



Development of Al₂O₃, ZrO₂ and Al₂O₃/ ZrO₂ thin film coating on mild steel using RF sputtering to improve corrosion protection for small scale industrial applications.

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ABSTRACT :

Mild steel is commonly used in engineering and manufacturing industries because it is inexpensive, easily available, and has good mechanical properties. However, it is highly susceptible to corrosion, particularly in industrial environments. Applying protective thin-film coatings to the steel surface is an effective method to improve its corrosion resistance. In this study, Al₂O₃, ZrO₂, and Al₂O₃-ZrO₂ (AZO) composite coatings were deposited on mild steel using radio-frequency (RF) sputtering. The coatings were deposited at a pressure of 2×10^{-2} mbar with an RF power of 70 W. X-ray Photoelectron Spectroscopy (XPS) confirmed the presence of aluminium and zirconium in the deposited coatings. X-ray Diffraction (XRD) and Raman spectroscopy were used to study the structural and bonding characteristics of the coatings. Raman analysis showed peaks in the 300–530 cm⁻¹ range for Al₂O₃ and AZO, with a major peak around 670 cm⁻¹ observed for the studied coatings. Field Emission Scanning Electron Microscopy (FESEM) showed a dense coating with a thickness of approximately 200 ± 20 nm. Atomic Force Microscopy (AFM) measured peak heights of 226 nm, 300 nm, and 104 nm for Al₂O₃, ZrO₂, and AZO coatings, respectively. The corrosion performance was investigated using Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy (EIS), and Potentiodynamic Polarization techniques. The results showed that the AZO composite coating provided better corrosion protection than the individual Al₂O₃ and ZrO₂ coatings. The improved corrosion resistance is associated with the dense protective coating, which reduces the contact between the mild steel surface and the corrosive environment.

Keyword: Al₂O₃; ZrO₂; Al₂O₃/ ZrO₂ composite; Mild steel; RF Sputtering; Thin film coating; Corrosion resistance; Electrochemical corrosion.

INTRODUCTION

In this paper, the authors have investigated the electrical and structural properties of a thin film of depositing by RF sputtering. In this paper a plasma enhanced atomic layer is mainly used for the solar cell passivation layer. Where X-rays diffraction results show the dominant peak of Al₂O₃. Al₂O₃ films were chosen to

investigate their electrical and structural characterization. And XRD results show no intensity peaks. The plasma enhanced atomic layer deposition of Al₂O₃ film is an excellent choice for solar cell passivation layer.¹ In this paper, Silicon rich Al₂O₃ films were co-sputtered from two separate silicon and alumina targets onto a long silicon oxide substrate. The formation of amorphous Si clusters upon the deposition process was found for the films. Where the low temperature measurement revealed the intensity of the behaviour expected for quantum confined Si-ncs. Such behaviour visible the PL bands differ from the quantum confined Si-ncs. The two main broad PL bands were observed at 500–900nm range and with peak positions at 575–600nm.² The Al/Al₂O₃ multilayers deposited with the help of RF sputtering on substrate with temperature ranging from -80-600 deg. Except in a high temperature Alumina films are amorphous with smooth surfaces. In metal films, multilayers present a granular surface. Where aluminium grains size was observed to increase with temperature. Where alumina is better structured at low deposition temperature than compared with high temperature. SEM results show that cross-section observations did not reveal any laminated structure.³ At different RF power and argon pressure values 50nm thick Al₂O₃ thin film were deposited at room temperature by using RF magnetron sputtering. After depositing the material were characterized by UV spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Where the deposited Al₂O₃ material was always highly transparent and amorphous in nature. The deposition of Al₂O₃ thin films at low argon pressure values the results shows was not detected because of incorporation of argon at 0.67 pa. The best passivation results are obtained by applying low RF power and high argon pressure during depositing thin films.⁴ Alumina thin films were deposited on Silicon by magnetron sputtering, where aluminium target and oxygen are 99.99% pure. At 100 W RF power the plasma was formed argon plus (Ar⁺), with a dwelling time of 3 hrs. After depositing the coated substrate were characterized with XRD, AFM, SEM and EDS.

