Corrosion & Micro Structural Property Analysis of Hard Coated SS304

Rilav B. Shah[a], Pina M.Bhatt[b], Naitik S.Patel[c],

[a] *Production Engineering (Mechanical Department), M.E.C, Mehsana- 384315, India*

[b] *Mechanical Department, R.K University, Rajkot, India*

[c] *Mechanical Engineering Department, M.E.C, Mehsana- 384315, India*

ABSTRACT

The aim with this experimental and analysis work is to extend the understanding of corrosion and micro structural behaviour of hard coated SS304 deposited with composite layers. Thin Films of TiAlN and TiCrN have been deposited on SS304 substrate using Cathodic Arc Evaporation (CAE-PVD) Method. The corrosion behavior of TiAlN and TiCrN coating layers on SS304 will be studied by Potentiodynamic Polarization Analysis and then their corrosion rates will be compared with uncoated substrate. The phases have been confirmed by carrying out X-Ray Diffraction (XRD) analysis and Energy Dispersive Spectroscopy (EDS). The microstructure of deposited film is studied using Field Emission Scanning Electron Microscopy (FESEM).

Keyword: *PVD Coatings, SS 304, Cathodic Arc Evaporation, TiAlN, TiCrN, Coating, FESEM, XRD.*

INTRODUCTION

Coating industry is one of the largest growing industries these days as coating has become a very important part of a manufacturing process. Coating highly enhances the working life of a component or an assembly, its working range as well as its working efficiency. But due to some of its major disadvantages, coating by micro and nano particles has took over the place of conventional coating materials like zinc. It enhances properties like hardness, corrosion resistance, thermal stability, wear resistance, etc. Due to its high adhesion property with the substrate surface as well as between their particles, it is highly recommended in compare to conventional coating materials. Materials like Titanium, aluminium, chromium, are deposited by processes like physical vapour deposition (PVD), magnetron sputtering, high velocity oxygen fuel (HVOF) in high vacuum medium of gases like nitrogen. Initially these coating layers were deposited as single layers. But to increase the working range of the substrate, two or more coating materials were combined either as successive layers or composite layers to get the most advantage of the component or an assembly. So coating industries started using coating materials like Titanium Aluminium Nitride (TiAlN), Titanium Chromium Nitride (TiCrN), etc on a huge scale.

Corrosion has always been a major issue for deterioting any material or a component during its working cycle and thus decreasing the life and efficiency of the component. Though materials like SS304 have the least chances to corrode but it has also some limitations with respect to some specific fluids. The atmosphere due to presence of these particular types of fluids can increase the corrosion rates of the component. This activity can be controlled by using dual or triad composite coating layers. To study the corrosion behaviour of any coating material, Potentiodynamic Polarization analysis is considered as one of the most effective tool in today's world. The anodic and cathodic behavior of the material is studied to find the corrosion rates of the material by supplying controlled electrical energy. This test feed us the information of the corrosion behavior of the material of short period or short time and then it can be compared to find out the actual corrosion time. The readings are obtained in graphical format and the corrosion rates are then calculated from the current and potential values. Like Potentiodynamic Polarization, one of the most effective ways to study the micro structures of any material is to examine it under a scanning electron microscope. But as SEM has its own limitations of magnification, Field Emission Scanning Electron Microscope is used instead of a normal SEM. FESEM gives a very detailed image of the coated substrate by the magnification range of around 50 000 X. This magnified image can give us many informative data regarding the micro structural behavior of the coated substrate material. In this paper, the study of corrosion and micro-structural behavior of SS304 which is coated with Titanium Aluminium Nitride (TiAlN) and Titanium Chromium Nitride (TiCrN) films has been mainly focused. And these behaviors have been studied using Potentiodynamic Polarization test and Field Emission Scanning Electron Microscope (FESEM).

EXPERIMENTAL DETAILS

Substrate Material

The complete work is executed taking Stainless Steel 304 grade as the main substrate material chemically composed of Carbon 0.047 %, Silicon 0.340 %, Manganese 1.320 %, Phosphorous 0.040 %, Sulphur 0.010 %, Chromium 18.650 % & Nickel 8.040 %. Stainless Steel is mainly used for applications where properties like corrosion have to be fought off majorly in working condition. It is a soft material in compare to its other grades like tool steel or mild steel. Before the actual coating process is executed, the substrate is cleaned by ultrasonic cleaning process.

