Optical, Wear and Corrosive Properties of Ti-Si-N Nanocomposite coatings

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ABSTRACT

In this paper Ti-Si-N nanocomposite coatings were prepared by reactive magnetron sputtering on to different substrates at different power 50, 100, 150 and 200 watt at substrate temperature 400°. The photoluminescence (PL) spectra of the films show good optical properties. Ti-Si-N shows improved wear resistance properties compared Bare MS, TiN.The Topography and roughness parameter obtained using AFM and Corrosion properties using Auto lab.

Keywords – Optical, Nanocomposites, Sputtering, Si and Ti

1.INTRODUCTION

Ti-Si-N has excellent combination of hardware Properties, Corrosion resistive Properties ,high temperature resistance and good wear stability plays prominent role in industrial applications like automobile spare parts, space applications [1-5] .Generally , techniques like Physical vapor deposition (PVD) ,Plasma assisted Chemical Vapour deposition are used for developing hard coatings on various substrates [6-8].

The aim of the present work is to study the Optical, wear and Corrosion resistance Properties of Ti-Si-N thin films[9].

2. EXPERIMENTAL DETAILS

The 316L substrate surface was ground with SiC paper to remove the oxides and other contamination. The polished substrates were degreased alkali solution containing sodium hydroxide, followed by rinsing with triple distilled water. These substrates were subsequently dipped in 5 vol.-%H2SO4 solution for 1 min and thoroughly rinsed in distilled water.

Ti-Si-N nanocomposite coatings were deposited on different substrates by reactive DC magnetron sputtering deposition unit HIND HIVAC. the substrate temperature was 400°C High purity argon was fed into the vacuum chamber for the plasma generation. The substrates were etched for 5 min at a DC power of 50 W and an argon

pressure of 10^{-6}Torr (1.33X 10^{-4}Pa). High purity (99.99%) T i and Si targets of 7.5 cm diameter was used as cathodes. The deposition parameters for Ti-Si-N sputtering are summarized in Table 2.1

2.1.Deposition parameters for Ti-Si-N nanocomposite coatings.

Table 2.1.Deposition parameters for Ti-Si-N

Objects	Specification
Target (2"Dia)	Ti & Si
Substrate	Glass, Si wafer, 316L Stainless steel
Target to substrate distance	60 mm
Ultimate vacuum	1×10^{-6} m bar
Operating vacuum	2×10^{-3} m bar
Sputtering gas (Ar: N_2)	2: 1
Power	50, 100, 150, 200 W
Substrate temperature	400 °C

Ti-Si-N nanocomposite films photoluminescence (PL) measurements were made using a Cary eclipse fluorescence spectrophotometer (VARIAN) employing a PbS photo detector and a 150W xenon arc discharge lamp as the excitation light source. The Raman spectroscopy measurements used an excitation wavelength of 632.8 nm. The data were collected with a 10s data point acquisition time in the spectral region of 200–1000 cm-1 The topography and roughness of the films was analyzed atomic force microscope (Model: A.P.E.Research A-100) and Conventional three-electrode cell assembly was used for polarization studies as well as for impedance measurements. Electrochemical polarization studies were carried out using Auto lab Electrochemical workstation