where, the results show that at high oxygen flow the alumina structure prevails in the coatings, while at low oxygen flow only aluminium was deposited in the coatings. If the oxygen flow is higher than the coatings decrease in the thickness and as well temperature is higher than the increase in their roughness and grain size.⁵ In this paper morphological and optical properties of aluminium and aluminium oxide thin films deposition were performed by RF magnetron sputtering. The films were grown by using a high purity Al target, containing argon and oxygen gas. After deposition, the substrate was characterized by techniques such as X-ray

diffraction, atomic force microscopy and UV spectroscopy. Where XRD shows phase identification and crystallite size estimation and AFM shows surface morphology and roughness analysis and UV spectroscopy shows optical transmittance measurements. The results showed that reducing target and substrate distance led to increased surface roughness and grain size, etc. The XRD analysis revealed that higher O₂ flows tended to suppress crystallinity and Al₂O₃ films are amorphous.⁶ Al₂O₃ film was deposited on Al₂O-TiC substrate by using RF diode sputtering. Al₂O₃ is 99.5% pure. The target RF power and substrate bias voltage were varied from 4-8kW and 80-180 V. The deposition time is 12.2 min, pressure 1×10^{-6} . After deposition, the substrate should be characterized by techniques such as, XRD, AFM and SEM. The results show that the elastic and hardness of Al₂O₃ were increased when RF power increased.⁷

In this paper ZrO₂ thin film deposition is done by using RF sputtering. Sputtering deposition is a process in which material is ejected from the surface of the target material when the argon gas hits. RF sputtering is used when the target material is an insulator. Where with increasing annealing temperature, grain size will also increase and a smooth surface is obtained. Annealing temperature of 500 deg enhances the ZrO₂ thin film quality by reducing leakage current and improving capacitance voltage. Deposition voltage and thermal annealing controls the

interfacial layer during thin film deposition.⁸ ZrO₂ films have been prepared by RF reactive magnetron sputtering at different O₂ concentration in the mixture sputtering gases. The deposited film has been characterized by XRD, SEM and EDX. The dominant phase of the films is the monoclinic phase of ZrO₂ found in films. When O₂ gas concentration was increased then the development of more columnar spacing was introduced.⁹ In this paper the aim is to work and develop zirconium ox nitride coatings by RF magnetron sputtering on Silicon substrate. Here the film's properties were analysed in two different inert gas atmospheres, namely argon and helium. The material is characterized by X-ray diffraction. The thickness of the film was measured by surface profiler and growth rate decreased to half of the original value for film deposited in argon atmosphere and when film deposited of helium atmosphere with increase of oxygen flux percentage. The surface roughness values are higher at low oxygen flux and decrease with increase in oxygen flux percentage for both cases. The results observed contact angle values are greater than 90 deg indicating the deposited films in both inert gas atmospheres are hydrophobic by nature.¹⁰ In this paper the aim of this work is to prepare thin film composite from ZrO₂ and MgO onto the Glass basis by plasma of RF magnetron sputtering and optical properties. The deposited substrate will be characterized by X-ray diffraction, scanning electron microscopy and atomic force microscopy. The SEM results show the grain size of the ready films. The AFM tests confirmed the homogenous distribution surface of the grains and grain distribution size.¹¹ ZrO₂-Y₂O₃ films with different Y₂O₃ concentrations have been prepared by RF magnetron reactive sputtering. And the deposited film has been characterized by XRD, SEM, EDX and Raman spectroscopy. The crystallite size increases with the increasing Y₂O₃ concentration. The extinction coefficient decreases because the scattering centre concentration decreases with the increase of Y₂O₃ concentration. Then the main reason for light loss in the films is the grain boundaries scattering.¹² In this paper the 316L stainless steel is a substrate and the ZrO₂ is a target material which is deposited on the substrate by RF magnetron sputtering system. After deposition, the substrate material was characterized by X-ray diffraction, atomic force microscopy and potentiodynamic polarization. The results show that the film thickness and roughness of the film is highly influenced by plasma parameters. The XRD results show that monoclinic phase. The ZrO₂ film deposited consisted of a poly-crystalline phase of monoclinic and tetragonal.¹³ In this study ZrO₂ thin films were produced by RF magnetron sputtering method on glass substrate. After deposition, the substrate was characterized by XRD, SEM, AFM and UV spectroscopy. The XRD results show the peaks of monoclinic and tetragonal phases at low growth pressure. All morphological and structural properties of the film had the potential to use the TCO industry.¹⁴