Coating Materials

Two hard coating films like Titanium Aluminium Nitride (TiAlN) & Titanium Chromium Nitride (TiCrN) is deposited on the surface of SS304 substrate. These are not deposited in successive layers one above the other in composite form. TiAlN hard coat is mainly for thermal applications where TiCrN is mainly for corrosion applications. TiAlN exerts dark ash colour whereas TiCrN exerts light silver colour.

Cathodic Arc Deposition Technique

The cathode spot is the extremely small and hot cathodic root of a high current low voltage arc. It melts and evaporate the cathode material forming a kind of micro crucible which has a diameter of about 1µm to 20µm. When it extinguishes, a new micro curable is formed near by the former one. This way, the cathode surface leaves irregular strings of small craters. The machine is equipped with eight cathodic semicircle sources. When the arc current is increased twice or thrice or so on, arc splits off. The spot velocity of the total number of micro droplets shows a maximum at an angle, which seems to be somewhere between 20º and 60º to the plane of the cathode depending on the experimental conditions. The mechanism is equipped through 6 cathodic arc sources. Nitrogen is supplied by a flow into the deposition chamber. The temperature of the deposition on the substrate material should be started from 25°C to 750°C. The nitrogen deposition pressure applied on to the coating material was 3.5Pa. The use of such coatings is aimed at improve efficiency through bettered performance and highly component life.

Coating Thickness

Thickness of the coating films is found out using Digital Coating Thickness Gauging system. This system senses the lowest as well as highest point on the surface of the coated substrate and gives us all the readings. From these readings, an average is calculated from these readings. The coating thickness of Titanium Aluminium Nitride (TiAlN) film and Titanium Chromium Nitride (TiCrN) film is given below in tabular form.

SS304 substrate coated with TiAlN film	23 µm
SS403 substrate coated with TiCrN film	30 µm

Potentiodynamic Polarization Test

Numerous corrosion phenomena may be explained when it comes to electrochemical reactions. It comes after then, that will electrochemical techniques can be used to study these types of phenomena. Size of current-potential interaction under carefully controlled conditions can generate information with corrosion rates, coatings along with films, passivity, pitting tendencies and also other important information. Potentiodynamic anodic polarization may be the characterization of your metal example of beauty by their current-potential relationship. The substrate potential is scanned slowly within the positive going direction and for that reason acts being an anode so that it corrodes or maybe forms a great oxide finish. These measurements are used to establish corrosion attributes of material specimens with aqueous conditions. A comprehensive current-potential plot of your specimen may be measured in some hours or, in certain cases, a few minutes. The test is conducted under scan rate of 5.0 mV/s in -500 mV to 800 mV potential in 0.25 cm^2 surface area.

Figure 1:- Potentiodynamic Polarization test

Field Emission Scanning Electron Microscopy

Microscopy techniques are utilized to create real place magnified images of any surface displaying what it appears to be. In basic microscopy data concerns surface area crystallography. It possesses a metallic sample as a pointed tip as well as a conducting neon screen encased in ultrahigh vacuum. The tip radius used is usually the order 100 nm. It comprises a metal that has a high melting point, including tungsten. The actual sample is held with a large negative potential (1-10 kV) in accordance with the neon screen. This provides electric field near the tip apex to become the order of 1010 V/m that is enough of for field emission regarding electrons to occur. This experiment is conducted at high voltage of 10.00 kV in the mode of scattered electron detected by everhart thronley detector magnified from 10000 X to 35000 X at a working distance of 15.4 mm examined at the size of 2 µm - 5µm.

