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Improvement of Corrosion Resistance by Vacuum Arc Evaporation PVD Thin Film TiN Coating

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Generally, engineering materials must have some specific characteristics and those characteristics which are important in selecting material for specific applications related with material structure and life-time. It is difficult to find all these features especially mechanical and surface properties in a single material. So the solution is found by increasing the strength of bulk material, and increasing wear and corrosion resistance of the surface. Therefore, engineering materials are selected from cheaper materials providing needed structural features, and the other surface characteristics are provided from coatings. Friction and wear of the sliding components in an automobile cause an increase in both fuel consumption and emission. Many engine components involved with sliding contact are all susceptible to scuffing failure at some points during their operating period. Therefore, it is important to evaluate the effects of various surface coatings on the tribological characteristics of the automobile parts. In this study, the corrosion protective properties of Vacuum Arc Evaporation PVD coatings were investigated and the relation between corrosion protective properties was investigated.

Keywords: Ceramic coating, Corrosion, PVD, TiN

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1 Introduction: This Corrosion is a severe problem which is defined as deterioration of material properties by its reaction with the environment. Most often, the reason behind corrosion is an electrochemical reaction of material in presence of a liquid or gaseous medium [1]. One of the most effective methods for preventing this harmful effect of corrosion is providing a protective barrier coating between the part and corrosive environment. PVD-ceramic coatings have been widely used as thin protective layers in many applications due to the excellent properties of thin films of ceramics such as high hardness, good wear and corrosion resistance, high electrical conductivity, chemical stability and good adhesion. TiN is one of the commonly used ceramic in tool industry for improving corrosion and wear resistance [2-5]. Titanium Nitride is an extremely hard, inert, thin film coating that is applied primarily to precision metal parts. TiN has an ideal combination of hardness, toughness, adhesion and inertness. TiN coating has the appearance of gold, but it is an ultra hard material, comparatively harder than carbide and three times harder than chrome. Can be applied to most metals to provide enhanced surface characteristics. Is highly inert and will not corrode because of its high chemical resistance. It has got extremely strong adhesion to the substrate metal. Thin film typically 2 to 3μm thickness is suitable for applications where good wear resistance is required [6]. Adhesion of the coating to the substrate is also an important factor with respect to corrosion protective properties. If the coating does not adhere well to the substrate the coating can easily delaminate, hence exposed substrate surface can increase. The adhesion properties of the coating to the substrate are a function of the coating type and surface cleanliness. Also high-energy ion bombardment and heating of the coated surfaces may cause diffusion of the metallic layer between the metal and the coating to the substrate, hence corrosion resistance of the substrate could be improved. Another possibility for the improvement of corrosion resistance is the deposition of inter layers and/or multilayered coatings. Such inter layers may be deposited by physical or electrochemical processes (PVD, ECD) [7]. In this study, the corrosion protective properties of PVD-TiN coatings were investigated and the relations between corrosion protective properties were studied.

2 Experimental Details: The TiN coated samples were prepared by vacuum arc evaporation (VAE) process on a 304 SS substrate of dimension 10 x 10 x 60 mm. The samples were polished as per requirement of VAE process standards. The coating thickness of the sample was analyzed using Fisherscope and adhesion was ensured by indentation method. The hardness of the coating layer was compared with that of substrate by Nano indentation method. The coated samples were inspected using SEM and TEM analysis for coating morphological study and compositional analysis. The corrosion properties of coated and uncoated samples were investigated using potentio-dynamic polarization method. Corrosion experiment parameters are described in Table 1.

Table (1): Corrosion Experimeter Parameters

Parameters	**Normal 304 SS**	**TiN Coated 304 SS**
Beta A (mV)	275.568	114.864
Beta C (mV)	281.601	238.669
Icorr (µA)	2.54e+00	1.68e-01
Ecorr (mV)	-452.714	-343.533
Corrosion Rate (mpy)	2.34e+00	1.55e-01

