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Corrosion Resistance Enhancement in Acidic solution for Austenitic Stainless Steel by Gas-Phase Hybrid Deposition Process

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Abstract: *In acidic environments the corrosion rate of stainless steels is considered high, this is due to pitting occurrence in concentrated chloride environments. The Austenitic steels such as type 316 stainless steel generally not recommended for Hydrochloric acid storage in petroleum planets except when solutions are very dilute and at room temperature, otherwise pitting may occur. In this work, a multicomponent coating (Ti-B-N-C) was deposited on the austenitic stainless steels (AISI 316) that used in petroleum industry. The coating process has been achieved by mixed vapor deposition technique; this was done in attempt to improve the resistance to pitting corrosion for austenitic stainless steels surface. The structural characterization for the deposited Ti-Base coating was done by using XRD technique, and the Scanning Electron Microscopy (SEM). Electrochemical corrosion tests have been performed by using electrochemical test in 0.25M hydrochloric acid (HCl) as an aqueous solution at 22˚C to obtain the anodic polarization curves for the coated surfaces. Several interesting observations have been made During the test. As expected, the surface of the AISI 316 suffers from a sudden increase in the current density at the potential above 1500 mV due to the occurrence of pitting corrosion. In addition, the Ti-B-C-N coating surfaces show great future in reducing the current density of the steel surface in the anodic region, indicating improved pitting resistance for all Ti-based coating samples. No evidence for pitting corrosion was observed in the coated surfaces during electrochemical test even at potentials up to 2000 mV, instead, general corrosion was observed for the samples that was deposited at 750˚C since low potential values was observed for these samples .*

Keywords- *AISI316,Titanium base coatings, pitting Corrosion, Hybrid gas phase, potentiostate*

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1. Introduction

Austenitic stainless steels constitute the largest stainless family that is widely used in various sectors of industry. Types 316 austenitic stainless steel have the broadest range of usefulness for storage vessels, pumps, and process equipment handling glacial acetic acid, which would be discolored by type 304 [1]. To stimulate production in petroleum industry, strong acids are often pumped into wells to increase formation permeability; this can lead to increase the corrosion rate of stainless steels due to pitting attack. Corrosion control is achieved normally by a combination of inhibition and limiting exposure time about 2 to 12 h [1]. In addition, high-temperature environments is required in many oil field applications. Most stainless steels, including austenitic and duplex grades, are known to be susceptible to elevated- temperature cracking, probably by a mechanism similar to chloride attack by stress corrosion cracking (SCC), thus the austenitic stainless steels such as type 316 stainless steel is not generally recommended for storaging the Hydrochloric acid in petroleum planets except when solutions are very dilute and at room temperature, otherwise pitting may occur, were the stainless steels are rapidly attacked by concentrated HCl because a passive film is not easily attained [1,2]. Pitting corrosion is a localized electrochemical dissolution process that in some cases can cause a catastrophic failure of passive metals such as the austenitic stainless steels [3]. The location of pits on metal surface

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that develop a passive films is often unpredictable, were pits usually tending to disperse randomly on the metal surface. The initial event in localized corrosion of stainless steels is passivity breakdown, followed by pit nucleation, growth, and in some cases re-passivation of these corrosion resistant metals [3]. In alkaline environments the corrosion rate of steel is fairly low, but in acidic environments the corrosion rate will increases markedly when the pH is less than 3 [4]. However, pitting corrosion of this type of alloy is very common in environments where the local dissolution rate of metal can be up to 12mm per year [4]. Titanium alloys are characterized by having excellent resistance to many environments that cause corrosion, especially oxidizing and chloride-containing process streams. This excellent resistance of titanium is due to extremely high reaction and extremely high affinity of titanium metal to oxygen, this will result in forming a layer of surface oxide films that will form spontaneously and instantly when metal surfaces exposed to air and / or moisture, and the damaged films of oxide can generally re-heal itself [4]. The formation of the chemically resistant, highly crystalline form of TiO_2 known as rutile is usually promote by High-temperature oxidation, whereas lower temperatures often generate the more amorphous form of TiO_2 anatase, or a mixture of rutile and anatase. The TiO_2 oxide is highly chemically resistant Thus, successful use of titanium alloys can be expected in highly oxidizing environments in which protective TiO_2 and Ti_2O_3 films form spontaneously and remain stable [4]. Because of decreasing cost and the increasing availability of titanium alloy products, Coated products that are produced by vapor deposition for corrosion-resistant applications are now widely used [5]. The process of vapor deposition can be divided into two basic types: the physical deposition process, which requires evaporation (through evaporation or laser ablation) and subsequent condensation for forming the surface coating layer [6]. The chemical deposition process of the metal vapour (CVD) is the second type of the gas phase deposition. It is produced by chemical reactions for the gas phase, which leads to the deposition of a solid film on a usually hot substrate [7]. For producing nanoscale or nanocomposite coatings, it may be necessary to combine two or more of the deposition methods into a single system. The hybrid gas phase coating technology can be considered as a new type that can be added to the other large technologies used in surface engineering, which resulted from the continuous developments in the deposition of physical and chemical vapor (PVD, CVD) technology during the last period [8]. The experimental method that was used to produce the Ti-Base layer in this work can be considered as a hybrid process, this is due to the rote that was used to produce the coating materials supplied in the form of the gas phase by evaporating a number of powders by using thermal energy (ie thermal reactive evaporation), while a deposition path on the surface of the base metal is based on the CVD technique.

