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Tungsten Oxide Nanoparticles as Corrosion Inhibitor of Stainless Steel in Saline Medium

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Abstract

Tungsten oxide (WO3) nanoparticles at various concentrations of 1.7×10^{-2}, 2.5×10^{-2} and 3.4×10^{-2} M were electrophoretic deposited onto stainless steel surface for corrosion inhibition investigations with respect to concentration as well as temperature by using potentiostatic polarization technique. Results obtained show that WO3 nano coating was used as a barrier layer for the corrosion protection of stainless steel in saline solution. The morphology of nanoparticles was examined using Scanning Electron Microscopy (SEM).The obtained results indicated that these nanoparticles are good inhibitors. All polarization curves yielded similar behavior pointing to stainless steel corrosion is controlled by the charge transfer process so that the stainless steel dissolution mechanism does not alter due to the presence of the nanoparticles. Generally, increasing the inhibitor concentration and temperatures leads to an increase in the inhibition efficiency. Thermodynamic parameters were calculated, and the energy of activation data obtained of the corrosion reaction was decreased with an increase of the concentration of nanoparticles. It is likely that the adsorption of WO3NP on the surface of stainless steel was chemical in nature.

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1. Introduction

Electrophoresis was utilized widely in biological, chemical and materials sciences, and bioengineering for the control and preparing of an assortment of natural materials (proteins, cells, and so on.), liquid phase and colloids [1]. In construct, electric field helped electrodeposition, chemical deposition, and electroplating, were utilized for various years in materials science, mechanical materials handling, and slender film applications including valuable metal coatings, composite artistic arrangement, and bio-dynamic materials, different paints and colors. Ongoing exploration [2] enthusiasm for nanoscience and nanotechnology has concentrated on finding easy systems to control materials that truly have demonstrated to be hard to deal with on account of their size. Practically, nanomaterials represent a significant test in their proficient treatment because of their lessened size. Of the large number of accessible systems to control the dissemination of these materials, the electrophoretic deposition (EPD) of nanomaterials seems, by all accounts, to be perfectly appropriate for the distribution and deposition of nanomaterials, giving an effortless, speedy intends to create firmly stuffed movies of nanoparticle, nanotubes, and other nanostructured materials. EPD joins parts of electrophoresis and the interpretation of charged particles, suspended in the medium, because of a surrounding, direct flow of an electric field and dielectrophoresis of the movement of dipolar, polarizable, or charged particles, likewise in arrangement, because of exchanging flow or inclination electric fields leads to precipitation of nanomolecules onto the electrode surface [3]. Tungsten oxide (WO_3) nanomaterial considered as corrosion inhibitor of metals and alloys due to its advantages such as low cost, low toxicity and easy production [4]. The precipitation of metal and/ or metal oxide nanoparticles composites allowed progress in the field of defensive coatings. Sajjadnejad et al. [5] improved the corrosion obstruction of zinc by TiO_2 nanoparticles co-deposition, while Zeng et al.[6] study the use of CeO_2 nanoparticles for improvement of the corrosion attitude of nickel coatings. Hence, there are no research reports in the literature known by the authors where (EPD) has been utilized for the deposition of WO_3 nanoparticles as protection films. Stainless steel alloy is an amalgam of iron with at least 10.5% Chromium. Chromium generated an oxide thin layer on the steel surface known as the 'passive layer'. This layer prevent occurrence of any further corrosion of the surface. Resistance to corrosion increased as the amount of Chromium increased. On the other hand, Steel also contains changeful measures of Manganese Silicon, and Carbon. Various components may be added, for example, molybdenum and nickel to improve other good properties, for example, improving susceptibility and increasing corrosion resistance [7].

This research aimed to performed electrophoretic deposition of tungsten oxide nanoparticles on stainless steel surface as corrosion inhibitor in saline medium. The effect of various concentrations of tungsten oxide nanoparticles and temperature on protective behavior of coated steel in 3.5 % sodium chloride solution was investigated by using Tafel polarization method. SEM images were also employed for investigating of the surface morphology and phase structure of coatings nanoparticles, respectively.