At a low temperature of 450 deg, Al₂O₃/ZrO₂ are synthesized by using RF magnetron sputtering. Films are deposited ranging from pure Alumina and pure Zirconia and the compositions were measured with Rutherford backscattering method. And the deposited substrate was characterized by X-ray diffraction. And the XRD results show the presence of monoclinic zirconia phase in pure zirconia films. No crystalline alumina was detected in both composite and pure alumina. The SEM results show a columnar growth mode in both pure zirconia and nanocomposite films. At higher alumina content the films were mostly amorphous and some evidence of small crystallites.¹⁵ In this paper the Al₂O₃ and ZrO₂ were dopants to investigate their effects on the properties of lithium niobate (LiNbO₃) amorphous thin films. LiNbO₃ was prepared by using sintering methods. And the film was deposited by using RF magnetron sputtering method. Both Al₂O₃ and ZrO₂ doping integrated into LiNbO₃ lattice, resulting in the presence of ZrO₂ phase in XRD pattern. Al₂O₃ and ZrO₂ increased from 90.5 % to 95.6% and 96.6% improved the sintering quality of lithium, niobate ceramics. The results showed there were no significant changes in the optical transmittance and microstructure of the thin films.¹⁶ In this paper the catalytic performance

of Ni-Co/ Al_2O_3 - ZrO_2 thin films prepared with the help of physical vapour deposition(PVD) method. RF magnetron sputtering methods that are used to sputter a layer of Al_2O_3 on a stainless-steel plate and then zirconia thin films were deposited by thermal evaporation. An RF sputtering method was used to deposit the Co doped Ni thin films on the Al_2O_3 - ZrO_2 . After deposition, the substrate was characterized by using XRD, FESEM and EDX analyses. The result shows the synthesized catalyst in this work, its simple preparation method. The FESEM image showed the nanocatalysts with 5% Co/Ni weight percentage. EDX analysis indicates a proper 4 min deposition time. The results say that PVD is significantly smaller amount of catalyst and having good stability compared to other methods.¹⁷ In this paper crystalline alumina-zirconia nanocomposites have been synthesized at 450 °C and 750 °C with RF magnetron sputtering. Composition of the films ranges from pure alumina to pure zirconia as measured with the ion beam method. After deposition, the substrate characterization showed the presence of monoclinic zirconia in the pure zirconia films and γ -alumina in the pure alumina films. And the grain size was ~ 5 nm for the nanocomposite compared to larger grains in the pure oxide films. The electron energy spectroscopy shows pure alumina to the pure zirconia.¹⁸ In this paper ZrO_2 - Al_2O_3 Nano laminate thin coatings is a new method to thermally stabilize at room temperature. These films were deposited with a laminated composite coating by using reactive magnetron sputtering with O_2 and Zr gas mixture at a constant temperature. The film presents an ZrO_2 polycrystalline phase and an Al_2O_3 amorphous phase. And they also deposited multilayers of ZrO_2 - Al_2O_3 Nano sized zirconia crystallites at room temperature without any use or dopants. The nanocrystal line size of ZrO_2 - Al_2O_3 multilayers indicates the average radius are equal to Nano layer thickness.¹⁸



Figure: RF magnetron Sputtering

PREPARATION OF SUBSTRATS AND EXPERIMENTAL PROCEDURE

1.1 Preparation of substrates: To investigate the coating material properties, mild steel is chosen as the base material. Mild steel metal sheet is cut into 20mm $\times$ 20mm $\times$ 3mm. The specimens are polished with SiC paper of grit sizes from 400 to 2500. The polished samples are cleaned ultrasonically in deionized water, then in acetone and isopropanol, and finally again in DI water, dried, and kept in a vacuum desiccator for further deposition. The fabricated target materials are used as source materials for RF magnetron sputtering, and the thin films were deposited at the following conditions.

