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Corrosion protection of mild steel using nanomaterials coating

ABSTRACT

Effectiveness of nanoparticle coatings in preventing corrosion of mild steel metal samples were experimentally determined. TiO_2 and ZrO_2 nanoparticles coatings were done by brush coating. Different samples were prepared by varying the parameters such as thickness of coatings, concentration of nanoparticles and temperature of heat treatment. Corrosion rate of both uncoated mild steel and coated using TiO_2, ZrO_2 samples was determined in the corrosive environments of 1M HCl and 3.5 wt% NaCl. From the experiments it was found that the coated mild steel samples prepared at temperature 80oC are more effective than samples prepared at 200 ^oC. It is observed that TiO_2 coatings prepared with ratio 2:0.3, 0.182 mm coating thickness and heat treated at 80^{o}C, and ZrO_2 coatings with thickness of 0.185 mm, prepared from nanoparticle paste of 1:0.3 ratios, heat treated at 80 ^{o}C, have shown better protection for mild steel in 1M HCl and 3.5% NaCl solutions compared with other TiO_2 and ZrO_2 coatings.

Keywords: *corrosion protection, nano composites; corrosion resistance, mild steel*

1. INTRODUCTION

Corrosion is a not a manmade process which deteriorate the metals in the form of its oxide, hydroxide or sulphide. It is the slow chemical or electrochemical process with their environment. Many structural materials are corroding in presence of wet condition or moisture air and the corrosion rate strongly affected by exposure to certain substances such as acids, alkalis, salt environment etc [1-3].

Corrosion in metals is such a serious issue that it may have a negative impact on the overall growth of the economy and may also be a cause for national concern. The global cost of corrosion is to be around US$ 2.5 trillion annually out of which large portion could be spent for the prevention of techniques. Corrosion prevention not only considered a financial issue but also one of health and safety concern. Corroded buildings, bridges, transport devise and other metal structures can cause injury and death. These losses can be reduced by protecting metals from corrosion [4-6].

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Corrosion protection is essential to increase the life and efficiency of metals. There are various methods of corrosion protection such as cathodic protection, corrosion inhibitors, metallic plating, hot dip galvanization, electroless plating, paints and coatings. A nanoparticle coating on the surface and polymeric chemical substances reduce the corrosion and act as resistance for corrosion. The coatings can have a monolayer or a multilayer and organized or unorganized structure based on the coating method used. These coatings can be done using different methods such as dip coating, spin coating, chemical vapour deposition, cold spray coating, brush coating, doctors blade [7-9] etc.

Shanaghiet al. [10] conducted research on corrosion protection of mild steel by TiO_2 nanoparticle by dip coating. Corrosion resistance of the coatings was assessed by tafel polarization curves carried out with potentiostat / galvanostat. They observed that TiO_2 nanoparticle coating resulted in highly improved corrosion resistance of mild steel in 3.5 wt% NaCl solution. They observed that temperature of 550^{o}C is suitable to get best coating quality and coating thickness 561 nm improved corrosion resistance.Kirtay et al., [11] conducted tests on mild steel for corrosion protection using SiO_2-TiO_2 sol gel coatings. Sol gel is prepared and coated on mild steel substrates using dip coating method and the samples were heat treated at 200 ºC and 300ºC to improve corrosion resistance. The corrosion resistance of coated and uncoated samples was evaluated in NaCl solution. The measured parameters indicated that the corrosion resistance is improved and ultimately crack free coating was observed at 200ºC. Anwar etal., [12] conducted experiments on corrosion performance in NaOH solution using ZrO_2 coated on mild steel. The dip coating was adjusted at 3, 5 and 7 times. The dipped sample annealed at 350°C for 2 hr by adjusting the heating rate at 1°C/min respectively. The corrosion resistance of uncoated and coated substrates was studied by polarization test and the coating efficiency was improved as the number of layer dip coated increased, which showed improvement in corrosion protection. Devaki and Gomathi Priya [13] conducted experiments on utilizing zeolite synthesized from fly ash for corrosion protection of mild steel. The zeolite was coated on mild steel using polymer binder (Polyvinylidene fluoride) and solvent (N-methyl-2-pyrrolidone). Thickness of coating was found to be 35μm on each side found using screw gauge. Coated samples were placed in sea water, hydrochloric acid, sulphuric acid, nitric acid for a month.