1. Experimental

1.1. Solutions Preparation

35g of sodium chloride salt of 99.9% purity, Sigma Aldrich was dissolved one litter of distilled water in order to prepare 3.5% of NaCl solution. Tungsten oxide nanoparticles was prepared in different concentrations of 1.7×10^{-2}, 2.5×10^{-2} and 3.4×10^{-2} M by adding a measurable quantity of it in 100 mL of absolute ethanol to prepare emulsion coating solutions and few amount of iodide is added to these solutions in order to increase their conductivity.

1.2. Electrophoresis Deposition of Emulsion (Coating Samples)

Electrophoresis deposition of tungsten oxide nanoparticles on stainless steel substrate was carried out by using direct current D.C voltage power supply from 0 to 15 V. A150 ml covered beaker has two slits with a distance of 1cm between them and the circuit is used by the AC meter. Measurement of the current generated between the electrodes. Meanwhile, the stainless steel rode used as inert electrode in deposition process cell and stainless steel specimen is caught by means of tong made of stainless steel. The deposition of specimens occurs at various time and finally, the specimens were thermally dried in an oven at 100 °C for 2 min. Following the above mentioned EPD, procedure a thick film was coated on stainless steel to ensure a uniform coating of the tungsten oxide nanoparticles film.

1.3. Electrochemical Consideration

Electrochemical studies were made using three-electrode potentiostatic device which respectively, reference (Saturated Calomel), auxiliary (platinum) and working electrode (stainless steel alloy) electrodes. The Wenking M Lab multi-channel system and the SCI-M Lab system for corrosion measurement obtained from Bank Electronics-Intelligent controls GmbH, Germany 2007 is used as a high tech electrical measuring device. M Lab is powered by Window XP desktop computer. The inhibition efficiency (%IE) of tungsten oxide in the inhibition of stainless steel in 3.5% of sodium chloride solution was calculated from relation[8]:

$$\mathrm{IE}\,(\%) = [\,(i^{o}_{corr} - i_{corr}) / i^{o}_{corr}] \times 100 \qquad (1)$$

Where, (i^{o}_{corr}) and (i_{corr}) are respectively the corrosion current density for blank and coated stainless steel with various (WO_3)NP coating concentrations at the same temperature. The surface coverage (θ) of stainless steel by (WO_3)NP is estimated by using this relation[9] :

$$\theta = (\%\,\mathrm{IE}/ 100) \qquad (2)$$

1.4. Scaning Electron Microscope technique

The SEM – SIGMA HV – Carl Zeiss Scanning Electron Microscope with Bruker Quantax 200 –

Z10 EDS Detector was used to investigate the surface morphology of the WO_3 nanoparticles.

2. Results and Discussion

2.1. Polarization Measurements

Figures 1 (a-d) illustrate the corrosion polarization plots of stainless steel in sodium chloride solution (3.5%) for uninhibited and inhibited solution by various concentrations of (WO_3)NP coatings at 293, 298,303,308 and 313 K. Electrochemical parameters such as corrosion potentials (E_{corr}), cathodic (b_c), and anodic (b_a) Tafel slopes and corrosion current densities (i_{corr}), are tabulated in Table 1. The data obtained show that the presence of (WO_3) NP coating caused an alteration in the E_{corr} data of stainless steel and the shifting range is toward more negative values with increasing temperature and less negative values with an increased concentration of coated inhibitor as indicated in Table 1. This behavior may be attributed to the basis of the decreased corrosion feasibility in the presence of (WO_3) NP and also due to increased coating concentration, indicating that the coated (WO_3) NP affects anode reaction rather than cathode reaction.