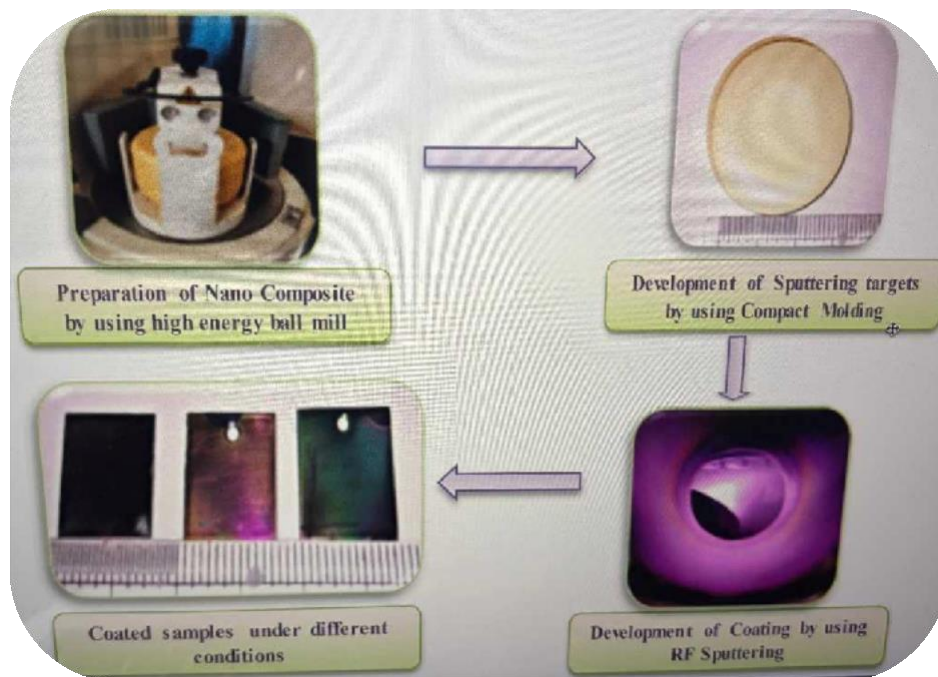
Table 1: Optimized Parameters

S.NO	Parameters	Value
1.	RF Power	70 W
2.	Substrate to target distance	7 cm
3.	Ar flow	45 SCCM
4.	Oxygen Flow	5 SCCM
5.	Deposition Pressure	2×10^{-2} mbar
6.	Deposition Temperature	400°C
7.	Duration	4 Hrs.

1.2 Monolithic and Nanocomposite Coating by using RF Sputtering:

In this investigation, thin-film deposition was performed using a sputtering system (Advanced Processing Equipment, India) with homemade targets. Initially, the sputtering chamber was set to 1×10^{-6} mbar, and deposition was performed at 2×10^{-2} mbar, with argon and oxygen atmospheres at 45 SSCM and 5 SSCM, respectively. Precursor gas flow was maintained at 5 SSCM. The deposition was carried out at an RF power of 70W, with the substrate holder rotating at 5 rpm and a substrate-to-target distance of 7 cm. The deposited samples are stored in a vacuum desiccator.

Figure1. Flow chart for nanocomposite coating process.



1.3 Experimental Procedure: The sputtering targets were made from As-purchased chemicals from Sigma-Aldrich, the micro powders were ball milled in wet media at 300 rpm for 10 hours and then allowed to dry. These dried powders are re-ground with a mortar and pestle and used to fabricate sputtering targets.

Materials:

1. Al_2O_3 (A)
2. ZrO_2 (Z)
3. $\text{Al}_2\text{O}_3/\text{ZrO}_2$ (50:50 wt.%) (AZO) composite.

The sintering temperatures for Al_2O_3 , ZrO_2 , and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite targets are 1200°C , 1300°C , and 1250°C , respectively, with holding times of 1 hr. each. Once the individual and composite sputtering discs have been prepared, the phases are characterized by X-ray diffraction, and further analysis is performed to understand the phases and structural morphologies.

RESULTS AND DISCUSSION

X-ray diffraction of the target materials and deposited specimens is recorded. The target material shows both Al_2O_3 and ZrO_2 phases, indicating a mixed phase in the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite target. Dominant ZrO_2 peaks are observed in the composite target given in Fig 2.

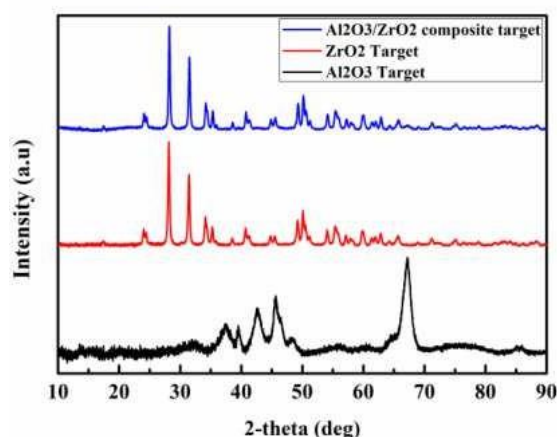


Figure 2. XRD pattern of Fabricated Sputtering Targets.

All deposited thin films were analysed by XRD (Cu-K α source) to determine any possible degree of crystallinity. Fig.3 shows the diffractograms for the Al₂O₃, ZrO₂, and Al₂O₃/ZrO₂ thin films deposited at 2×10^{-2} mbar and 70 W RF power. As shown, no distinct peak was detected in the diffractograms of Al₂O₃, indicating a lower crystallinity. This amorphous nature was observed in all the deposited films, including Al₂O₃ and AZO thin films. On the other hand, in an attempt to determine whether this ZrO₂ could be attributed to the initial nucleation, which is dominant in very thin films with dominant peak position a 2θ - 28.1 with lattice planes (-1 1 1) which is in according to the JCPDS No:01-070-2491(Monoclinic Space Group: P21/c(14)), the recorded diffractograms was three deposited films are presented in Fig.3, which means that, for the studied conditions, the Al₂O₃, AZO are amorphous state is independent of the substrate temperature and they need more thermal energy to exhibit crystallinity. The ZrO₂ is trending toward nucleation at 400°C and shows a crystalline nature.

