

Investigation on Corrosion Behaviour of ZrN Thin Films in Industrial Environment

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Abstract: Zirconium Nitride (ZrN) coatings produced by Physical Vapor deposition (PVD), are increasingly being used for their excellent mechanical and tribological applications in various industrial sector. These coatings are particularly attractive for their excellent corrosion which further enhances their lifetime and service quality. In the present investigation corrosion resistance of ZrN thin films of varying thickness ($1.5\mu\text{-}2.0\mu$) in environments having different 3.5%NaCl, 11pH Na_2SO_4 and 0.1NHCl are studied. D.C polarization and A.C impedance spectroscopy studies have also been carried out. The results indicate that 2.0μ ZrN have better corrosion resistance, 2.861mpy in 3.5%NaCl than 1.5μ ZrN (22.7 mpy). Similar behaviour is observed for 0.1NHCl. The difference is less in case of 11pH Na_2SO_4 indicating formation of stable film in alkaline environment.

Keywords: Cathode arc Evaporation, SEM, Potentiodynamic test, EIS.

1. Introduction

The majority of material failure originates at surface by mechanism involving wear, corrosion and fatigue. [1] The deposition of ceramic phases onto conventional metallic materials results in good combination of bulk toughness and load support with desirable surface characteristics and also making forming of complex shapes easier. [2]

In certain applications coating suffer combined corrosion attack and wear. Some examples include tools for plastic processing such as moulds for extrusion or injection molding which are in contact with corrosive media (eg. Softener and colors and free hydrochloric acid contain in certain polymers) and cutting tools where cutting fluid may contain sulphur. In some applications combined properties in terms of tribology, corrosion and fatigue are required. For example, pumps in chemical industries subjected to aggressive environments bearings and gears exposed to marine environment such as in naval aircraft which suffer from pitting corrosion due to localized attack by chloride ions.[3] In applications such as chemical apparatus processing and the food industry, however the mechanical loads occurring are superimposed by corrosive attack. Requirements for coatings withstanding this complex load include chemical inertness in the media concerned, but also microstructure demands a smooth surface, dense morphology without micro porosities and diffusion pathways, a homogeneous stoichiometry and a good adhesion between the coating and the substrate material [4]

Hence in practice wear, corrosion and fatigue are major concerns and coating life time is in many circumstances closely related to surface degradation problems. [3] In the present investigation, ZrN of varying thicknesses (Film thickness was chosen as the controlling parameter) were deposited on 316 stainless steel by cathode arc evaporation technique. Since stainless steel is an important metal used in daily life, AISI 316 stainless steel (316 SS) was chosen as the metal substrate for evaluating the applicability of these coatings in the present study.[5] The deposited coatings were subjected to characterization technique like SEM(Scanning electron microscope) and EDX(Energy dispersive X rays) after Corrosion (Potentiodynamic test and Electrochemical impedance spectroscopy(EIS)) in industrial corrosive environment).

2. Experimental Part

2.1. Thin film deposition

The deposition of ZrN thin films on 316 stainless steel of 4cm diameter was done at Cathode arc evaporation chamber of Multi Arc (I) Ltd. Umargoan. The cathode materials was Zr (99.95%) The surface to be coated was finely ground. After pre cleaning the samples of 316 Stainless steel (S.S) were placed in 64x 40 cm cylindrical chamber with rotating substrate holder The chamber was evacuated to a base pressure of 5×10^{-5} torr and the substrates were heated to about 200°C to remove adsorbed gases from the surfaces. Before deposition surface were etched with Argon plasma. High purity nitrogen gas with a maximum limit of all impurities -32 ppm was later introduced. The target to substrate distance was maintained at 20cm. A thin intermediate layer of Zr metal was deposited between substrate and ZrN . The substrate bias voltage for ZrN was 600 V for about 2-3 min initial bombardment and for thin intermediate layer, it was kept at 300V, later kept at 150-600V at evaporation current of 60 amp and nitrogen pressure of 0.005-0.008Mbar, 65 amp. and Nitrogen partial pressure of 0.005-0.008Mpa.