Corrosion rate determined using weight loss method and electrochemical method. The optimum zeolite to binder ratio was reported as 1:0.3. The zeolite coated samples had excellent corrosion inhibition efficiency in sea water (above 85%) and above 80% in acid solutions.The literatures reported various methods to prevent corrosion by nano composite coating. In his investigation TiO_2 and ZrO_2 nano material is synthesized and attempted to test the Mild steel corrosion protection using weight loss method and test the corrosion resistance rate with nano coating and without nano coating.

2. MATERIALS AND METHODS

TiO_2 nanoparticles were prepared with titanium isopropoxide as precursor with ethanol, distilled water and ammonia catalyst. The reactants were mixed using magnetic stirrer for 30 min. The precipitate formed was centrifuged to separate nanoparticles. Then the nanoparticles were dried at 80ºC for 24 hrs. They were calcined at 700ºC for 1 hr.ZrO_2 nanoparticles were prepared with zirconium propoxide as precursor with ethanol, distilled water and ammonia catalyst. The reactants were mixed using magnetic stirrer for 30 min. The precipitate formed was centrifuged to separate nanoparticles. Then the nanoparticles were dried at 80ºC for 24 hrs. They were calcined at 650ºC for 1 hr.

2.1. Nanomaterial preparation and coating

Nanoparticle pastes were prepared with different binders and solvents. Paste 1: TiO_2 paste was prepared with ethanol and sodium dodecyl sulphate (SDS) as binder. It was coated on mild steel plate manually. Steel coupon was dried at 150ºC for 30 min. Paste 2: TiO_2 paste was prepared with polyvinylidene fluoride (PVDF) as binder and ethanol as solvent. Cleaned steel substrate was coated manually and heat treated at 80ºC for 10 hrs. Paste 3: TiO_2 paste was prepared with PVDF as additive and N-methyl-2-pyrrolidone as solvent. Coated on steel and heat treated at 80ºC. Similarly, ZrO_2 paste was prepared with PVDF as additive and N-methyl-2-pyrrolidone as solvent. Coated on mild steel and heat treated at 80ºC.The samples prepared with paste 3 was found adhered well to the surface after heat treatment. The coated samples are shown in the Figure 3 and. Hence, this paste was used to prepare different samples by varying the parameters such as thickness, concentration of nanoparticle and temperature. Various coating ratio, temperature and coating thickness were shown in the Table1.

Table 1. Different condition followed to coat the nano particle on the mild steel

Tabela 1. Uslovi za premazivanje nano čestice na mekom čeliku

Sample	Nano particle	Coating name	ratio	Temperature, (°C)	Coating thickness, (mm)
Mild Steel	TiO_2	Coated I	1:0.3	80	0.12
		Coated II	1:0.3	80	0.20
		Coated III	2:0.3	80	0.182
		Coated IV	2:0.3	200	0.130
	ZrO_2	Coated I	1:0.3	80	0.120
		Coated II	1:0.3	80	0.185
		Coated III	2:0.3	80	0.185
		Coated IV	2:0.3	200	0.185

2.2. Corrosion environment and Metal used

The metal used was mild steel obtained from local market. 1M HCl and 3.5 wt% NaCl solution were used as corrosive environments at room temperature. Weight loss method is used to determine the corrosion rate of metal substrates using brush coating method is used to coat the sol-gel over metal substrates.

2.3. Wight loss method and corrosion rate estimation

A simple test for measuring corrosion rate is weight loss method. The method involves exposing a known weight of metal exposed to the corrosive environments for a specific period of time. Then the sample weight is measure to determine the weight loss. The weight loss for each week is obtained using the weighing balance and the difference in weigh was calculated. Corrosion rate was determined using the formula

$$C_R = \frac{k \times \Delta w}{A \times t \times \rho} \tag{1}$$

where,

C_R= penetration (corrosion) rate (mm/yr),

Δw= weight loss (g)

A= exposed surface area of metal,

ρ = density ofmetal (g/cm^3),

t = time of exposure (hr),

k = constant for unit conversion = 8.76×10^4.