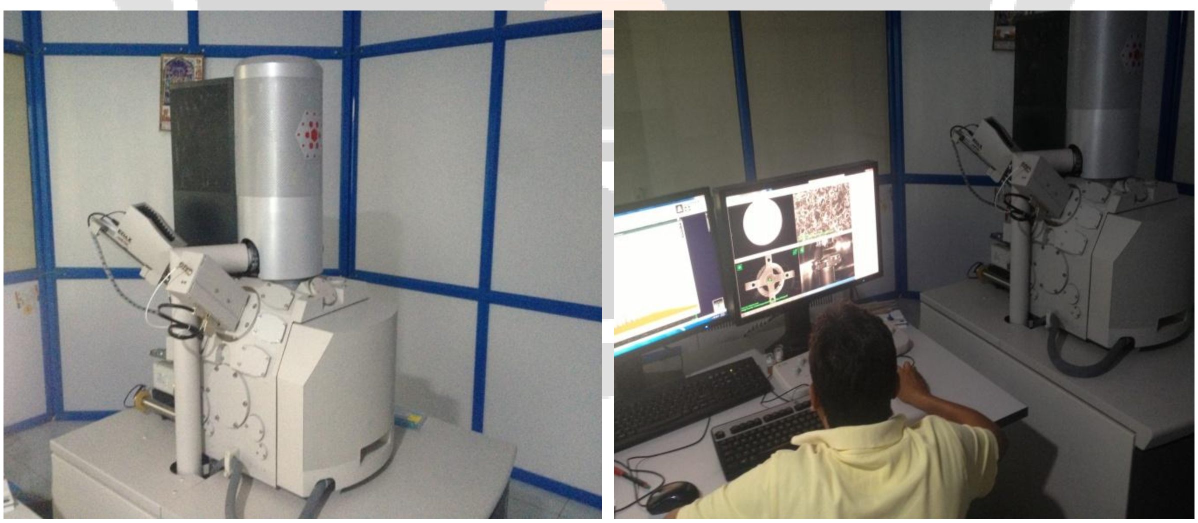


Figure 2:- Experimental setup of Field Emission Scanning Electron Microscopy

RESULT AND DISCUSION

Corrosion Analysis

- Images of Potentiodynamic Polarization scan of uncoated and substrates coated with TiCrN and TiAlN films presented individually.

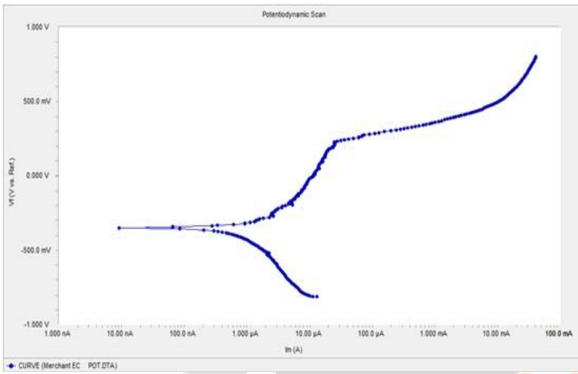


Figure 3:- Potentiodynamic Polarization Scan of Uncoated SS304

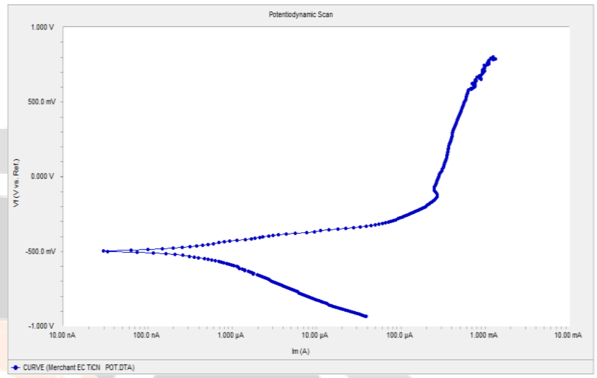


Figure 4:- Potentiodynamic Polarization scan of SS304 substrate coated with Titanium Chromium Nitride (TiCrN)

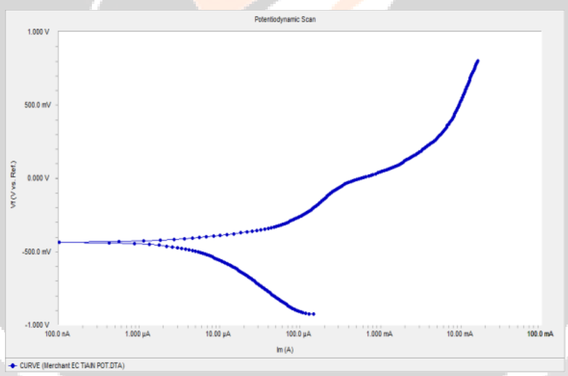


Figure 5:- Potentiodynamic Polarization Scan of SS304 substrate coated with Titanium Aluminium Nitride (TiAlN) film