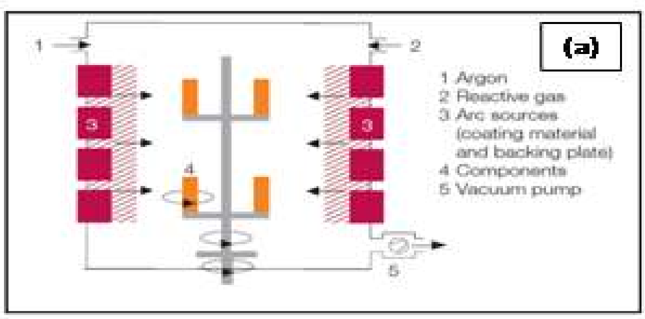


Figure (1a): Schematic diagram of PVD vacuum arc evaporation technique

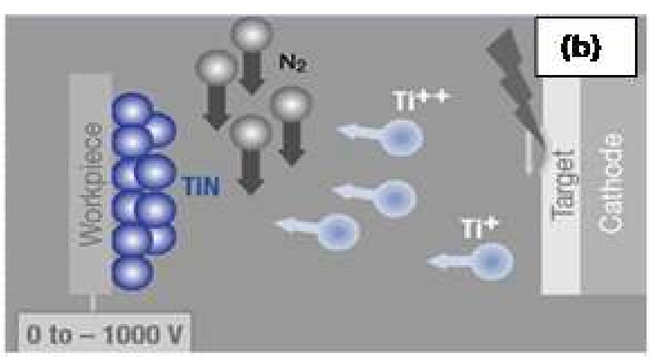


Figure (1b): Schematic representation of VAE mechanism.

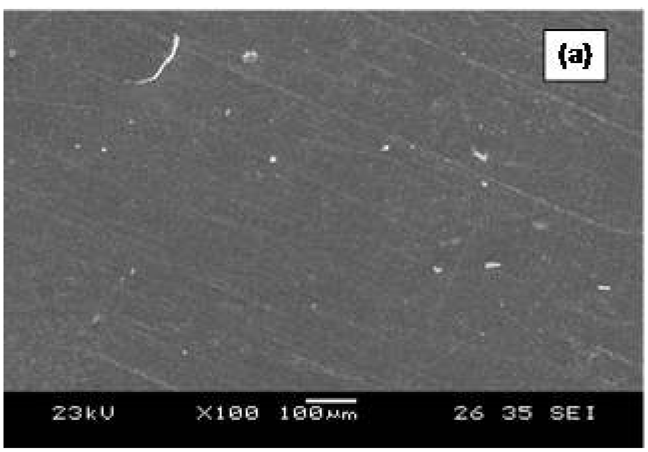
3 Results and Discussion:

Coating characterization: The coating thickness was checked using a Fisherscope and found to be in the range 1.9 µm. A coating thickness of 2 µm has been found to give the best tool life in steel tools [8]. The coating adhesion test was done by indentation method and was found good. The hardness of the VAE PVD applied coating layer was checked using Nano-indentation method. And the result are as furnished in Table 2.

Table (2): Nano indentation test results

Max Depth (nm)	Load (Nm)	Hardness (Gpa)	Young's modulus (Gpa)
69.68	2.86	14.9	243.71
111.85	5.85	11.64	224.79
146.7	8.89	13.24	181.89
194.5	11.74	11.25	174.28
222.84	18	15.28	183.04
334.87	26.25	12.44	149.85
337.76	28.65	11.51	193.22
449.51	37.7	11.79	128.77
504.63	47.75	12.91	122.58
521.36	51.9	13.83	122.1

The average coating hardness found to be 12.879 Gpa i.e. 1312 HV where as the substrate hardness is about 128.5HV.



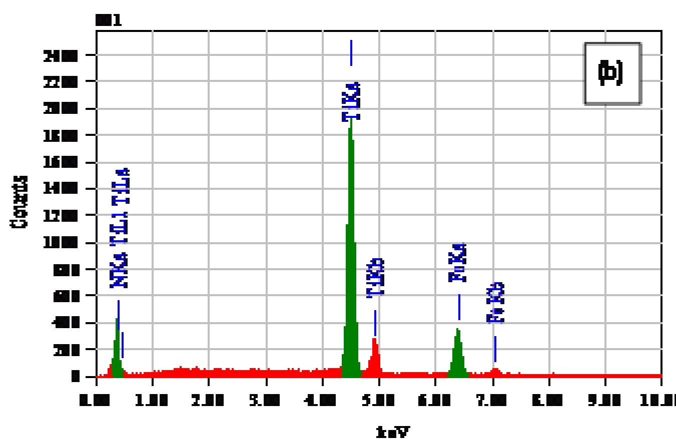


Figure (2a): SEM Image of TiN Coated Sample. Figure: (2b): EDS MAPPING of Coated Sample.