2. Experimental

An experiment that was aimed at the evaluation of the microstructure and the corrosion resistance were made by using Austenitic stainless steel AISI 316 as the substrate material in this work. The chemical composition of this steel is listed in Table 1. Samples were prepared for the required tests according to the requirements of each of these tests. For phase characterization samples (XRD), and structural morphology (SEM), the samples were prepared with the dimensions of 2 x 10 x 5 mm for thickness, height and width, respectively. For the electrochemical tests Specimens of 1 cm^2 surface area were used in this work. A mechanical grinding for all samples was also performed on the emery paper of 240 grits and then the soaking of samples with acetone ultrasonic cleaning was used for the samples in ethanol for 15 minutes directly before each deposition process. The constituents of the different phases were detected by using an X-ray diffractometer (XRD-6000 x Shimadzu X-ray diffractometer with using an incident angle of 0.154nm with copper-Kα radiation). For the topographical features of the upper surface of the Ti-B-C-N coating, the TESCAN Vega 3SB electronic scanning microscope test was performed with a voltage acceleration of 200V to 30KV and a magnification force of 6X to 100,000X. Multicomponent coatings (Ti-B-N-C) were deposited on austenitic stainless steel (AISI 316) by mixed gas phase deposition process technique (PVD and CVD); a schematic diagram for this new technique is shown in Fig.1 as anew rote for the coating film deposition. In this work, the deposition process that was used for the coating contains four units as follows: 1- The unit used to evaporate powders. 2 - The unit for the processing of different gases 3 - The deposition chamber unit 4 - The exhaust gas unit.

Table1 Chemical composition (wt.%) of theAISI316 work substrate

Element	wt.%
C	0.020
Si	0.49
Mn	1.28
P	0.029
S	0.003
Mo	2.09
Ni	11.19
Co	0.16
Cr	17.13
N	0.032

The powder evaporation unit used in this work is a high-temperature tubular furnace of -1600-60X that was used for supplying the required metal gases for the deposition process; the powders have been contained in alumina boat and placed in the center of the evacuated alumina tube [9]. During the deposition process, the gas flow rate and the reaction temperature were carefully controlled. The deposition of the Ti-B-C-N film was performed by the powders evaporation for the pure titanium, titanium carbide, and pure boron, in the presence of NH3 gas, which acts as reactive gas in this hybrid deposition system. The Ti-B-C-N deposition process were performed at different deposition temperatures (750,850, and 950 ° C), and by using the same nitrogen flow rate at a flow of 2.5SLPM (standard litter per minute). The deposition experiments in this work were carried out using the nitrogen flow rate which represents the best conditions for the reactive gas flow based on our previous work for the same coating system (Ti-B-C-N) on the hard surface, which will results in a producing of a denser structure and a more uniform surface layer that is free of cracks with preferable surface roughness for the reactive evaporation process [9]. The electrochemical corrosion tests have been performed by using a WIKING M-Labsci Potentiostat from Bank-Elektronik Using the analysis and requisition system as well as computer data logging. The sample used for the test was installed on the corrosion cell, which exposed 1.0 CM2 from the surface of the sample used to the electrolyte. A Pt electrode operated as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The electrolyte solution was designed to cause pitting corrosion by a high concentration of chlorides; the electrolyte that was used for the tests was 0.25 M hydrochloric acid (HCl) aqueous solution in deionized water. Anodic curves were recorded for polarization by using a sweep speed of 2 mVs_1. At a temperature of 22 ° C for measuring curves for anodic polarization of uncoated and coated surfaces.

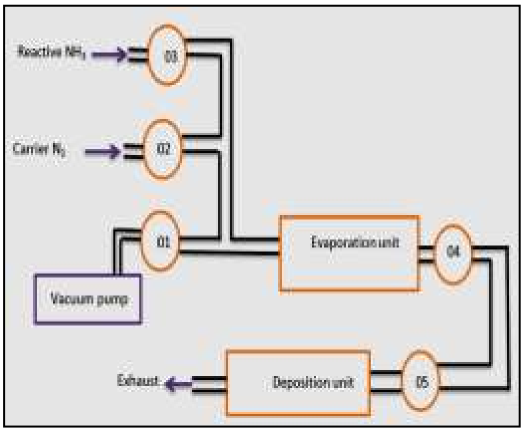


Figure 1: Schematic diagram of the mixed gas phase deposition process system equipment

3. Results and Discussion

I. XRD Results

The possible chemical reactions in the coating and on the interfaces between the coating and the base metal are of great importance because these reactions help to predict the nature and properties of the coating layer. Since the exact composition of the coating is affected by, the flow rate of NH_3 as well as by the deposition temperature, and by applying the thermodynamics and the ternary-phase diagram of the alloy Ti(C)-B-N (Figure 2), all possible reactions in this system can be predicted. In our coating system for Ti-B-C-N, following reactions can occur.