3. RESULT AND DISCUSSION

3.1. TIO_2 and ZrO_2 nanomaterial

The prepared nanoparticle is analyzed using XRD method and the spectrum is shown in the Figure1 and Figure 2 for TiO_2 and ZrO_2 particle respectively. The experimental XRD pattern agrees the 2θ at peak 25.4° confirms the TiO_2 nanoparticles and the peak at 2θ = 28.23° in the figure 2 confirms the ZrO_2 nano particles. The XRD pattern the TiO_2 and ZrO_2 nanoparticle formed were also confirmed and the particle size were determined using Debye-Scherrer equation

$$D = \frac{K\lambda}{\beta cos\theta} \tag{2}$$

D is the mean size of the crystallites;

K is crystalline shape factor;

λ is the wavelength of X-ray;

β is the half high width of the diffraction peak of the sample;

θ is diffraction angle(deg);

TiO_2 particle size was found to be 26 nm and ZrO_2 particle size was found to be 8 nm.

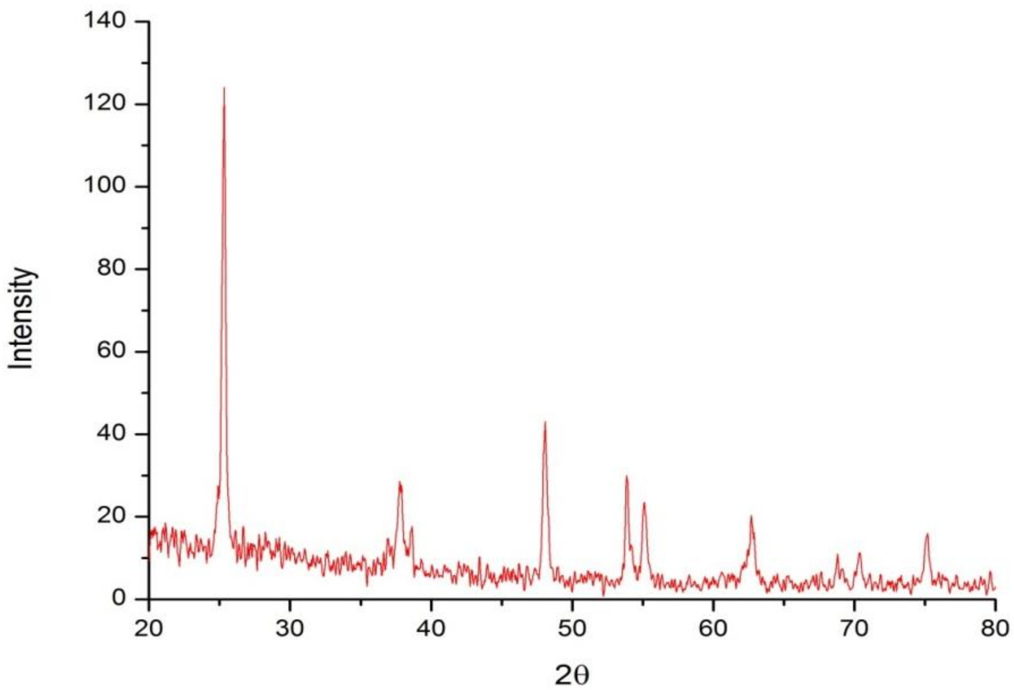

Figure 1. XRD analysis of synthesized TiO_2 nanoparticle

Slika 1. XRD analiza sintetizovane TiO_2 nanočestice

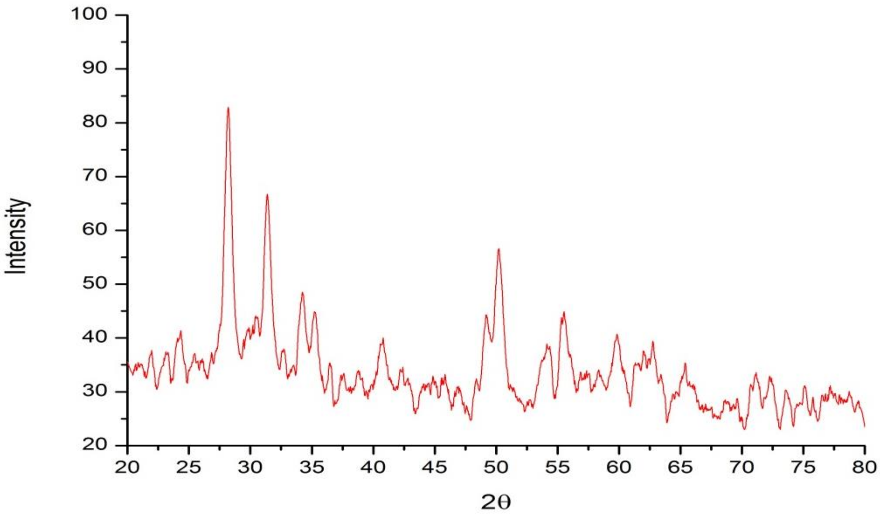

Figure 2. XRD analysis of synthesized ZrO_2 nanoparticle

Slika 2. XRD analiza sintetizovane ZrO_2 nanočestice


a)


b)

Figure 3. TiO_2 Coated Mild steel (b) ZrO_2 Coated mild steel

Slika 3. Meki čelik obložen TiO_2 (b) Meki čelik obložen ZrO_2

3.2. Corrosion Protection measurement

The various coating ratio is applied to the mild steel for the HCl environment and 3.5wt% NaCl solution and the effectiveness of the coating is shown in the Table 2-5. The table 2 and 3 shows the protective efficiency of TiO_2 coatings on mild steel in 1 N HCl solution and 3.5 wt% NaCl solution respectively.

Table 2. Influence of the Experiment Duration on the Protective Efficiency of TiO_2 coatings on Mild Steel in 1N HCl Solution

Tabela 2. Uticaj trajanja eksperimenta na zaštitnu efikasnost TiO_2 premaza na meki čelik u rastvoru 1N HCl

Experiment duration	Protective effectiveness of TiO_2 coating(%)			