2.2. Potentiodynamic Test

Electrochemical corrosion measurements were performed with conventional three electrode cell. A computer assisted potentiostat (EG&G PAR 273A was employed to apply and scan the potential and display data resulting current density Vs potential curve. Data were analyzed using model M273 and M398 software .The corrosion coupons of 4cm diameter were masked with lacquer on surface but 10mmx10mm window was left on coated surface. A saturated calomel electrode (SCE) was used as the reference electrode (RE) to measure the potential across the electrochemical interface. A high-purity graphite rod was used as the counter electrode. The sample was placed in such a way that the Luggin capillary of the reference electrode was close to the working electrode and this distance was maintained for all the tests. The polarization curves were measured after 1 hr of stabilization at the corrosion potential so that a quasi-stable potential was reached. The curves were obtained by sweeping the potential from the direction of the cathode to the anode. The sweep-rate setting was 0.2 mV/sec The electrolyte used was various industrial environment like 3.5% NaCl (marine environment), 0.1N HCl(reducing acid and used in chemical conversion reactions) and 11pH Na_2SO_4 (paper and pulp industry). All tests were carried at surface open to air. The test was in accordance to Potentiodynamic (ASTM G59) practice. The plot of E vs. log I was obtained and was super imposed for various thicknesses in particular environment.

As a small amplitude sinusoidal signal is used throughout the EIS measurements, this technique does not significantly accelerate the corrosion reactions and, therefore, the coating surface is not affected too much and can be considered as a non-destructive method. In the present investigation the EIS data are plotted in terms of Bode Plot (Freq/Impedance/Phase angle)/ (Frequency/Impedence). The testing was in accordance with A.C Impedence (ASTM G106) Test.

3. Results And Discussion

3.1 Corrosion behaviour in 3.5%NaCl Environment

The corrosion potential of the steel substrate is about -0.446V . The corrosion potential of coated samples has a lower value than E_{corr} of the steel without a coating because the thin coating, having a high porosity, causes an electrochemical heterogeneity of the surface contacting the electrolyte. This heterogeneity is the reason for a physico-chemical instability of the substrate coating system in an aggressive environment. [6] The corrosion current density (i_{corr}) is an important parameter to evaluate the kinetics of corrosion reactions, normally proportional to the corrosion current density measured via polarization. The lower the i_{corr} , the lower corrosion rate the sample is. In the present test the i_{corr} value obtained is less than bare Stainless steel substrate. The i_{corr} values of the coatings in the anodic region are lower than stainless steel indicating protection of substrate. [7] As observed in Polarisation curve, in cathodic polarization region the coated samples starts at a current lower than the stainless steel, but near the corrosion potential the coated sample current increases until it becomes almost equal to that of stainless steel. This phenomenon can be explained by pitting of the coatings at

defect sites. [8] As indicated in Bode's plot fig(a) the difference in the impedance of $1.5\mu\text{ZrN}$ and $2\mu\text{ZrN}$ is less at high frequency whereas at low frequency difference is more indicating although both the coatings are having similar capacitive property, however $2\mu\text{ZrN}$ has better corrosion resistance property than $1.5\mu\text{ZrN}$, this may be due to increased number of defects in $1.5\mu\text{ZrN}$. [9] SEM studies were carried out to determine morphology of coating after typical anodic polarization tests in 3.5% NaCl.

Table. 1 Results for potentiodynamic test in 3.5% NaCl

	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a	β_c	mpy
S.S	-449.6	101.9	8.480	1.229	45.99
$1.5\mu\text{ZrN}$	-585.9	50.27	739.1E^{-3}	839.8E^{-3}	22.70
$2\mu\text{ZrN}$	-545.6	6.336	272.6E^{-3}	305.8E^{-3}	2.861

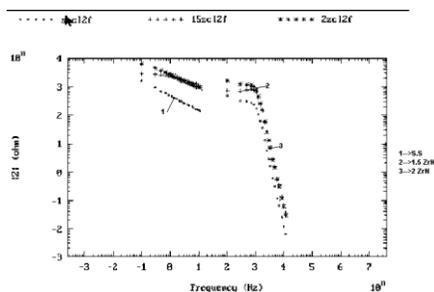
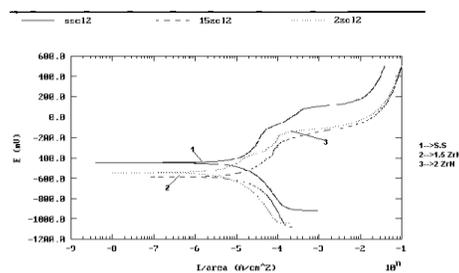
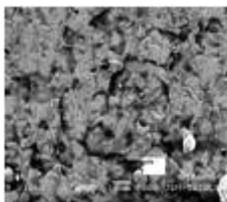


Fig 1(a) Bode curve for 3.5% NaCl



(b) Potentiodynamic curve for 3.5% NaCl

Fig 2 Typical SEM morphologies of the $2.0\mu\text{ZrN}$ coatings which had been subjected to the anodic polarization test in 3.5% NaCl

