



## Electrochemical Deposited Zinc Titanate Film on Mild steel Surface for Enhanced Corrosion Protection Characteristics

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### ABSTRACT

Zinc titanate particles were synthesized by using electrochemical techniques. The synthesized zinc titanate was in-situ deposited on mild steel surfaces. The deposition of zinc titanate was confirmed by XRD analysis. The corrosion protection of mild steel with surface deposition of zinc titanate particles were evaluated by immersing in neutral water (tap water) for different durations. Weight loss methods, open circuit potential measurements, and potentiostatic polarization techniques were used to measure the corrosion behaviour of mild steel in water. The corrosion rate of zinc titanate deposited mild steel shows lower values compared to pure mild steel in aqueous medium

**Keywords:** Mild steel, Zinc titanate, XRD, Polarization.

### 1. INTRODUCTION

Mild steel is a widely used material due to low cost and easy availability. The main problem associated with mild steel is the corrosion nature of the metal, especially when the metal is in contact with an electrolyte. There are many techniques used to prevent corrosion of mild steel in aqueous environment and most common technique is the use of corrosion inhibitors. Organic compounds especially those having N, S and O showed significant inhibition efficiency. The organic compounds adsorbed on the metal surface and there by forming a protective layer, which prevent further oxidation of the metal [1, 2]. Unfortunately, most of these compounds are not only expensive but also toxic to living beings

A new method of corrosion protection of mild steel was developed by in-situ deposition of zinc titanate on the surface of mild steel. Zinc titanate ceramics attracts the researchers due to their various applications as paint pigments [3], gas sensors [4] and catalysts [5]. There are several methods to prepare ZnTiO<sub>3</sub> powder including solid state reaction [3], sol gel synthesis [6] and molten salt synthesis [7]. A new method for the synthesis of zinc titanate is studied by coupling electro-deposition technique and co-precipitation method. The zinc titanate particle were prepared is simultaneously and deposited on mild steel surfaces by electrochemical method. The mild steel specimen in electrochemical couple oxidized to Fe<sup>2+</sup> / Fe<sup>3+</sup> by interacting with the electrolytic bath for zinc titanate preparation. Zinc titanate formed will react with oxidized iron species in the surface of mild steel and there by producing iron zinc titanate on the surface of the mild steel. This

sacrificial action of zinc and protective coating of titanate is able to reduce the corrosion of mild steel.

### 2. EXPERIMENTAL

#### 2.1. Substrate (mild steel)

The substrate selected for depositing zinc titanate was mild steel. The composition of the substrate is given in table 1.

**Table 1.** Composition of metal specimen.

Sl. No.	Elements	Quantity (%)
1	Carbon	0.2
2	Silicon	0.1
3	Manganese	0.7
4	Chromium	0.02
5	Nickel	0.01
6	Molybdenum	0.10
7	Fe	Balance

Rectangular strips of size 4cm x 2.5cm x 0.2cm were cut from mild steel. These strips were abraded with fine emery papers. Then all the strips were subjected to alkaline cleaning using 5% NaOH solution, acid cleaning using 3% HCl and sensitization using stannous chloride solution (10 g/L SnCl<sub>2</sub> + 40 ml/L conc. HCl) Each process was carried out for 1 minutes successively and the strips were cleaned with water and dried.

#### 2.2. In-situ Deposition of zinc titanate on mild steel

500 ml of 0.2 M TiCl<sub>4</sub> (solution A) was prepared and the solution is taken in an electrochemical cell having a volume capacity of 1000 ml. A mixed solution of 400 ml (solution B) is prepared by

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admixing 20 ml of 30%  $\text{H}_2\text{O}_2$  solution, 15 ml of 28% aqueous ammonia solution and rest of distilled water. The mixed solution was taken in a burette. A pure zinc electrode (surface area  $5\text{ cm}^2$ ) immersed in the electrochemical cell act as the anode. Mild steel act as the cathode. The dimension of mild steel for deposition of zinc titanate particle is  $4\text{ cm} \times 2.0\text{ cm}$ . The un-required area was covered and insulated using a teflon tape. A saturated calomel electrode (SCE) served as the reference electrode for measuring the potential of working electrode. The potential between the working electrodes is suitably set by adjusting the current flowing across the anode and cathode by using rheostats. The multi-meters are used to measure the current and voltage in the system. Dry cell batteries are the DC power source in the electrochemical cell. A potential of 0.6 V vs. SCE is maintained in the anode material kept in the electrochemical cell containing 0.2 M  $\text{TiCl}_4$  (solution A). To this electrochemical cell mixed solution (solution B) is added drop wise drop till 400 ml solution is consumed in the cell.

### 2.3. Characterization of Coatings

The deposited material were carefully scratched from the specimen surface and analyzed by XRD. X-ray diffraction was performed on powder scratched from metal surface by using  $\text{CuK}\alpha$  radiation (Rigaku XRD instrument). Average crystalline size was calculated from the peak width using Scherer formula.

### 2.4. Evaluation of Samples

#### 2.4.1. Corrosion rate

The accurately weighed mild steel specimens (bare and coated with zinc titanate) were immersed in 500 ml of water for a period of 30 days. After 30 days of exposure in aqueous environment, the specimen were taken out cleaned by using pickling solution dried in air oven and weighed, corrosion rate is measured from the difference in weight of the specimen before and after immersion in water. The open circuit potential of the metal in aqueous media is measured against the potential of saturated calomel electrode and reported as V vs SCE.