The image of SEM analysis Figure (2a) shows a continuous film of coating on the substrate and the EDS graph ensures Figure (2b) that the coating material is TiN. Since the film coating is in 2 micron range the EDS analysis shows the peaks of Iron from substrate.

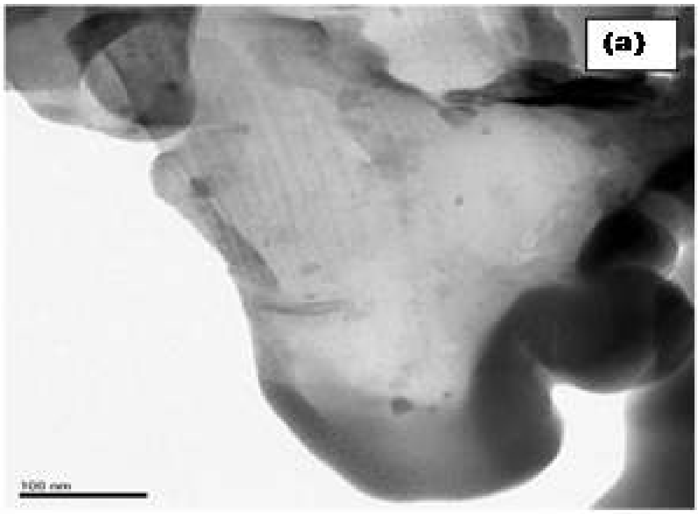


Figure (3a): TEM Image of Coated Sample.

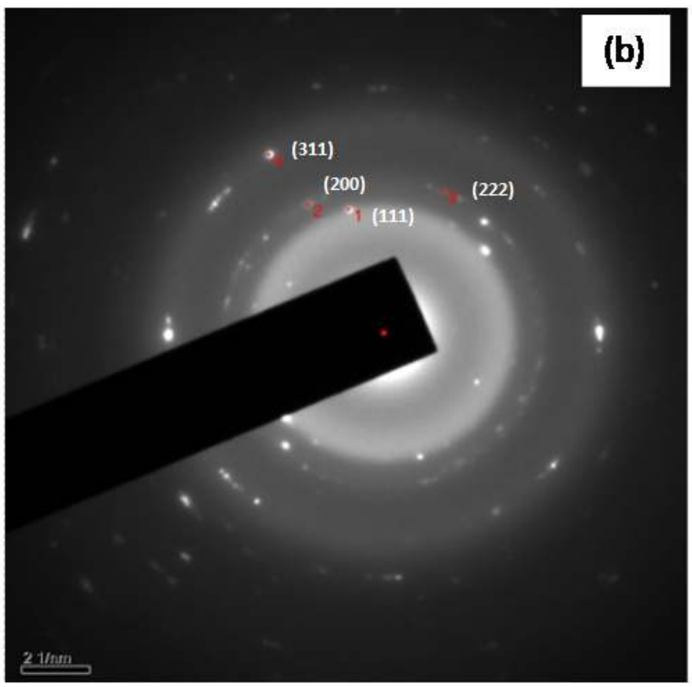


Figure (3b): SAD Pattern of TiN Coated Sample.

TEM is an indispensable analytical tool in the study of the microstructure of coatings. TEM analysis results as shown in Figure (3a), (3b) provides a strong backing of coating continuity and it also gives an indication of mixed nature that is amorphous and crystalline nature of TiN. The d-Spacing indexing of SAD Pattern ensures the particle is TiN. Since Coating is done through VAE PVD Method, the TiN may be partially converted to amorphous in nature, which will improve the corrosion resistance.

Corrosion Studies: In corrosion tests, the corrosion medium was prepared by dissolving 3.5 gm NaCl in 100 ml water and all the tests were carried out at room temperature, with the help of a Faraday's Box. The sample surfaces were cleaned by acetone and distilled water. The Corrosion studies were done using by potentio dynamic polarization technique. The results were plotted by taking Icorr (Corrosion current) in X-axis and its abscissa is Ecorr (Corrosion potential). The cathodic and anodic polarization curves are noted from the plots and the corrosion rates in terms of mpy (milli inches per year) are estimated.