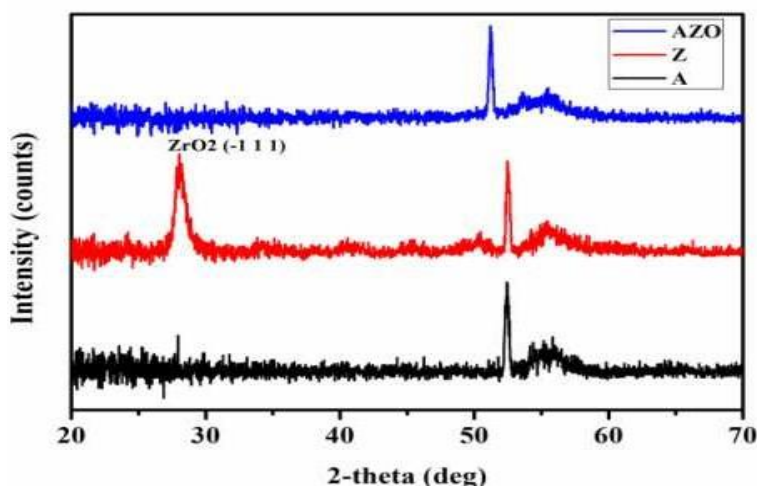


Figure.3 XRD pattern of deposited thin films on a silicon substrate.

Raman spectroscopy was performed using a Lab Raman (Horiba) spectrometer with a solid-state green laser (532 nm) operating at an initial power of 50 mW. Raman Spectra of each thin film were recorded using a CCD detector (Peltier-cooled CCD) in confocal configuration with a $\times 100$ objective and grating with 1200 lines per mm,

offering a spectral resolution of 1 cm^{-1} . Spectra were acquired over the range 100 cm^{-1} to 1200 cm^{-1} . The lower Raman shift cannot be achieved with the filter used in this setup.

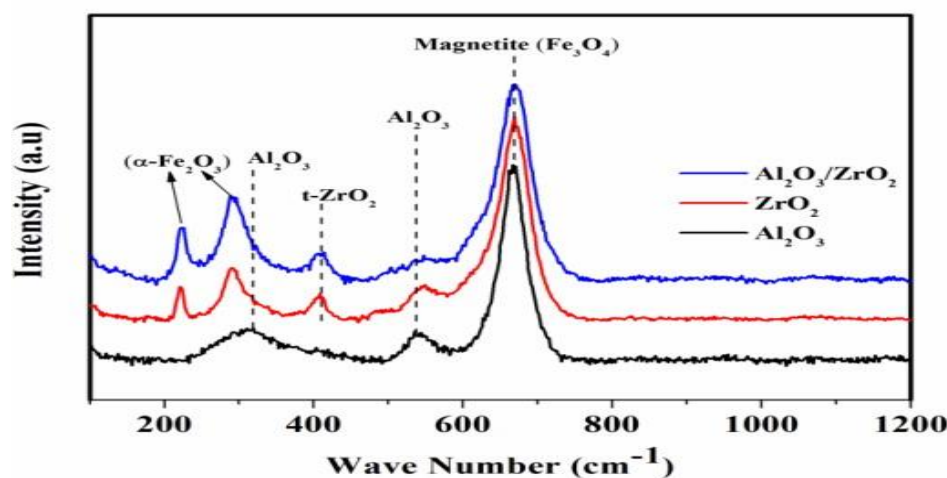


Figure 4. Raman spectra of deposited thin films on mild steel substrate.

Amorphous alumina (Al_2O_3) often shows broad scattering bands rather than sharp peaks, typical of a disordered, non-long-range crystalline structure. The deposited films are amorphous in nature. Raman signals are often very weak or yield broad peaks in the 300 cm^{-1} – 530 cm^{-1} range, indicating the presence of alumina in the deposited thin film.

The Raman bands in the spectra are observed around 408 cm^{-1} , corresponding to tetragonal zirconia, for all compositions, with a small amount of shifting. Alumina and Zirconia composite phases are detected in the spectrum as characteristic Raman bands. The additional peaks at 220 cm^{-1} and 280 cm^{-1} correspond to $\alpha\text{-Fe}_2\text{O}_3$, and a 670 cm^{-1} high-intensity peak is also observed for Magnetite (Fe_3O_4), in good agreement with previous literature on heat-treated mild steel. The characteristic alumina and zirconia low-intense peaks confirm the presence of both materials.