	Coating I	Coating II	Coating III	Coating IV
1st week	16.46	19.10	29.11	13.02
2nd week	10.05	12.07	23.36	3.67
3rd week	9.20	9.84	13.52	-
4th week	1.80	9.52	12.99	-
5th week	-	-	-	-

Table 3. Influence of the Experiment Duration on the Protective Efficiency of TiO_2 coatings on Mild Steel in 3.5 wt% NaCl Solution

Tabela 3. Uticaj trajanja eksperimenta na zaštitnu efikasnost TiO_2 premaza na meki čelik u 3,5 tež% rastvora NaCl

Experiment duration	Protective efficiency of TiO_2 coating(%)			
	Coating I	Coating II	Coating III	Coating IV
1st week	40.48	20.51	69.04	13.72
2nd week	15.22	19.04	38.46	8.69
3rd week	7.691	15.22	32.61	-
4th week	17.64	9.80	21.57	-
5th week	-	-	-	-

Table 4. Influence of the Experiment Duration on the Protective Efficiency of ZrO_2 coatings on Mild Steel in 1N HCl Solution

Tabela 4. Uticaj trajanja eksperimenta na zaštitnu efikasnost ZrO_2 premaza na meki čelik u 1N rastvoru HCl

Experiment duration	Protective efficiency of ZrO_2 coating(%)			
	Coating I	Coating II	Coating III	Coating IV
1st week	31.22	36.77	27.74	20.23
2nd week	14.79	21.99	11.37	-
3rd week	10.46	20.99	4.97	-
4th week	0.76	18.20	2.49	-
5th week	0.68	16.60	0.911	-

Table 5. Influence of the Experiment Duration on the Protective Efficiency of ZrO_2 coatings on Mild Steel in 3.5 wt% NaCl Solution

Tabela 5. Uticaj trajanja eksperimenta na zaštitnu efikasnost ZrO_2 premaza na mekom čeliku u 3,5 tež% rastvora NaCl

Experiment duration	Protective efficiency of ZrO_2 coating(%)			
	Coating I	Coating II	Coating III	Coating IV
1st week	30.95	47.61	42.85	23.52
2nd week	12.82	41.02	15.68	9.52
3rd week	10.0	29.41	6.52	8.69
4th week	7.84	26.08	6.15	7.69
5th week	2.17	17.5	5.0	-

´—´ represents the protective coating is not effective

The protective efficiency of the coating is calculated using the corrosion rate uncoated sample and coated sample of mild steel using the following equation [13]

$$Protective\ effectiveness\ (\%) = \frac{C_{UC}-C_C}{C_{UC}} \times 100 \quad (3)$$