Figure 3 shows E_{corr} versus I_{corr} potentiodynamic polarization plot of uncoated SS304 substrate. The I_{corr} value is 359.0 nA and E_{corr} is -353.0. The final corrosion rate value comes as 0.541. There are no oxidation layers formed during experiment as it shows no 's' curve in cathodic range. Figure 4 shows E_{corr} versus Icorr potentiodynamic polarization plot of SS304 substrate coated with Titanium Chromium Nitride (TiCrN) layer. The I_{corr} value is 252.0 nA and E_{corr} is -499.0. The final corrosion rate value comes as 0.380. We can easily observe that the corrosion rate of SS304 substrate coated with TiCrN in compare to uncoated SS304. This is due to the oxidation layers formed during experiment as it shows's' curve in cathodic range.

Figure 5 shows E_{corr} versus I_{corr} potentiodynamic polarization plot of SS304 substrate coated with Titanium Aluminium Nitride (TiAlN) layer. The I_{corr} value is 2.280 µA and E_{corr} is -437.0. The final corrosion rate value comes as 3.437. We can easily observe that the corrosion rate of SS304 substrate coated with TiCrN in compare to uncoated SS304. There are no oxidation layers formed during experiment as it shows no 's' curve in cathodic range.

- Image of comparison of Potentiodynamic Polarization scans of uncoated and substrates coated with TiAlN and TiAlN films.

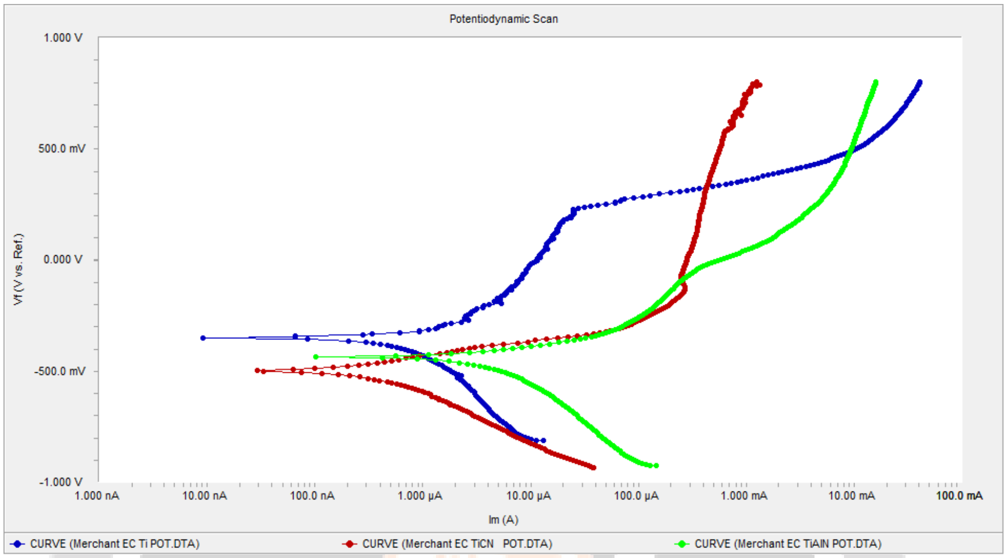


Figure 6:- Comparison of Potentiodynamic scans of uncoated & substrates coated with TiCrN & TiAlN films

Figure 6 shows the comparison of potentiodynamic scans of uncoated SS 304 substrate and coated with Titanium Chromium Nitride (TiCrN) & Titanium Aluminium Nitride (TiAlN) in 3.5 % NaCL solution.The uncoated SS304 Austenite Stainless Steel exhibits passivation behaviour and having active potential of -357 mV.It is corroded at the rate of 0.541 mpy in 3.5 NaCL. From the above results it can be concluded that there is an improvement in corrosion resistance of uncoated SS 304 when it is hard coated with Titanium Chromium Nitride (TiCrN). But there is a slight increase in corrosion rate when it is hard coated with the layer of Titanium Aluminium Nitride (TiAlN). So it has been suggested that the Austenite Stainless Steel 304 should be hard coated with the layer of Titanium Chromium Nitride (TiCrN) to enhance its corrosion resistance property.