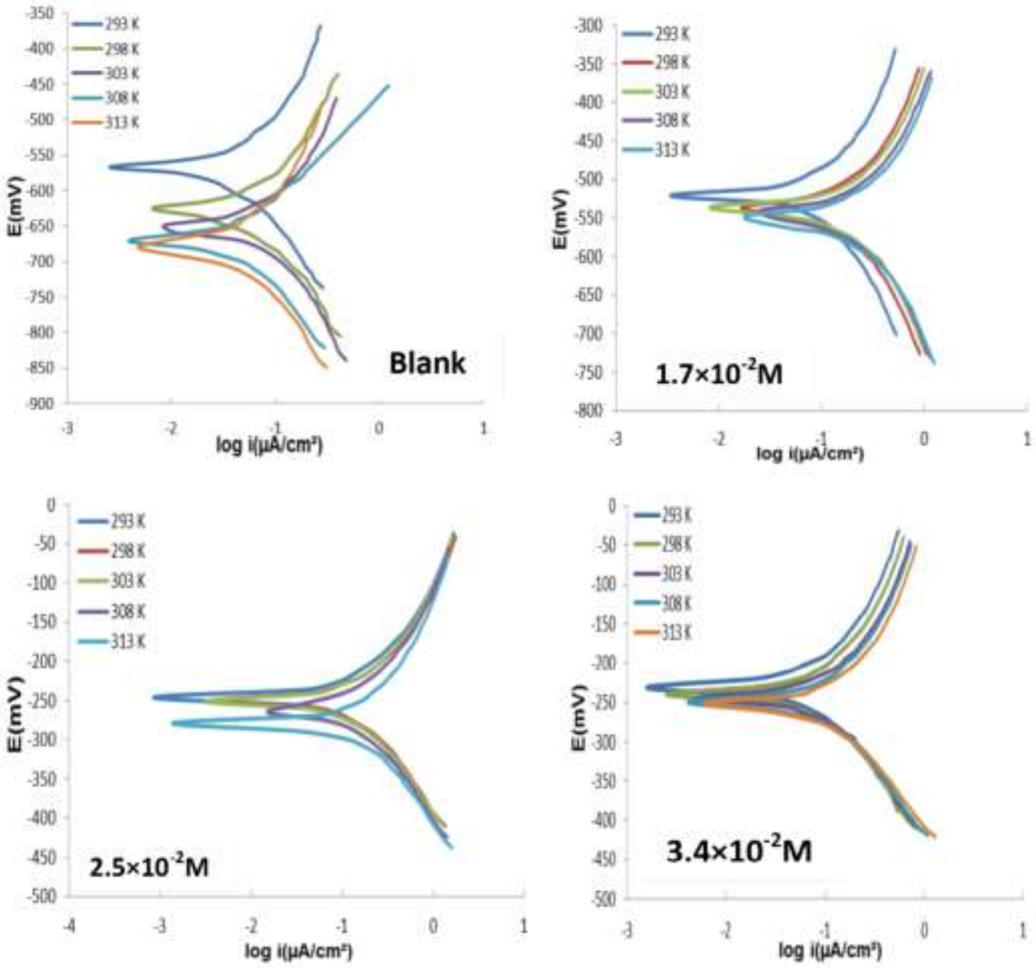

Figure 1. Polarization curves for stainless steel corrosion in 3.5% sodium chloride solution in the absence and presence of different coated concentrations of tungsten oxide nanoparticles at various temperatures in the range (293-313) K.

At a constant WO_3NP coating concentration, E_{corr} were moved toward active values with the rise of temperature. Thus, the increased temperature makes corrosion of stainless steel more convenient as shown in Table 1. On the other hand, the values of the corrosion current density (i_{corr}) at constant tungsten oxide nanoparticles coating concentration were increased with the rise of temperature. Meanwhile, i_{corr} data decreased with increasing tungsten oxide concentration and this behavior may be due to the better corrosion protection of WO_3NP adsorbed on the surface of steel. Therefore Tafel discussion of WO_3NP illustrates the restricted mobility of electrolyte ions to the steel surface in saline medium. This is indicative that WO_3NP coating reflects the remarkable anticorrosion properties for steel alloy [10]. Therefore, Increasing coating WO_3NP concentration leads to an increase of the protection efficiencies (%IE) due to good adhesion property of WO_3NP coating and strong compact adsorbed films which are formed on the surface of the stainless steel with increase of the temperature. This implies the increase in surface coverage (θ) with increase in the coating concentration. Thus, the maximum inhibition efficiency of 79.66% was achieved at the highest WO_3NP coating concentration of 3.4 $\times 10^{-2}$ M and at 313K. Cathodic and anodic Tafel slopes data are changed at all WO_3NP coating concentrations and temperatures as shown in table 1. These results indicate a change in the charge transfer mechanism to chemical precipitation or to electrochemical desorption the cathodic reactions and also to the variation of the anodic (dissolution) reaction of stainless steel alloy [11].