C_{UC}- Corrosion rate of uncoated sample;

C_C- Corrosion rate of coated sample

By observing the obtained data, it is found that TiO_2 coated sample prepared with ratio 2:0.3 and heat treated at 80ºC, exhibited good protection for mild steel in 1M HCl solution when compared to the other TiO_2 coated samples. This is due to coated III (2:0.3, 80°C , 0.182 mm coating thickness) is adhered to the steel well and the protective efficiency is good for all the weeks. The coated IV (2:0.3, 200°C, 0.13mm coating thickness) shows irregular in value of corrosion rate due to less thickness of coating and poor binding ability with nanomaterial. Similar results were observed for mild steel present in the 3.5% NaCl solution for the TiO_2 coating. The protective efficiency decreases with increasing time. This can be improved by increasing the thickness of the coating with high binding ability to the mild steel. The table 4 and 5 shows the protective efficiency of ZrO_2 coatings on mild steel in 1 N HCl solution and 3.5 wt% NaCl solution respectively. According to Tables 4 and 5, the ZrO_2 coated samples of coating thickness 0.12mm showed a significantly lower protective effectiveness: after 5 weeks of exposure, it almost disappeared. By observing the obtained data, it was found that the ZrO_2 coated samples of coating thickness 0.185 mm, prepared from nanoparticle paste of 1:0.3 ratio, heat treated at 80ºC (Coating II), showed better corrosion protection for mild steel in 1MHCl and 3.5 wt% NaCl solution. This is due that the binding ability, coating thickness and the heat treatment important parameters to determine effectiveness of the nanomaterial coatings.

4. CONCLUSION

Effectiveness of nanoparticle coatings in preventing corrosion of mild steel metal samples were experimentally determined. TiO_2 and ZrO_2 Nanoparticles coatings were done by brush coating. Good adhered coatings were obtained using brush coating. Different samples were prepared by varying the parameters such as thickness of coatings, concentration of nanoparticles and temperature of heat treatment. Corrosion rate of uncoated mild steel, and TiO_2, ZrO_2 coated samples were determined in the corrosive environments 3.5 wt% NaCl and 1M HCl. From the observations it was found that the coated mild steel samples prepared at temperature 80ºC are effective than samples prepared at 200ºC. When comparing TiO_2 (Coating III) and ZrO_2(Coating II) coated samples showed good protection against corrosion for mild steel in 1MHCl and 3.5 wt% NaCl solutions. However the protective effectiveness of the coatings decreases markedly over time, so they can be recommended for use in the short term. The important parameters to prevent the corrosion of the mild steel are binding materials, the coating thickness, and treatment temperature of the coated samples. These parameters will increase the protective effectiveness of the material for the longer period of time.

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Data Availability Statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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IZVOD

Zaštita od korozije mekog čelika korišćenjem premaza od nanomaterijala

Eksperimentalno je utvrđena efikasnost premaza nanočestica u sprečavanju korozije uzoraka metala od mekog čelika. Oblaganje nanočestica TiO_2 i ZrO_2 urađeno je premazivanjem četkom. Različiti uzorci su pripremljeni variranjem parametara kao što su debljina premaza, koncentracija nanočestica i temperatura termičke obrade. Stopa korozije i neobloženog mekog čelika i obloženog uzorcima TiO_2, ZrO_2 određena je u korozivnom okruženju 1M HCl i 3,5 tež% NaCl. Iz eksperimenata je ustanovljeno da su obloženi uzorci mekog čelika pripremljeni na temperaturi 80oC efikasniji od uzoraka pripremljenih na 200^{o}C. Uočeno je da su se bolje pokazali TiO_2 premazi pripremljeni u odnosu 2:0,3, debljine prevlake 0,182 mm i termički obrađeni na 80^{o}C i ZrO_2 prevlake debljine 0,185 mm, pripremljene od paste nanočestica u odnosu 1:0,3, termički obrađene na 80^{o}C. zaštita mekog čelika u 1MHC i 3,5% rastvorima NaCl u poređenju sa drugim TiO_2 i ZrO_2 premazima.

Ključne reči: *zaštita od korozije, nano kompoziti; otpornost na koroziju, meki čelik*

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