- Table representing Ecorr values versus Icorr values of uncoated and coated SS304 substrate with TiCrN and TiAlN layers with their respective corrosion rates.

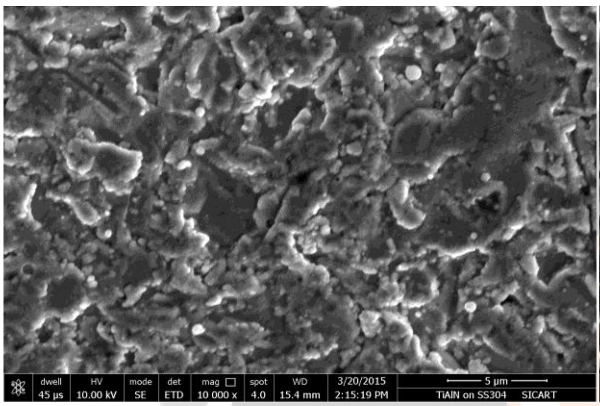
Sr. No	Sample	Icorr	Ecorr (mV)	Corrosion Rate (mpy)
1	Uncoated SS304	359.0 nA	-353.0	0.541
2	SS304 coated with TiCrN	252.0 nA	-499.0	**0.380**
3	SS304 coated with TiAlN	2.280 µA	-437.0	3.437

Table 1:- E_{corr} values versus I_{corr} values of uncoated and coated SS304 substrate with TiCrN and TiAlN layers with their respective corrosion rates.

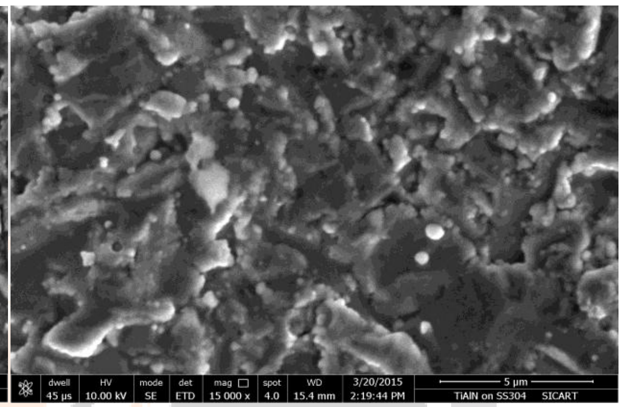
The above Table 1 shows the comparison of all E_{corr} values versus I_{corr} values of the potentiodynamic polarization plot of uncoated SS304 substrate with coated SS304 with Titanium Chromium Nitride (TiCrN) layer and Titanium Aluminium Nitride (TiAlN) layer respectively. From the corrosion rate values received from these plots and the table given below, we can easily observe that the corrosion rate of SS304 substrate coated with the layer of Titanium Chromium Nitride (TiCrN) is slightly less than that of the uncoated substrate. This is due to the‘s’ curve formed in the cathodic zone due to oxidation layer formed during the experiment. On the contrary, corrosion rate of SS304 substrate coated with the layer of Titanium Aluminium Nitride (TiAlN) is higher than uncoated substrate as well as the substrate coated with TiCrN layer.

Micro Structural Analysis

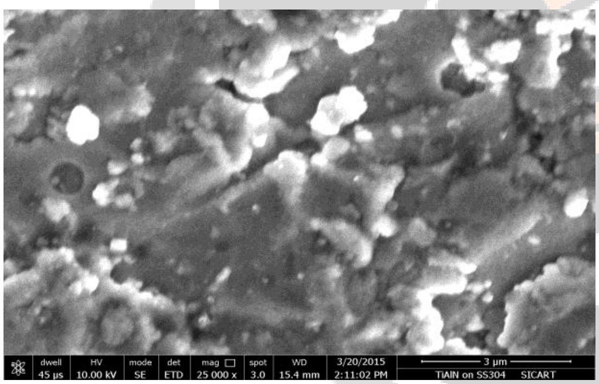
The microstructure of the substrate is captured by FEG-SEM NANO NOVA 450 Instrument. The below images are scans of the substrate coated with Titanium Aluminium Nitride (TiAlN) film. Four images were captured at different magnifications of 10 000 X, 15 000 X, 25 000 X and 35 000 X.