Table 1. Corrosion parameters of stainless steel in 3.5% sodium chloride solution in the absence and presence of different coated concentrations (1.7×10^{-2}, 2.5×10^{-2} and 3.4×10^{-2}) M of tungsten oxide nanoparticles at various temperatures in the range (293-313) K.

In $\times10^2$ [M]	T [K]	$-E_{corr}$ [mV]	i_{corr} [μA/cm^2]	Tafel slope [mV/dec] $-b_c$	$+b_a$	θ	%IE
0	293	567.7	48.21	123.8	89.9	-	-
	298	625.8	55.05	115.3	78.7	-	-
	303	650.8	59.47	108.8	73.6	-	-
	308	669.1	65.49	151.9	92.7	-	-
	313	681.4	73.60	143.4	88.6	-	-
1.7	293	524.4	32.39	165.9	96.5	0.328	32.81
	298	540.0	35.38	142.4	90.1	0.357	35.73
	303	545.5	37.37	123.7	76.8	0.371	37.16
	308	548.6	40.68	116.4	74.4	0.378	37.88
	313	554.4	44.06	128.4	81.0	0.401	40.13
2.5	293	246.3	21.13	60.8	44.0	0.561	56.17
	298	249.1	23.12	55.5	41.6	0.580	58.00
	303	252.5	23.16	75.6	50.8	0.610	61.05
	308	263.3	23.99	88.3	56.7	0.633	63.36
	313	280.1	25.73	93.0	58.2	0.650	65.04
3.4	293	229.7	12.42	72.6	43.4	0.742	74.23
	298	238.2	13.56	76.5	44.7	0.753	75.36
	303	244.2	14.04	88.6	48.5	0.763	76.39
	308	249.8	14.40	105.0	53.0	0.780	78.01
	313	251.1	14.97	109.2	55.0	0.796	79.66

2.2. Corrosion Kinetics

Temperature dependence of i_{corr} data was investigated by drawing a log i_{corr} versus (1/T) plots of blank stainless steel and coated with WO_3NP in sodium chloride solution in according to Arrhenius equation [12]:

$$\log i_{corr.} = \log A - [E_a / 2.303\, RT] \qquad (3)$$

Where i_{corr} means the rate of corrosion in temperature (T). E_a is activation energy and A is a pre- exponential factor data, respectively, were obtained from the slopes and intersection of Arrhenius diagrams as shown in figure 2. It is clear that the correlation between log i_{corr} and (1/T) in the absence and presence of different concentrations of the coated WO_3NP fit with straight lines in all cases. The increased WO_3NP concentration leads to decrease the value of the calculated temperature coefficient E_a values, showing that the protection efficiency increases as the temperature increase and chemisorption adsorption is more probable [13]. A high value of E_a is attached to a high value of A and vice versa is true also, as E_a is lower for the inhibited solution than for the uninhibited one. This behavior was explained on the basis that WO_3NP are chemically holed on the surface of the metal, as a result of an increase in the surface area of the metal covered by inhibitor molecules and adsorbed film formation from the reaction product due to an increase in temperature [14,15]. Hence a chemisorption mode of adsorption is more likely. The transition state of Arrhenius equation was used in order to evaluate the enthalpy (ΔH*) and entropy (ΔS*) of activation as indicating from the following [16]:

$$i_{corr.} = (RT/Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$$

where N and h are respectively, Avogadro's number and Planck's constant. Figure 3 shows a schematic diagram of lni_{corr} data versus 1/T data in which values of ΔH* and ΔS* were determined, respectively, from the slope and intercept, and data obtained are tabulated in table 2. ΔH* values are positive and they decrease with increasing the (WO_3) NP coated concentration indicating that corrosion process is endothermic [17]. Otherwise, ΔS* data is negative and negativity increased by increasing the concentration of coated (WO_3) NP. The obtained negative values of ΔS* revealing that the association step of activated complex is more likely to occur rather than dissociation step in the rate determining step, which means a decrease in disorder [18, 19].