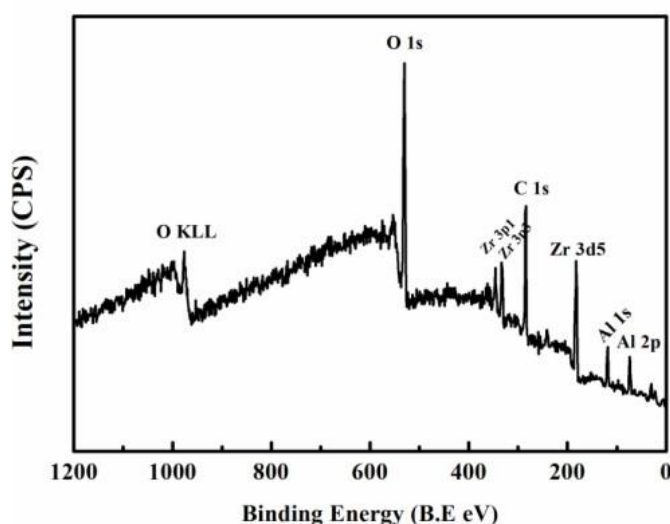


Figure 5. XPS survey spectra of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite-coated thin film.

The XPS spectra of the deposited AZO thin film collected

samples are shown in Fig. 5. The Al 2p, Al 1s peak position was around 73 eV and 119 eV , respectively, and the position of the Zr 3d_{3/2} peak was around 185 eV , Zr 3p_{3/2} peak at 329 eV , which proves that both Al and Zr are observed corresponding to Al_2O_3 and ZrO_2 composite. The signal at around 285 eV corresponds to adventitious carbon. Samples exhibit a secondary structure with a higher binding energy of the main lattice oxygen peak at 529

eV. The XPS survey spectrum of the composite thin film confirmed the presence of Zr, Al, O, and C, suggesting the formation of interfacial Zr-O and Al-O linkages.

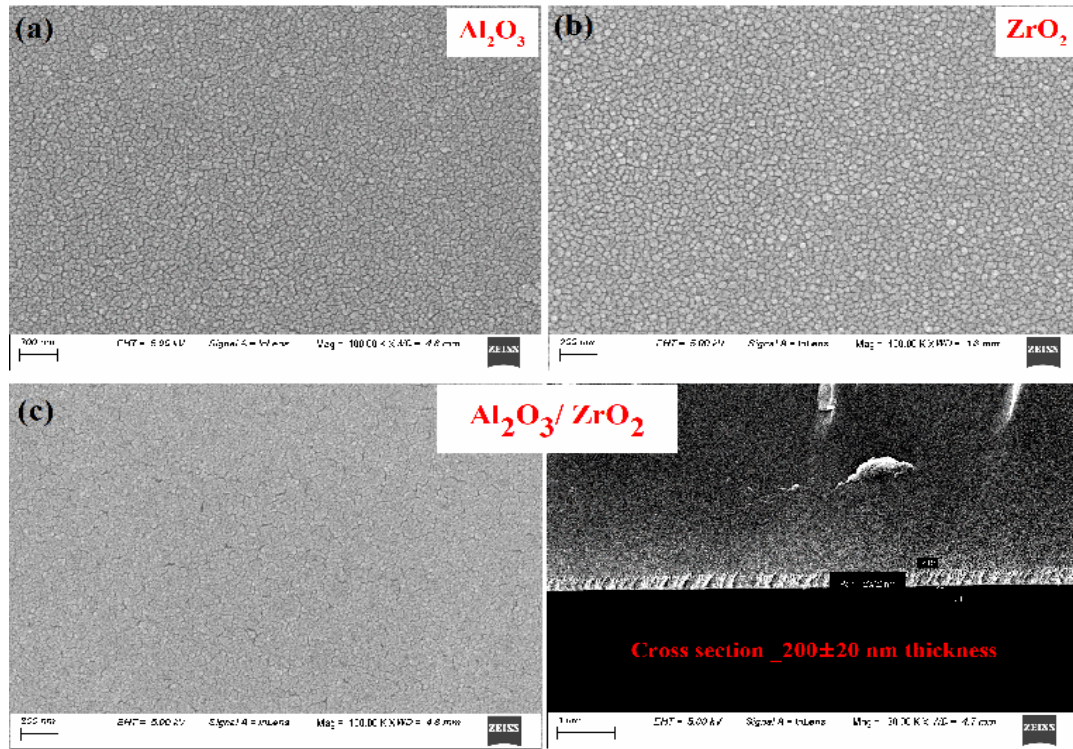


Figure 6. FESEM surface morphologies and cross-section photographs of (a) Al_2O_3 , (b) ZrO_2 , and (c) $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite coatings, and cross-section for thickness estimation.