Surface image of the $2.0\mu\text{ZrN}$ coated alloy after corrosion tests is shown in Fig 3. When the SEM image was examined, it was seen that the coating layer was broken from the substrate as large pieces, causing removal of the larger pieces. The formation of the coating defects is very much difficult to avoid totally. Consequently, when subjected to a corrosive atmosphere, coated materials will form galvanic cells at the defects near the interface since ceramic coatings are electrochemically more stable than most substrate materials. Once aggressive ions such as chlorides penetrate the coating through these small channels, driven by capillary forces, the exposed area will begin to experience anodic dissolution, which will usually extend laterally along the interface between the coating and the substrate. Finally the pits to be formed linked up each other, causing removal of the entire coating by flaking. The coating defects e.g., pores, pinholes, cracks, observed at the SEM images before corrosion tests lead the electrolyte to reach to the substrate and contribute to developing of the corrosion. [3,10,11]

3.2 Corrosion Behaviour in 0.1N HCl Environment

The corrosion potential of the steel substrate is about -0.528V . The corrosion potentials (E_{corr}) of the coated specimens are only slightly away from that of stainless steel, within 25 mV, which indicates that the corrosion of the ZrN coated-specimens are mainly from the dissolution of the metal substrate and not from the ZrN film. Since corrosion potential is a thermodynamic property of the substrate material the variation of E_{corr} is not supposed to be far away from that of bare steel. [12,13]

The corrosion current density (i_{corr}) is an important parameter to evaluate the kinetics of corrosion reactions normally proportional to the corrosion current density measured via polarization. The lower the i_{corr} , the lower

corrosion rate the sample is. In the present test the i_{corr} value obtained for all the thickness is always less than bare Stainless steel substrate indicating protection of substrate. [14]

Table 2. Results for potentiodynamic test in 0.1NHCl

	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a	β_c	mpy
S.S	-460.6	1.827(mA/cm^2)	100.1 E^{24}	358.1 E^{-3}	825
1.5 μ ZrN	-471.5	63.28	227.6 E^{-3}	236.8 E^{-3}	28.57
2 μ ZrN	-491.1	12.53	190.5 E^{-3}	290.2 E^{-3}	5.6

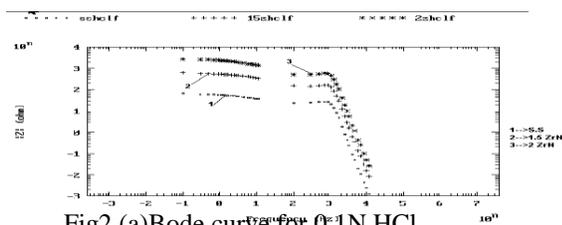
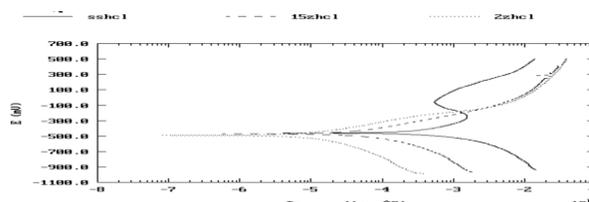


Fig2 (a)Bode curve for 0.1N HCl



(b)Potentiodynamic curve for 0.1NHCl

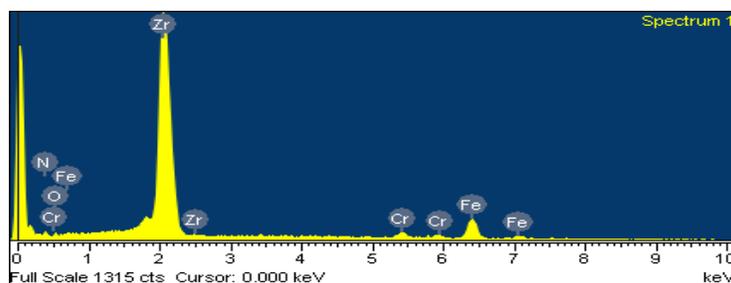
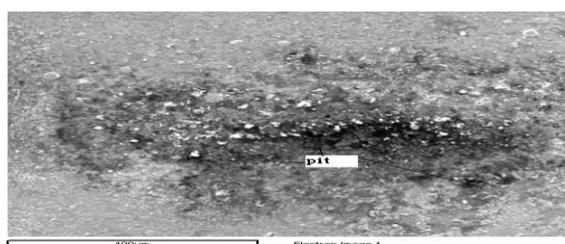


Fig3 The EDX analysis of 1.5 μ ZrN thin film subjected to potentiodynamic test in 0.1 N HCl

Surface image of the 1.5 μ ZrN coated alloy after corrosion tests is shown in Fig 3. The EDX indicates the intense peak of Zr, and less intense peaks of Fe, Mn. The coating system at 100X shows few very small and shallow pits.