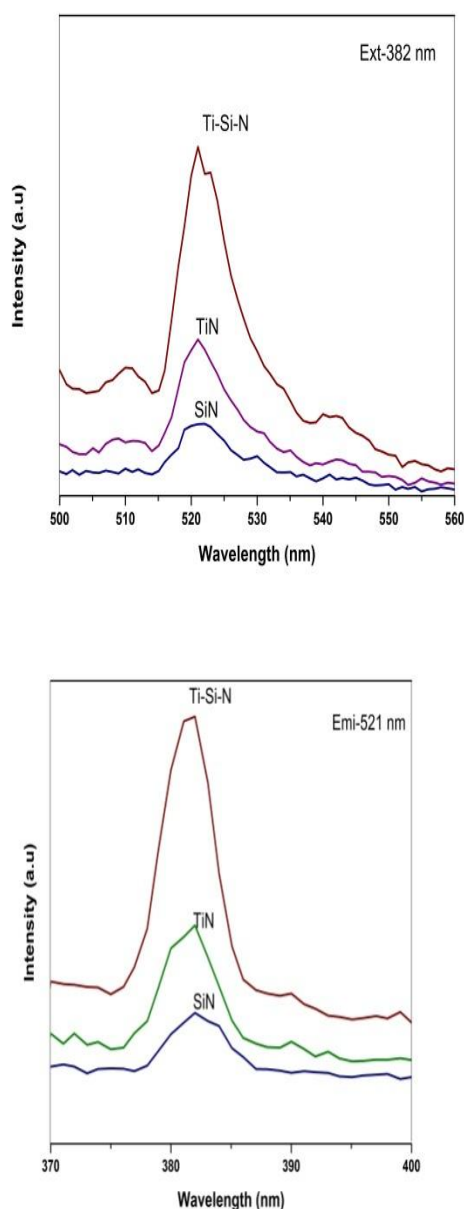## 3.RESULTS AND DISCUSSION
3.1. Photoluminescence spectra

Fig.3.1. PL spectra of SiN, TiN and Ti-Si-N coatings (a) emission (b) excitation spectra.

The photoluminescence (PL) spectra of Ti-Si-N, SiN and TiN coatings excitation peak at 382 nm are shown in Fig.3.1and emission peak at 522 nm. The nanocomposite coatings shows shift towards lower wavelength region by mixing of Si concentration TiN lattice.
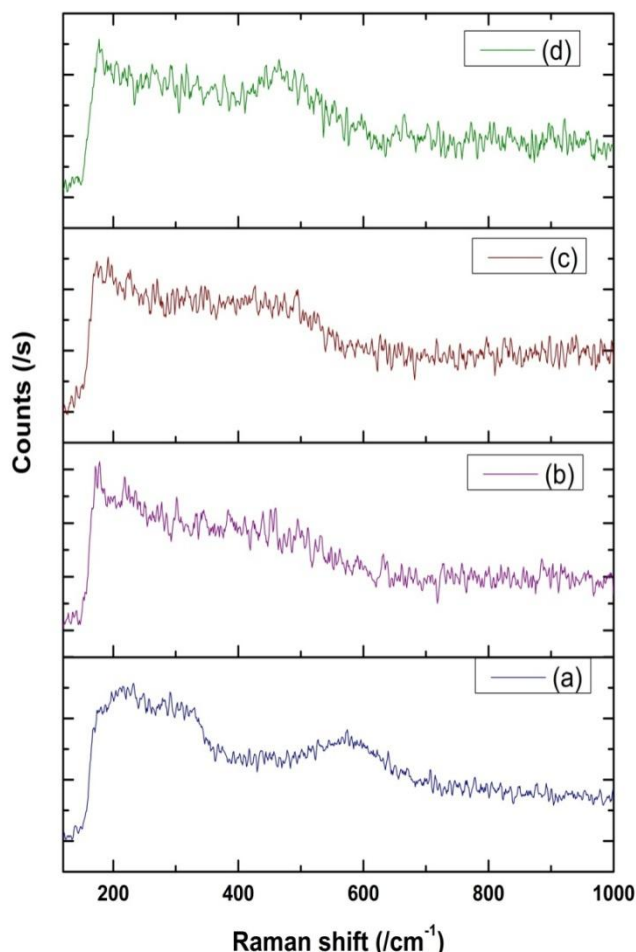
3.2. Laser Raman spectroscopy

Fig3.2. Laser Raman spectra of Ti-Si-N nanocomposite coatings at different powers.
(a)   50 watt   (b)100 watt (c) 150 watt (d) 200 watt

Raman microscopy is to elucidate the behavior of the optic and acoustic phonon modes of the (cubic) crystalline lattices. The phonon bands of Ti-Si-N have attributed the scattering in the acoustic range is determined by the vibrations of the heavy Ti ions (typically 150–300 cm^{-1}) and in the optic range by vibrations of the lighter N ions (typically 400–650 cm^{-1}).The characteristic peaks at 230, 300 and 580 cm^{-1}, related to transverse acoustic (TA) / longitudinal acoustic (LA), second-order acoustic (2A),and transverse optical (TO) modes of TiN, respectively, were observed in the Raman spectra of TiN films (**Fig 3.2**) prepared by reactive sputtering process. This is in good agreement with the reported values for Ti-Si-N films. Increasing the deposition power there is a slight shift to lower vibrations was observed and it is shown in Fig.3.2.