The Al_2O_3 surface appears like a compact coating, and the ZrO_2 coating has a typical columnar structure with a rough surface. The $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite coating microstructure appears compact and uniform, with a structure similar to that of the ZrO_2 coating (Fig.6). The usual columnar and dense structure found in sputtered coatings prepared at 400°C temperature is clearly identified in the micrograph. The composite coatings also show a columnar structure.

However, the RF-deposited coatings are dense and uniform, with uniform coverage across the substrate.

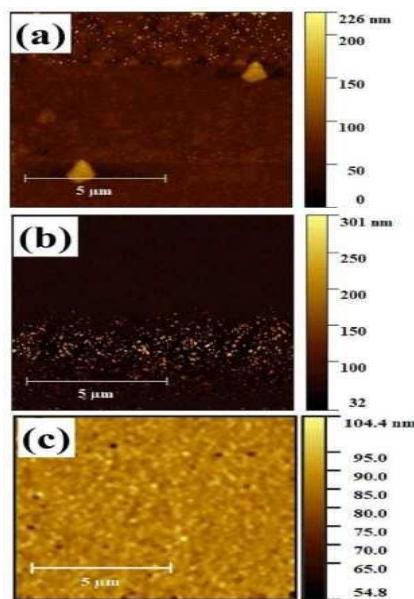


Figure 7. AFM surface profiles of (a) Al_2O_3 , (b) ZrO_2 , and (c) $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite coatings.

The surface profiles of the deposited layers were analysed using a Bruker Instruments (Innova) instrument. The thin films grown were highly uniform, amorphous, smooth, and fine-grained. As observed on AFM, the peak height for all three RF-sputtered ultra-thin films varies with individual Al_2O_3 , ZrO_2 , and AZO composites as follows: 226 nm, 300nm, and 104 nm, respectively. The morphology is highly sensitive to the sputtering composition of Al_2O_3 and ZrO_2 , power, and other parameters. Combining the two materials often results in further reductions in grain size, surface roughness, and peak heights.

A typical top-view AFM image of the Al_2O_3 films with larger grains is shown in fig. 7(a). Using these surface profiles, uniformity was estimated. The microstructure observed in the deposited film is dense and fine-grained.

1.4 Corrosion studies: Electrochemical corrosion resistance studies provide an effective means of evaluating both the corrosion resistance of coating systems and the underlying base metal. In accordance with ASTM G59, the Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements, corrosion behaviour is generally represented by polarization curves (Tafel curves) and electrochemical impedance spectroscopy (EIS) using a three-electrode cell configuration. The working electrodes include deposited and base metals, with a saturated calomel electrode (SCE) as the standard reference electrode, and a platinum mesh employed as the counter electrode for measurements.

The electrochemical corrosion properties of deposited Al_2O_3 , ZrO_2 , and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite coatings, as well as base mild steel, were investigated in a 3.5 wt.% NaCl solution using an electrochemical workstation. The corrosion current density (I_{corr}) was determined by extrapolating the polarization curve. Polarization tests

were conducted at a fixed sweep rate of 0.5 mV/s over a potential range centered on the open circuit potential (OCP) relative to the SCE. Impedance tests were performed at a stable potential across a frequency range of 1 Hz to 100 kHz with an amplitude of 10 mV. The exposed area of each sample in the solution was 1 cm². Prior to each set of measurements, all test samples were immersed in a 3.5 wt% NaCl solution for one hour to achieve an equilibrium potential. To ensure test results' reliability, electrochemical tests were typically conducted on three sets of samples.

