiO_2–33%NiO and 80%TiO_2–20%NiO the two sols prepared separately were mixed. These values correspond to a molar ratio of 0.94, 1.91 and 3.70 for Ti:Ni, respectively.

316L stainless steel was used as the substrate. The composition of the 316L stainless steel is shown in Table 1. Samples having dimensions of (20×10×2) mm were ground with no. 400 to 2500 emery papers and polished with 1 micron diamond paste to obtain mirror finished surfaces. Before the coating process, samples were carefully cleaned in acetone, ethanol and distilled water. These substrates were dip coated in the sol solutions at a withdrawal speed of 4 cm/min. After natural drying in air flow, samples were heated in an oven at 120 °C for 15 min. Such an operation was repeated to form different coating thicknesses under 100 nm. The samples were then heat-treated at 600 °C for 90 min to enable oxide conversion and to remove the solvent and residual organics.

2.2. Characterization

For the purpose of thermal analysis, X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FTIR) tests, powder samples were prepared by drying the final sols in an oven at 120 °C for 24 h. The powder samples were heat treated in a manner similar to that used for processing the coated coupons. The annealing time of powder samples was chosen a little longer than that of the coatings. This difference comes from two reasons. First, since these coatings normally have nanometric thicknesses, the amount of heat that they experience is more than that of the powder samples. The second reason for decreasing the annealing time of coatings was to avoid sensitization of the substrate and thus diminishing its corrosion resistance properties. Thermal effect was investigated by differential thermal analysis (DTA) and thermogravimetric analysis using the apparatus PL-STA-1640 (Polymer Laboratories, Stanton Redcraft, UK) at a constant heating rate of 5 °C/min from room temperature up to 1000 °C. The microstructures of powder samples having different compositions were examined using XRD analysis and FTIR spectroscopy. XRD patterns were obtained using JEOL JDX-8030 diffraction system with Cu K_α radiation ($\lambda = 1.5406$ A°) at a scanning rate of 0.1°/min for 2θ ranging from 20° to 80°. FTIR spectroscopy was performed in a Shimadzu instrument (Japan) at a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1}. Surface morphology of the coatings was examined using scanning electron microscopy (SEM) (Tescan Vega, USA) at an operating voltage of 30 kV. The surface topography of the coatings was characterized using scanning probe microscopy (SPM) with 0.1-nm accuracy in Z-axis direction. The SPM (DualScope C-26, DME) used in non-contact mode. The roughness and grain size of the coatings were determined based on the SPM images. The measurements of Tafel polarization curves and electrochemical impedance spectroscopy (EIS) were carried out in a three-electrode cell in a 3.5% NaCl solution using an EG&G Instruments Inc., model 273/A Electrochemical Measurement System. The coated 316L stainless steel specimens were used as working electrodes. The test cell was comprised of a platinum auxiliary electrode and a saturated calomel reference electrode (SCE). The specimen surfaces in contact with the solution had a constant area of 0.283 cm^2. The Tafel curves were measured between +500 mV and −250 mV (vs. SCE) at the open circuit potential at the rate of 1 mV/s. Tests were started 1 h after immersion of samples in the solution. The Tafel polarization curves were analyzed using SoftcorrIII software. The EIS measurements were performed at open circuit potential. The range of applied frequencies was from 10^5 to 10^{-3} Hz using voltage perturbation amplitude of 10 mV. The impedance data were analyzed using PowerSuite and ZView softwares.

Table 1
The composition of 316L stainless steel used as substrate.

Element	C	Si	Mn	Cr	Ni	Mo	P	S	Fe
Weight percent	0.03	0.8	1.2	17.55	13.65	3.1	0.04	0.03	Balance

3. Results and discussion

3.1. Thermal analysis

The TG-DTA curves for the powder sample having a composition of 67%TiO_2–33%NiO are shown in Fig. 1. It can be seen that there are three weight loss regions in the TG curve. The weight loss below 170 °C is related to the removal of absorbed water and evaporation of the organic materials. The weight loss in the temperature range of 170 °C–260 °C is due to the decomposition and combustion of organic materials in the material and the exothermic peak at 205 °C is a witness to this phenomenon [9]. The next weight loss ranging from 260 °C to 360 °C is related to the burnout of the ethyl acetoacetate and the residues of organic materials. This region has an intense exothermic peak at 260 °C due to the burnout of surfactant agent [8]. In the temperature range of 360 °C to 580 °C we can see a broad weak exothermic region which is related to the formation of anatase crystallites from the amorphous matrix. The small rather broad exothermic peak at about 620 °C shows the formation of crystalline $NiTiO_3$ phase. Also the other small exothermic peak at 680 °C is due to the conversion of anatase to rutile in agreement with X-ray diffraction results.

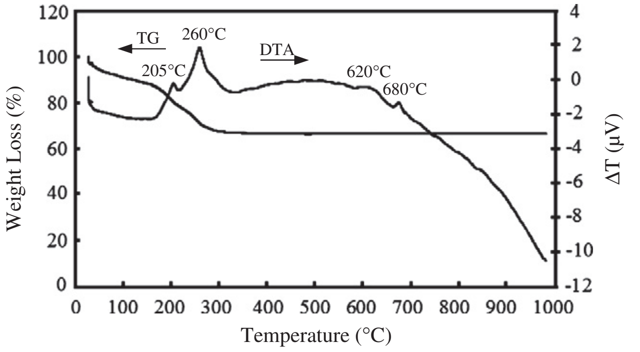

Fig. 1. TG/DTA curves of powder sample having a composition of 67%TiO_2–33%NiO.