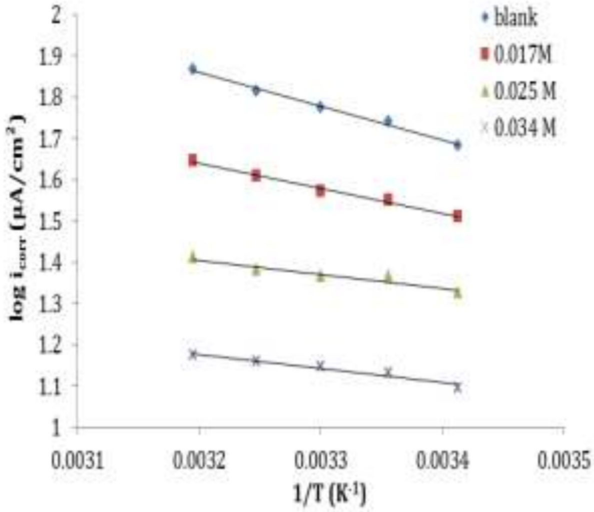

Figure 2. log i_{corr} versus 1/T of stainless steel corrosion in 3.5% sodium chloride solution in the absence and presence of different coated concentrations of tungsten oxide nanoparticles

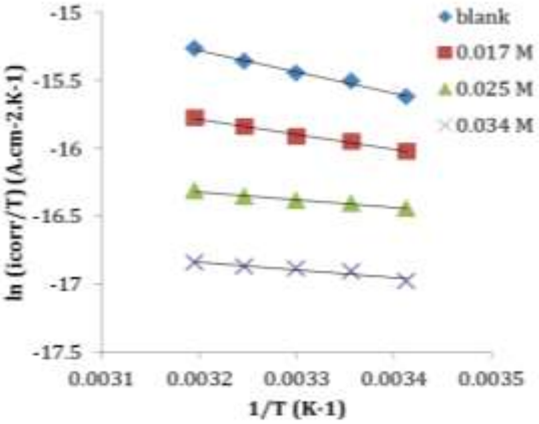

Figure 3. Plots of ln (i_{corr}/T) versus (1/T) for stainless steel in 3.5% sodium chloride solution in the absence and presence of different coated concentrations of tungsten oxide nanoparticles

Table 2. Activation energy (E_a), enthalpy (ΔH_a), and entropy (ΔS_a) of activation for the corrosion of stainless steel in 3.5% NaCl solution for blank and coated with various tungsten oxide concentrations.

Con×102 [M]	Ea [kJ.mol-1]	A×10^{28} [molecule cm-2.s-1]	ΔHa [kJ.mol-1]	-ΔSa [J.K-1.mol-1]
-	15.55	1.73	13.03	282.85
1.7	11.5	0.22	8.98	300.02
2.5	6.57	0.019	4.71	318.18
3.4	6.54	0.011	4.52	323.06

2.3. Scanning Electron Microscopy (SEM)

SEM is a good technique for determining the morphology and particle size of samples. Figures 4 (a-d) illustrate the SEM image of stainless steel sample. The SEM result shows that the surface of the coated alloy is found more smoothly than the uncoated. As well as, WO_3 nanoparticles are clearly observed rod. Figure 4d shows that there was significantly less damage to the surface of WO_3NP coated steel by 0.034 M. Accordingly, it was concluded that the adsorption film was able to efficiently delay the corrosion of the steel specimen [20].