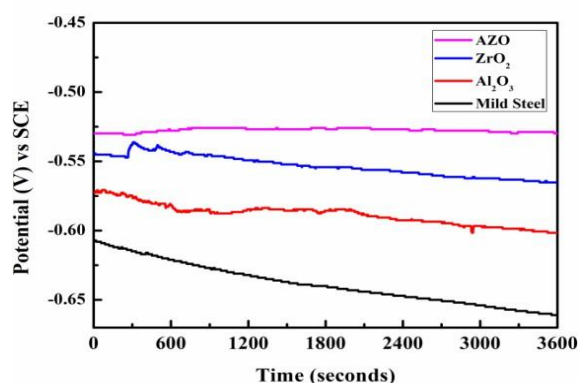
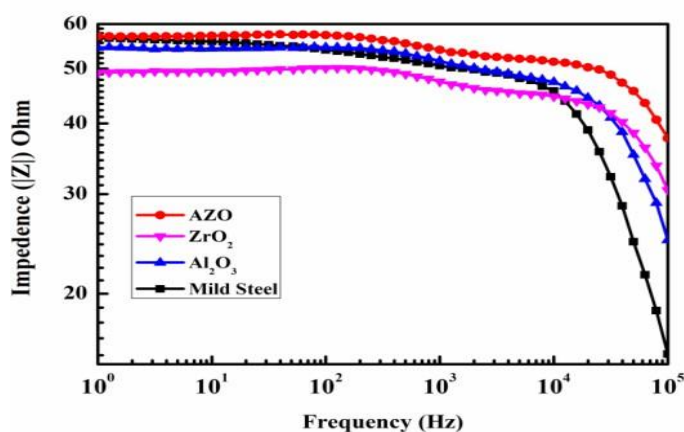


Figure 8. Open Circuit Potential of bare and coated steels.

Open-Circuit Potentials of bare and coated steels are measured at steady-state conditions for 60 min. A positive shift in potential is observed for coated substrates, and the OCP values are tabulated. The highest OCP is observed in the AZO-coated mild steel around -0.52 V.

Figure 9. Impedance (EIS) vs Frequency analysis of coated and bare mild steels.



The impedance studies also follow the same trends as OCP. For all three coated surfaces, the coating area exceeds the base substrate area. The largest area under the impedance curve is observed for AZO-coated mild steel in 3.5 wt.% NaCl is observed.

The destructive analysis of coated mild steels is conducted using potentiodynamic polarization (PDP) studies. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) are determined by extrapolating the anodic and cathodic Tafel lines from the potential vs. log current density plots to their intersection point. It is observed that the cathodic curves exhibit greater polarization than the anodic curves, and the coating on steels performs more effectively at cathodic sites. The reduction in both anodic and cathodic current densities indicates that the AZO composite coating effectively suppresses these reactions. Tafel extrapolations reveal a significant shift in the corrosion potential (-0.77 V) of AZO-coated mild steel compared to bare mild steel. The lower current densities (1.3×10^{-3} mA/cm²) observed in AZO-coated mild steel further confirm that the protective properties of mild steel are enhanced when its surface is coated with AZO.

Table.1: Parameters of Potentiodynamic polarization studies.

Metal/Coating	Corrosion Potential (E_{corr} V)	Current density (I_{corr} mA/cm ²)
Mild Steel	-0.79	2.5×10^{-3}
Al ₂ O ₃	-0.77	1.9×10^{-3}
ZrO ₂	-0.70	1.7×10^{-3}
Al ₂ O ₃ /ZrO ₂ (AZO)	-0.77	1.3×10^{-3}

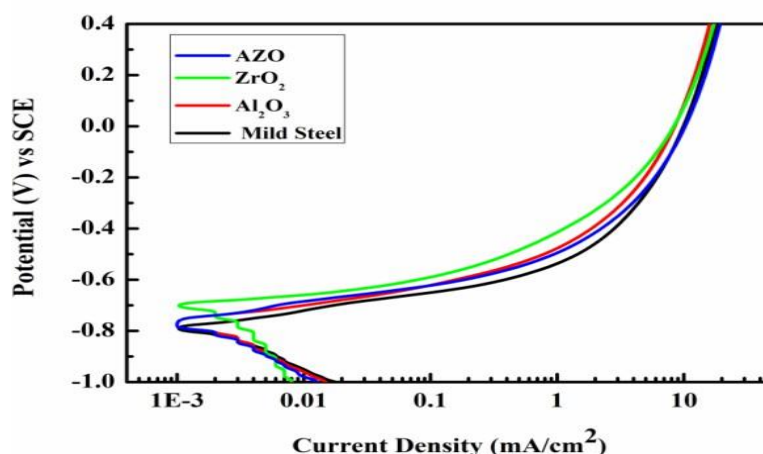


Figure 10. Potentiodynamic polarization studies of coated and bare mild steels.

CONCLUSION

- The RF-sputtered coating on the mild steel surface was uniform, non-porous, and well-adhered.
- The formation of Al₂O₃, ZrO₂, and AZO composite coatings was confirmed by XPS analysis.
- XRD confirmed the phase composition and crystalline structure of a coated material.
- Raman spectroscopy confirms the molecular structure, crystal phases, and chemical bonding of a coated material.
- OCP, EIS, and potentiodynamic polarization measurements revealed the corrosion protection property of AZO coating.
- FESEM, AFM images of coated specimens confirm the formation of a dense passive layer on the metal surface.

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