3.3 Corrosion behaviour in 11pH Na_2SO_4 Environment

The corrosion potential of the steel substrate is about -0.508V . The corrosion potential of coated samples has a lower value than E_{corr} of the steel without a coating because the thin coating, having a high porosity, causes an electrochemical heterogeneity of the surface contacting the electrolyte. This heterogeneity is the reason for physico-chemical instability of the substrate coating system in an aggressive environment. [6]

It is well known that, the corrosion current density (i_{corr}) is an important parameter to evaluate the kinetics of corrosion reactions, normally proportional to the corrosion current density measured via polarization. The

lower the i_{corr} , the lower corrosion rate the sample is. In the present test the i_{corr} value obtained is less than bare Stainless steel substrate.

Table 3. Results for potentiodynamic test in 11pH Na_2SO_4

	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a	β_c	mpy
S.S	-725.6	30.99	51.91 E^{30}	288.6 E^{-3}	13.99
1.5 μ ZrN	-449.6	14.86	1.032	928.8 E^{-3}	6.710
2 μ ZrN	-490.4	7.928	831.6 E^{-3}	659.4 E^{-3}	3.598

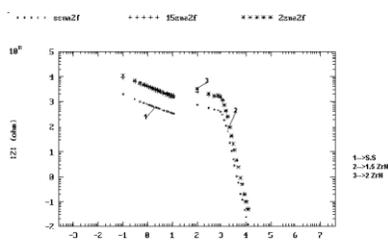
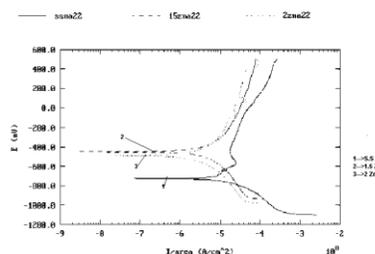


Fig 4 (a) Bode curve for 11pH Na_2SO_4



(b) Potentiodynamic curve for 11pH Na_2SO_4

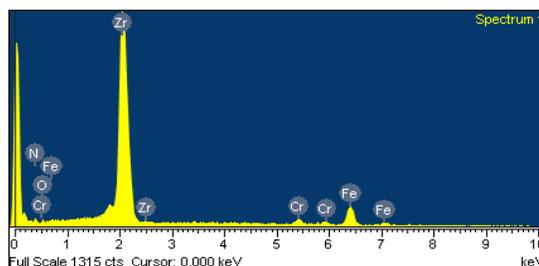
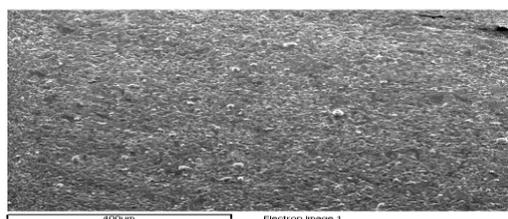


Fig 5 The EDX analysis of 2 μ ZrN thin film subjected to potentiodynamic test in 11pH Na_2SO_4

The EDX analysis of 2 μ ZrN thin film in Fig 5 indicates the large peak of Zr and small peaks of Fe, Mn. This indicates uniform and mild corrosion on the surface of coating.

Metals typically develop a passivation layer in moderately alkaline (high pH) solutions, which lowers the corrosion rate as compared to acidic (low pH) solutions. The passivation layer provides a measure of immunity to further corrosion, this is reason for higher corrosion resistance in 11pH Na_2SO_4 compared to 3.5% NaCl and 0.1N HCl

4. Conclusion

Electrochemical properties of ZrN coated on stainless steel was evaluated by potentio dynamic polarization and EIS test in 3.5% NaCl, 0.1N HCl and 11pH Na₂SO₄. Compared to stainless steel, coated samples show better corrosion resistance in all the cases. The corrosion resistance of thin film not only depends on composition and thickness but also on environment to which it is subjected to. As stated by Ellina Lunarska et al [15], it could be concluded that chloride ions are more aggressive than sulfate ions for stainless steel. It can be said that the presence of chloride ions in the solution affects the passivity of stainless steel substrate more negatively than that of sulfate ions. The effect of chloride ion is more aggressive in HCl compared to NaCl as the bonding in HCl is ionic and hence even when small potential is applied, its dissociation occurs whereas that in case of NaCl bonding is covalent resulting in better stability. However evolution of hydrogen decreases the in homogeneity in the corrosion behavior depicted by difference in E_{corr} values of coating and substrate in 3.5% NaCl, 11pH Na₂SO₄ and 0.1N HCl.[16]

5. References

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