3.3. Morphological studies
The surface topography of the Ti-Si-N coatings was studied using Atomic force

microscopy (AFM). The basic study comprised 2D and 3D representations for a scanned area of 2X 2 μm, which are shown in **Fig 3.3.** The roughness value, estimated from these images was 5.3 nm, which shows that the films were very smooth in nature[7]
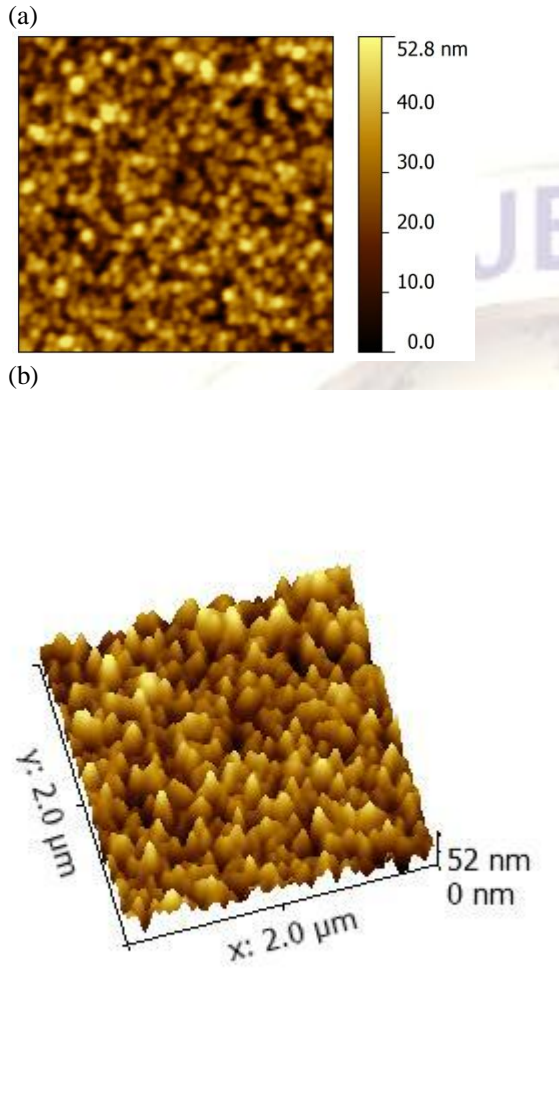
(a)

(b)

Fig .3.3. AFM Images of Ti-Si-N (a)2D Image (b)3D Image

3.4. Wear studies

The tribological characteristics of Ti-Si-N films were measured using block-on-ring test. The ring material used for this test is high chromium high carbon tool steel (850HV) for 120s. Ti-Si-N has more wear resistance than substrate, due to low coefficient of friction. Compared to TiN coatings, the wear rate of Ti–Si–N coating obviously decreased [9, 10].

Table.3.1.Wear rate for coated and uncoated substrates.

Substrate material	Wear rate (10^{-6} gm/mm)
Bare mild steel	6.5
TiN coated mild steel	6.3
Ti-Si-N coated mild steel	3.7

3.5. Electrochemical corrosion studies:

Electrochemical impendence spectroscopy and potentiodynamic polarization measurements were done using an Autolab system. A three electrode electrochemical cell system was used with a platinum counter electrode, saturated calomel electrode (KCl) as the reference electrode and sample as the working electrode. The sample was kept in the solution for 60 min prior to the potentiodynamic polarization study in order to establish the open circuit potential (E_{ocp}) or the steady state potential. The Tafel plot was obtained after the electrochemical measurements. The corrosion potential (E_{corr}) and the corrosion current density (I_{corr}) were deduced from the Tafel plot (that is log I Vs E plot). Impedance measurements were conducted using a frequency response analyzer. The spectrum was recorded in the frequency range of 10 mHz-100 kHz.