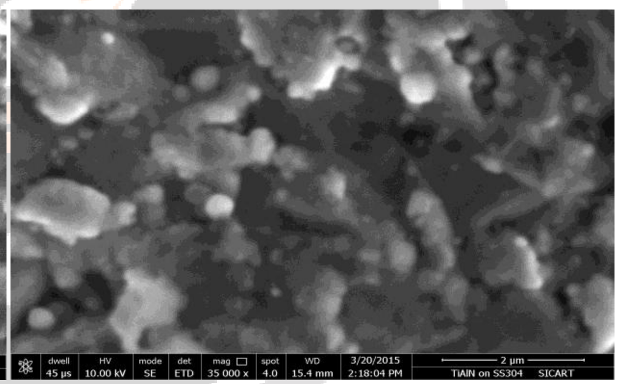
(a)



(b)



(c)



(d)

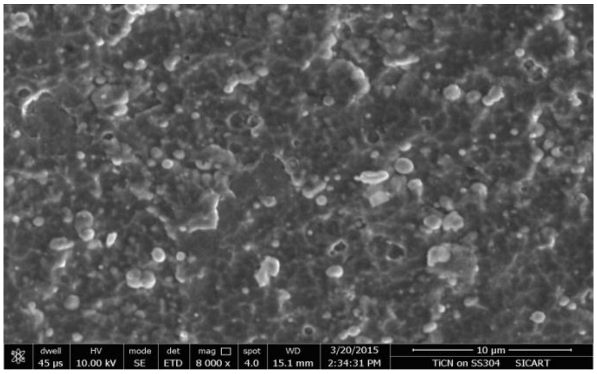
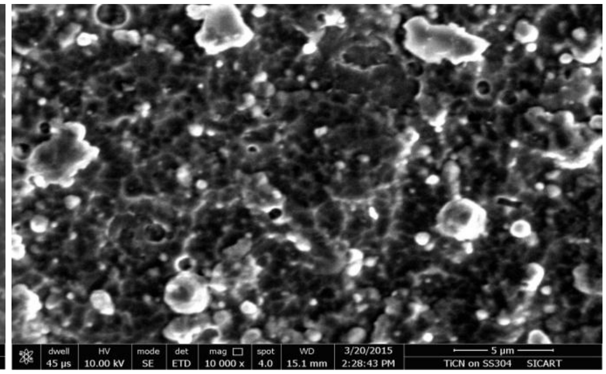
Figure 7:- (a) FESEM Image which shows particles at 10 000X Magnification and observing on the 5µm size of the TiAlN coated Specimen

(b) FESEM Image which shows particles at 15 000X Magnification and observing on the 5µm size of the TiAlN Coated Specimen

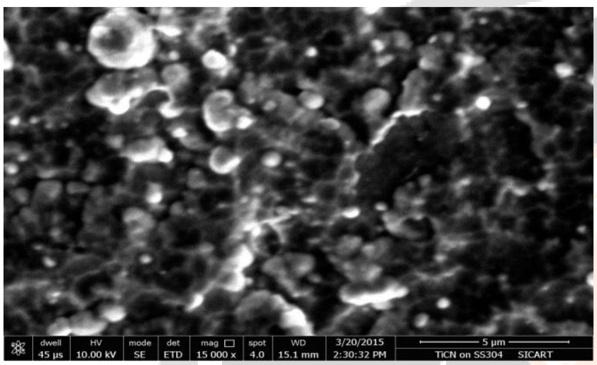
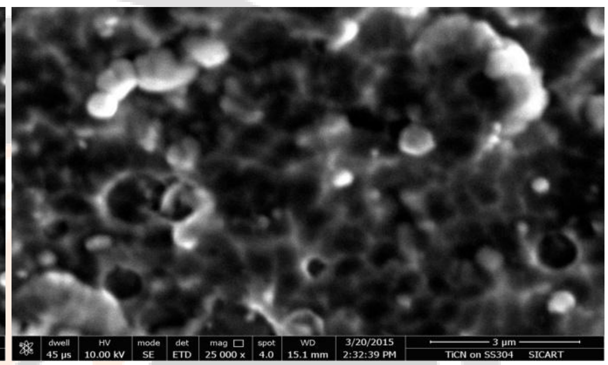
(c) FESEM Image which shows particles at 25 000X Magnification and observing on the 3µm size of the TiAlN Coated Specimen