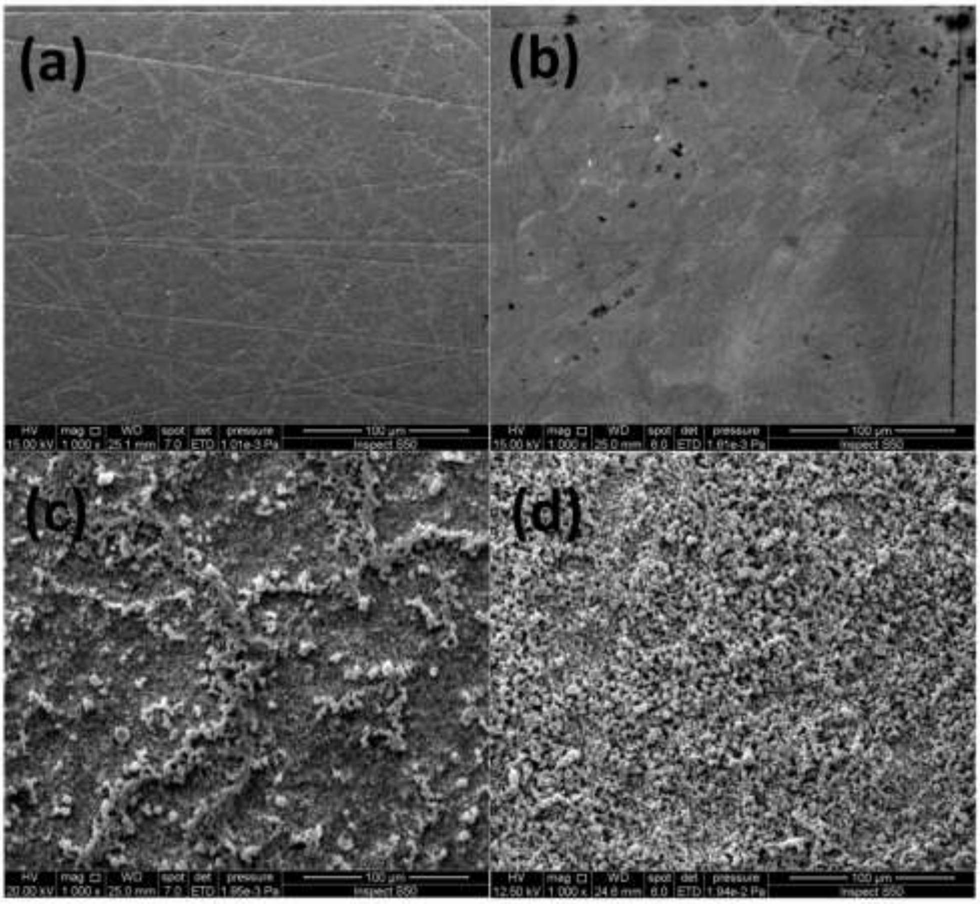

Figure 4. SEM images for stainless steel (a) uncoated (b) immersed in 3.5% sodium chloride solution for 24 h. (c)coated with WO3 NPs (0.034 M) and (d) immersed in 3.5% NaCl for 24 hr. after coating.

3. Conclusions

The anti-corrosion performance of nano-Tungsten oxide was studied by experiments calculations. All coatings concentrations have good corrosion protection performance and their protective efficiencies calculated from the polarization curves are consistent. Moreover, electrophoresis deposited of WO_3 NPs on stainless steel substrate was explained for a thin layer coated for corrosion inhibition studies. The effect of the WO_3 NPs concentration on the coatings morphology and its corrosion behavior were investigated. Based on the obtained results, the use of nanoparticles of tungsten oxide improved the corrosion resistance of coatings. The overall results indicated that corrosion behavior of stainless steel depends on the coated concentration in corrosion media. The nano composite coating that its emulsion WO_3 NPs solution contains 0.034 M nanoparticle has the lowest corrosion rate between all coatings. SEM images showed that before corrosion experiments, the surfaces of stainless steel specimen coated with tungsten oxide nanoparticles was completely smooth and homogeneous by absorption, indicating that the coated nanoparticles had action as a barrier against corrosive environment. Using the tungsten oxide nanoparticles also created a uniform surface.

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