3.5.1 Corrosion studies in 3.5% Nacl solution

Electrochemical impedance spectroscopy measurement of the mild steel coated substrate spectrum shows higher resistance. The increase in R_{ct} value and decrease in C_{dl} values as shown in Table.3.2. For the Ti-Si-N on MS system confirm its better corrosion resistance property compared to the TiN, SiN and the bare substrate. It shows (Fig.3.5a.) the increase in corrosion resistance of the Ti-Si-N coatings compared to other coatings. Fig.3.5b. shows the bode plot of MS, SiN, TiN and Ti-Si-N nanocomposite coatings. The plots show higher charge transfer resistance for coated substrate[11].

Fig.3.5c. shows the polarization curves of mild steel (MS), SiN, TiN and Ti-SiN nanocomposite coatings in 3.5% NaCl solution. The E_{corr} and I_{corr} values have been calculated using the tafel extrapolation method and are given in Table.3.2.   The corrosion potential of the MS substrate is about -0.712 V. The coated samples shows positive corrosion potential, when compared to the MS substrate. The positive shift of E_{corr} indicates better corrosion resistance of the coated samples. The corrosion current is observed to be minimum 0.41×10^{-6}A/ cm^2 for the Ti-Si-N on MS

substrate compared to single layer and bare substrate. The corrosion rate has also minimum for Ti-Si-N nanocomposite coated substrate.

From the polarization test results, the protective efficiency, P_i (%) of the films can be calculated by Eq. (1)

$$P_i\left(\%\right)=\left[1-\left(\frac{i_{corr}}{i_{corr}^{0}}\right)\right]\times100 \qquad (1)$$

Where i_{corr} and i^{0}_{corr} indicate the corrosion current density of the film and substrate, respectively. The Ti-Si-N nanocomposite coating shows the highest protective efficiency of 97.2% caused by lowest corrosion current density of 0.41×10^{-6} $\mu A/cm^{2}$, compared to TiN and SiN coatings.

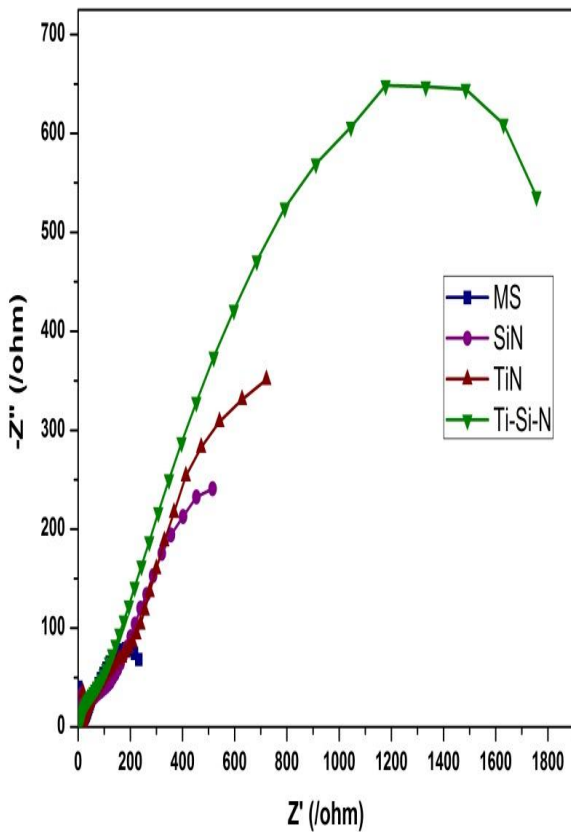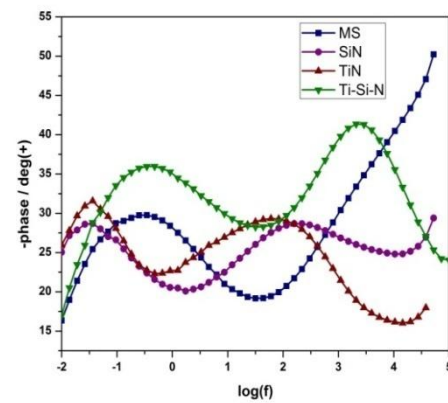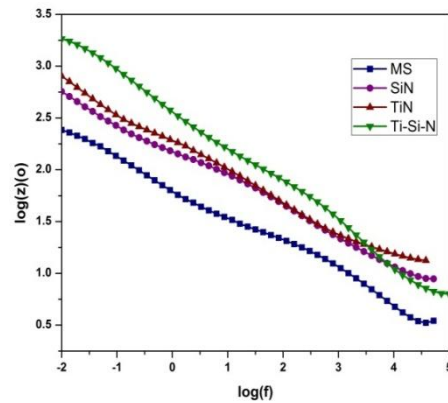Fig.3.5.b. Bode plot for (a) MS, (b) TiN, (c) SiN and (d)Ti-Si-N coatings in 3.5% NaCl solution.