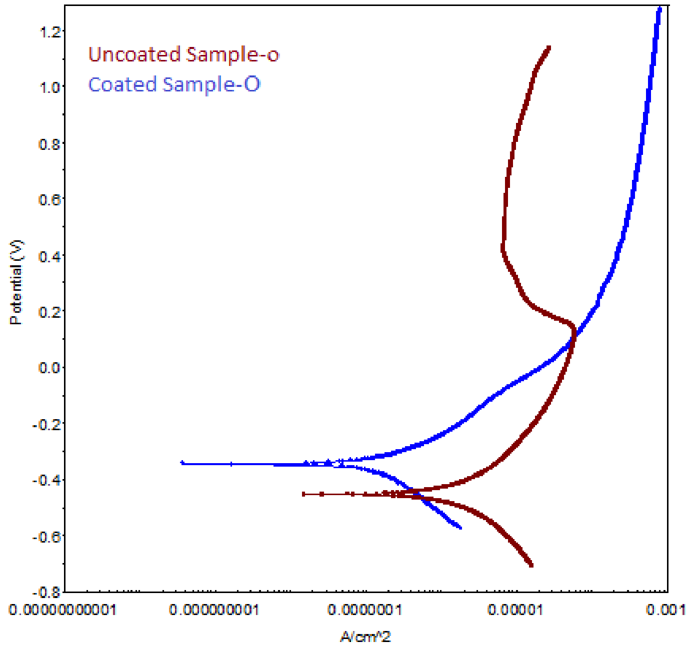


Figure (4): Voltage versus current plot of the potentio-dynamic polarization corrosion test.

From the above graph Figure (4) the superior corrosion resistance of TiN coated sample is evident. And the corrosion rates are estimated from the individual plots as below.

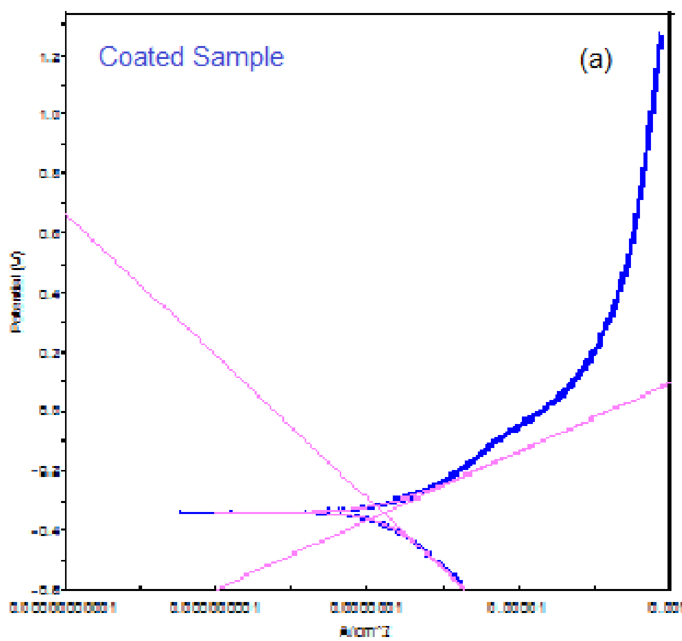


Figure (5a): Extrapolating the anodic and cathodic curves to estimate the corrosion rate of TiN coated sample.

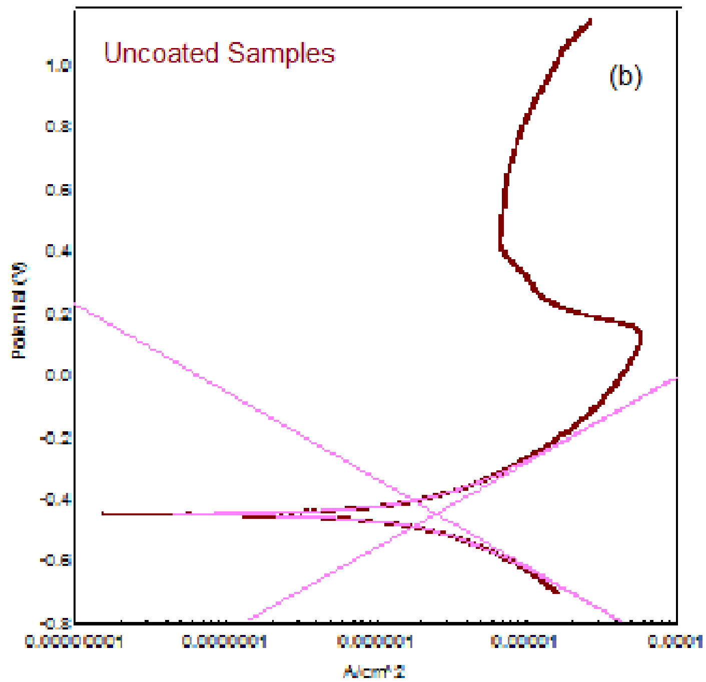


Figure (5b): Extrapolating the anodic and cathodic curves to estimate the corrosion rate of uncoated sample.