(d) FESEM Image which shows particles at 35 000X Magnification and observing on the 2µm size of the TiAlN Coated Specimen

The below images are scans of the substrate coated with Titanium Chromium Nitride (TiCrN) film. Four images were captured at different magnifications of 8 000 X, 10 000 X, 15 000 X and 25 000 X.

(e) (f)

(g) (h)

Figure 8:- (e) FESEM Image which shows particles at 8 000X Magnification and observing on the 5µm size of the TiCrN coated Specimen

(f) FESEM Image which shows particles at 10 000X Magnification and observing on the 5µm size of the TiCrN Coated Specimen

(g) FESEM Image which shows particles at 15 000X Magnification and observing on the 3µm size of the TiCrN Coated Specimen

(h) FESEM Image which shows particles at 25 000X Magnification and observing on the 2µm size of the TiCrN Coated Specimen

FESEM micrographs analysis for TiAlN & TiCrN coated ASTM 240, TYPE 304 Austenitic stainless steel substrate subjected for the investigation of grain morphology with FEG-SEM NANO NOVA 450 Instrument. Both micrographs shows non-uniform and dense morphology of the TiAlN & TiCrN films on the surface of SS304 substrate. But still the substrate coated with Titanium Chromium Nitride (TiCrN) exhibits more uniformity than the substrate coated with Titanium Aluminium Nitride (TiAlN). The morphology of grains is dense because CAE-PVD Method for coating material was deposited on the surface of SS304 subtrate at higher temperature upto around 750oC. At this temperature, surface & bulk diffusivity occurs by means of the higher energized evaporated atoms from the target material on to the substrate. The adherence achieved is good in case of using CAE- PVD Method on ASTM, 240-12, TYPE 304 Austenitic stainless steel substrate due to the source of the nitrogen for the development of the coating. It is because nitrogen not only acted as working or reacting gas but also due to nitrogen gas coming from the substrate, making diffusion and proper mixing of elements in the interface layer easy. Normally in the case of CAE – PVD Method, due to inhomogenity because of occurrence of many drop shaped & elongated micro particles on the substrate surface, micro porosity develops. But here in our analysis the images did not show any type of micro porosity such that our structure due to uniformity and enough density in the distribution of coating material on the substrate surface. Both the coating layers deposited on the surface of SS304 substrate also showed a characteristic columnar & fine graded structure.

CONCLUSION

From the Potentiodynamic Polarization scans and from the corrosion rates found out by carrying the experiment, we can easily conclude that under specific coating deposition parameters, the substrate coated with Titanium Chromium Nitride (TiCrN) imparted maximum corrosion resistance by showing least corrosion rate of 0.380 mpy in compare to the substrate coated with Titanium Aluminium Nitride (TiAlN) as well as uncoated substrate. The substrate coated with TiAlN showed minimum corrosion resistance by showing maximum corrosion rate of 3.437 mpy in compare to the TiCrN layer as well as uncoated SS304 substrate. In case of uncoated SS304 substrate, it showed more corrosion resistance than substrate with TiAlN coating layer but showed a little less corrosion resistance than substrate with TiCrN coating layer by showing corrosion rate of 0.541 mpy which is more than substrate with TiAlN layer and less than substrate with TiCrN layer. From the images captured by Field Emission Scanning Electron Microscope (FESEM) at different magnifications, the surface morphology showed dense formation of grains, non-uniformity in deposition and less porous coatings on the surface of SS304 substrate. This in turn can enhance mechanical and tribological behaviour of these coating layers in any possible way.