Fig.3.5a. Nyquist plot for (a) MS, (b) TiN, (c) SiN and (d)Ti-Si-N coatings in 3.5% NaCl solution.
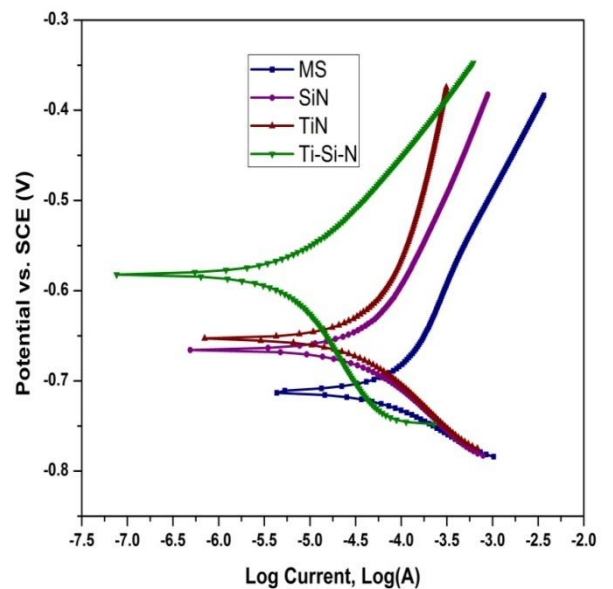

Fig.3.5c. The potentiodynamic polarization curve for (a) MS, (b) TiN, (c) SiN and (d)Ti-Si-N coatings in 3.5% NaCl solution.

Table.3.2. Polarization and impendence data obtained from Tafel and Nyquist plots.

Sample	E_{corr} V	b_a V dec^{-1}	b_c V dec^{-1}	I_{corr} $\times 10^{-6}$ Acm^{-2}	Corrosion rate mpy $\times 10^{-2}$	R_{ct} ohm cm^2	C_{dl} $\times 10^{-6}$ F/cm^2	P_i (%)
MS	-0.712	0.014	0.035	14.79	55.45	230	8.712	-
TiN	-0.665	0.016	0.005	2.98	11.17	508	1.299	79.8 %
SiN	-0.653	0.007	0.010	1.84	6.91	708	0.640	87.5 %
Ti-Si-N	-0.582	0.011	0.012	0.41	1.56	1754	0.140	97.2 %

I. CONCLUSION

Ti-Si-N nanocomposite coatings were prepared by reactive magnetron sputtering on to different substrates at different power. The photoluminescence (PL) spectra of Ti-Si-N shows excitation peak at 382 nm and emission peak at 522 nm. Ti-Si-N has more wear resistance than the bare substrate, due to low coefficient of friction. The Topography and roughness parameter obtained using AFM analysis indicated that the coatings were regular with smooth structure around 5.3nm roughness. From Electrochemical corrosion studies Ti-Si-N on MS system confirm its better corrosion resistance property compared to the TiN, SiN and the bare substrate

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