#### 2.4.2. Electrochemical Parameters

Cathodic and anodic polarization curves were recorded on the metal electrode surface ( $1\text{ cm}^2$ ) immersed in aerated drinking water by sweeping at a rate of 1 mV/s over a range of 100 mV vs. Saturated Calomel Electrodes (SCE) where stainless steel SS 316 L ( $20\text{ cm}^2$ ) act as counter electrode.

## 3. RESULTS AND DISCUSSION

### 3.1. XRD studies

Table 2 shows the XRD data of  $\text{ZnTiO}_3$  powders scratched from the zinc titanate deposited mild steel surface. The XRD spectra shows sharp intense peak corresponding to well crystalline  $\text{ZnTiO}_3$  phase. The entire peak corresponding to  $\text{ZnTiO}_3$  phase were well matched with database in JCPDS. The particle size calculated using the Scherer formula showed average particle size of 65 nm of  $\text{ZnTiO}_3$  synthesized.

### 3.2. Corrosion Rate Measurements

The corrosion rate of mild steel with and without surface deposition of zinc titanate in neutral water for 15 days of exposure is given in table 3. The open circuit potential (V vs. SCE) for different time of immersion of samples were also given in the same table. The OCP shift to anodic value for mild steel samples incorporated with zinc titanate. The corrosion rate also decreased for mild steel samples surface impregnated with zinc titanate. zinc titanate protect the metal against corrosion in two ways. Anodic potential of zinc is higher than that of mild steel and zinc undergo sacrificial action (sacrificial anode) and protect mild steel against corrosion when zinc and mild steel couple were immersed in water. The titanate act as barrier layer for mild steel samples exposing to electrolyte medium and also shift the corrosion potential of metal to anodic regions and there by reducing the corrosion kinetics of the metal.

The results of the potentiostatic polarization study of the mild steel specimen with and without surface impregnation of zinc titanate is given in table 4. The  $E_{\text{corr}}$  value of zinc titanate deposited mild steel was found to be -0.262V where as the bare electrode it was noted as -0.520V. Similarly the logarithmic value of corrosion current density ( $\log i, i_{\text{corr}}$ ) was found to be  $-0.890\ \mu\text{A}/\text{cm}^2$  for zinc titanate coated electrode and the bare electrode the value was found to be  $-0.120\ \mu\text{A}/\text{cm}^2$ . Deposition of zinc titanate on mild steel samples shifts the slope of anodic and cathodic polarization curves and there by decreasing the corrosion current density ( $i_{\text{corr}}$ ) of the metal. The corrosion current density shows more negative value for zinc titanate deposited electrode implies the lower corrosion rate compared to bare metal.

## 4. CONCLUSIONS

The zinc titanate particles were synthesized and deposited on the surface of mild steel by the combination of electrochemical technique with co-precipitation method. The zinc titanate deposition on mild steel surface was confirmed by XRD studies. The deposition of zinc titanate on mild steel shifts the open circuit potential of the metal towards anodic direction (passive regions) and reduces the corrosion rate of the metal. The more

**Table 2.** XRD data of specimens

Specimens	Peak at 2θ	Peak corresponding	$\beta^{1/2}$ (radians)	Particle size (nm)
Deposited sample on mild steel surface	34.4	ZnTiO <sub>3</sub>	0.001668	82.0
	37.1		0.002552	53.4
	44.9		0.001768	77.3
	49.4		0.002462	55.5

**Table 3.** Corrosion rate of mild steel (bare and zinc titanate deposited) in potable water

Specimen	OCP (V vs SCE)					Corrosion rate (mpy)
	1 hr	2hr	6hr	12hr	24 hr	
Mild steel	-0.510	-0.512	-0.555	-0.552	-0.512	2.72
Mild steel with zinc titanate on surface	-0.255	-0.250	-0.260	-0.240	-0.258	1.25

**Table 4.** The polarization data of mild steel sample with and without surface incorporated with zinc titanate

Specimen	OCP, V vs SCE	E corr V vs SCE	Log i ( $\mu\text{A}/\text{cm}^2$ )
Mild steel	-0.512	-0.520	-0.120
Zinc titante deposited mild steel	-0.250	-0.262	-0.890

positive corrosion potential ( $E_{\text{corr}}$ ) for the zinc titanate deposited mild steel was due to the shifting of anodic and cathodic slope in the polarization curves. The zinc titanate deposited electrode shows lower the current density and there by lower corrosion rate compared to bare electrode. The corrosion rate calculated based on weight loss method shows that the value for the zinc titanate deposited electrode was 1.25 mpy where as bare metal the corrosion rate was 2.72 mpy. This sacrificial action of zinc and protective coating of titanate is able to reduce the corrosion of mild steel.

## 5. REFERENCES

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## Bibliographical Sketch



**Dr. K. S. Beenakumari** passed M. Sc in Analytical chemistry, University of Kerala during the year 1996 with 2nd Rank. She completed Ph. D in Electrochemistry from Kerala University in 2008. She had published 20 papers in International journals. She presented three papers in National and International journals. She is now working as Assistant Professor in Department of Chemistry, All Sanits' College, Thiruvananthapuram, Kerala. Current Research topics include, bio-electrochemistry, Water quality improvements, Synthesis of nano particles, photo chemistry, Corrosion etc.