From the graph described in Figure (5) , it can measured out that The TiN coated sample's corrosion rate is 1.55 milli inches per year (mpy) , where as the corrosion rate of the uncoated sample is 323.4 mpy.

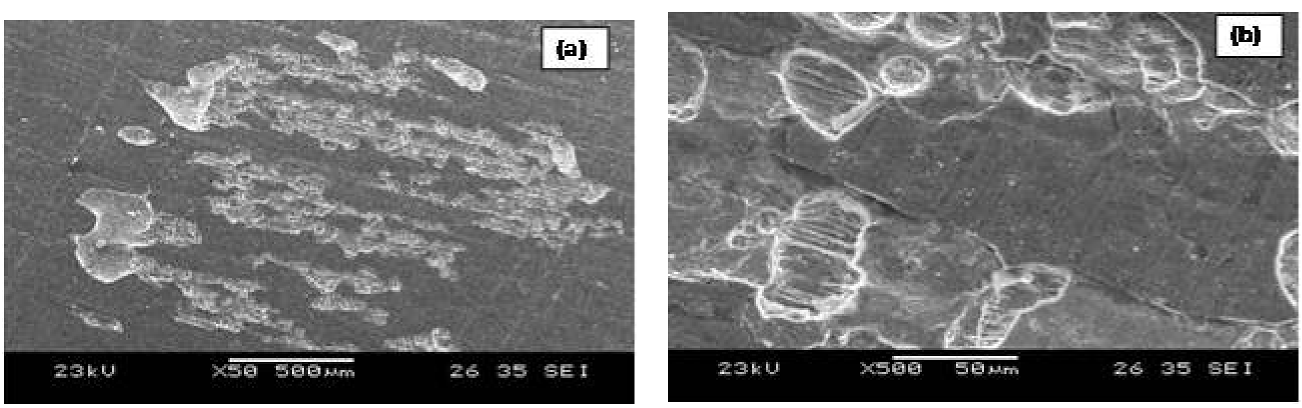


Figure (6): SEM images of the corroded area on the TiN coated sample after the corrosion test.

Figure (6) shows SEM images of corroded area the TiN coating layer after the potentio-dynamic polarization corrosion test. Ceramic coatings are chemically inert in neutral or acidic media, but generally have inherent micron level porosity and some coating defects. Therefore, 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 (e.g. steels). Once aggressive ions such as chloride penetrate the coating through these small channels, driven by capillary forces, the exposed area will begin to experience anodical dissolution, which will usually extend laterally along the interface between the coating and the substrate. Corrosion may be then accelerated to high rates since the coating presents a large cathodic area compared to the very small exposed substrate, which serves as an anode. Thus the protection of the substrate is no longer effective, leading to a strong local corrosion attack [8].

4 Conclusions: According to the testings done on the TiN coating deposited on 304 stainless steel substrate using the vacuum arc evaporation PVD technique the conclusions are as follows:

- The coating thickness measured with Fischerscope showed the thickness to be 1.9 μm which is the optimum coating where there is sliding friction.
- The Rockwell adhesion test gave good adhesion of coating layer to the substrate.
- The nano indentation test showed the TiN coating hardness.
- The SEM and TEM analysis confirmed the coating layer material as TiN and the presence of 2 phases crystalline and amorphous which enhances corrosion resistances.
- The SEM and TEM analysis confirmed the coating layer material as TiN and the presence of 2 phases crystalline and amorphous which enhances corrosion resistances.
- The corrosion testing results shows that Ceramic coating on ss-304 reduces corrosion rate from 23.4 mpy to 1.54 mpy and it proves that Ceramic coatings like TiN improve the corrosion resistance of the system because coating materials are normally relatively noble and coating layer acts as a protective barrier between the part and corrosive environment.

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