REFERENCES

1. Hui-Ping Feng , Cheng-Hsun Hsu , Jung-Kai Lu , Yih-Hsun Shy, “Effects of PVD sputtered coatings on the corrosion resistance of AISI 304 stainless steel”, Materials Science and Engineering,2003, A347, 123 – 129
2. J.A. Alegrı´a-Ortega, L.M.Ocampo-Carmona , F.A.Sua´rez-Bustamante, J.J.Olaya-Flo´ rez, “Erosion–corrosion wear ofCr/CrN multi-layer coating deposited on AISI-304 stainless steel using the unbalanced magnetron (UBM) sputtering system”, Wear , 2012, 290, 149-153.
3. C. Reinhard , A.P. Ehiasarian, P.Eh. Hovsepian, “CrN/NbN superlattice structured coatings with enhanced corrosion resistance achieved by high power impulse magnetron sputtering interface pre-treatment”, Thin Solid Films, 2007, 515, 3685 – 3692.
4. M. Leonia, P. Scardia, S. Rossia, L. Fedrizzia, Y. Massiani, “(Ti,Cr)N and Ti/TiN PVD coatings on 304 stainless steel substrates: Texture and residual stress”, Thin Solid Films,1999, 345, 263 – 269.
5. K. Singh , P.K. Limaye , N.L. Soni , A.K. Grover , R.G. Agrawal , A.K. Suri,” Wear studies of (Ti–Al)N coatings deposited by reactive magnetron sputtering”, Wear, 2005, 258, 1813 – 1824.
6. Bin Tian , Wen Yue , Zhiqiang Fu , Yanhong Gu , Chengbiao Wang , Jiajun Liu, “Microstructure and tribological properties of W-implanted PVD TiN coatings on 316L stainless steel”, Vacuum, 2014, 99, 68 -75.
7. E.S. Puchi-Cabreraa , M.H. Staia , E.A. Ochoa-Péreza, D.G. Teerc, Y.Y. Santana-Méndeza, J.G. La Barbera-Sosaa, D. Chicotd, J. Lesaged, “Fatigue behavior of a 316L stainless steel coated with a DLC film deposited by PVD magnetron sputter ion plating”, Materials Science and Engineering, 2010, A 527, 498 – 508.
8. A.I. Fernández-Abia, J. Barreiro, J. Fernández-Larrinoa, L.N. López de Lacalle, A.Fernández-Valdivielso, O.M. Pereira, “Behaviour of PVD coatings in the turning of austenitic stainless steels”, Procedia Engineering, 2013, 63, 133 – 141.
9. Cheng-Hsun Hsu , Kuan-HaoHuang, Ya-HueiLin, “Microstructure and wear performance of arc-deposited Ti–N–O coatings on AISI304 Stainless Steel”, Wear, 2013, 306, 97 – 102.
10. Shujun Gaoa, Chaofang Donga , Hong Luob, Kui Xiaoa, Xiaoming Pana, Xiaogang Liaa, “Scanning electrochemical microscopy study on the electrochemical behavior of CrN film formed on 304 Stainless Steel by magnetron sputtering” , Electrochimica Acta, 2013, 114, 233 – 241.
11. Y. Khelfaoui , M. Kerkar , A. Bali , F. Dalard, “Electrochemical characterisation of a PVD film of titanium on AISI 316L Stainless Steel”, Surface & Coatings Technology,2006, 200, 4523 – 4529.
12. J.L. Endrino , G.S. Fox-Rabinovich , C. Gey, “Hard AlTiN, AlCrN PVD coatings for machining of austenitic Stainless Steel”, Surface & Coatings Technology, 2006, 200, 6840 – 6845.
13. C.H. Hsu , C.K. Lin , K.H. Huang , K.L. Ou, “Improvement on hardness and corrosion resistance of ferritic Stainless Steel via PVD-(Ti,Cr)N coatings”, Surface & Coatings Technology, 2012, 231, 380 – 384.
14. M. Nordin, U, R. Sundstroma, T.I. Selinder , S. Hogmark, “Wear and failure mechanisms of multilayered PVD TiNrTaN coated tools when milling austenitic Stainless Steel”, Surface and Coatings Technology, 2000, 133 – 134, 240 – 246.
15. Lei Shan , YongxinWang , JinlongLi , XinJiang , JianminChen, “Improving tribological performance of CrN coatings in seawater by structure design”, Tribology International, 2015, 82, 78 – 88.