Ti–B-C-N system:
(1) $Ti+2B=TiB_2$ or $3Ti+4B=Ti_3B_4$ or $Ti+B=TiB$ (2) $TiN + BN + N_2$ (3) $TiB_2 + B + BN$ (4) $TiB_2 + TiN + TiN_{1\_x}$ (5) $TiB_2 + TiB + TiN_{1\_x}$ (6) $TiB + Ti + TiN_{1\_x}$

The selection of precursors and the temperature during deposition can greatly affects the chemical composition produced, the amount of crystallized phase, and the properties affecting the friction of coating. The deposition rates can also be controlled by the change in the temperature of deposition, which can control surface roughness [11]. In Figure 3 the XRD pattern is shown for Ti-B-C-N samples that were coated at 750 °C (deposition temperature) and 2.5SLPM (ammonia flow rate). This coating contains iron (ferrite with a cubic structure of 100%Fe). This coating also contains titanium oxide mixed with iron, 36.81Fe wt%, 31.63O wt% and 31.56Ti wt% (Rumbohedral) for both titanium and iron in the coating structure. The presence of titanium-boron compounds with a chemical formula of α-TiB12 with 73.04B wt% and 26.96Ti wt% of the tetrahedral structure has been identified in this pattern. The increase in temperature during deposition to 850 °C will result in a change in the presented phases, were this change resulted from the higher deposition rates compared to the previous coating film, which was deposited at lower temperatures. The effect of the increase in deposition temperature and its effect on the chemical composition and the microstructure of the new coating film leads to the presence of new phases that are can find in this pattern. The boron nitride phase was identified by a chemical formula of BN, which is characterized by cubic structure, which contains 43.56% B and 56.44% N in this XRD pattern. At higher deposition temperatures (950°C) and with the use of 2.5SLPM ammonia flow rate, a sharper pattern was observed with increased intensity for this film (Table 2). This pattern was like to the crystallized form of Ti-B-C-N more than the rest of the previous patterns. It should also be noted that No diffraction peaks were observed for the TiN phases in all Ti-B-C-N coating samples, which were produced by using this HDP system. This absence of TiN phase can be due to the use of conditions that are not preferred to form stable compounds of TiN. In addition, different amounts of titanium oxide phase have been shown in all Ti-B-C-N coating samples. This can be explained by the fact that there is a great affinity between oxygen and titanium, leading to an interaction that will result in formation of an oxide surface layer when performing deposition in the air.

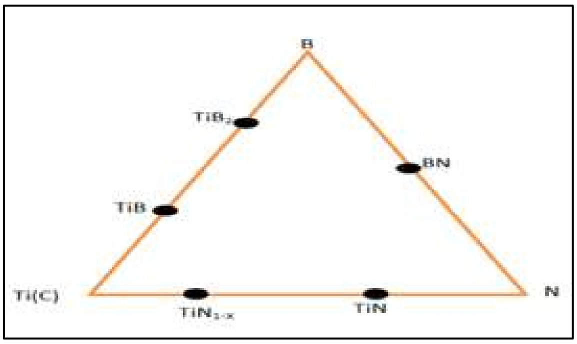


Figure 2: Chemical composition of Ti-B-C-N coatings plotted in the Ti©-B-N phase diagram [10]

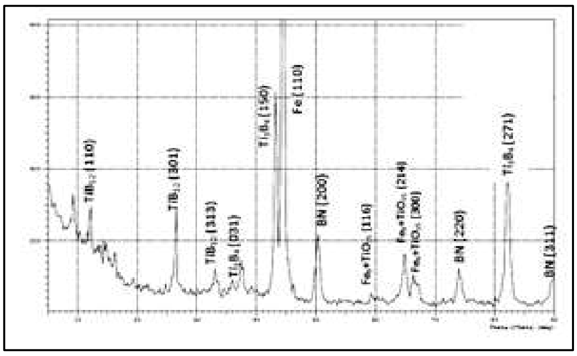


Figure 3: XRD pattern of Ti-B-C-N Film deposited at temperature of 750 °C and with 2.55LPM Ammonia flow rate

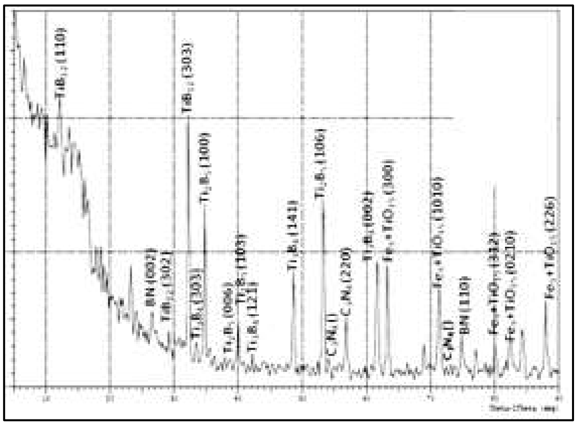


Figure 4: XRD pattern of Ti-B-C-N Film deposited at temperature of 850 °C and with 2.55LPM Ammonia flow rate

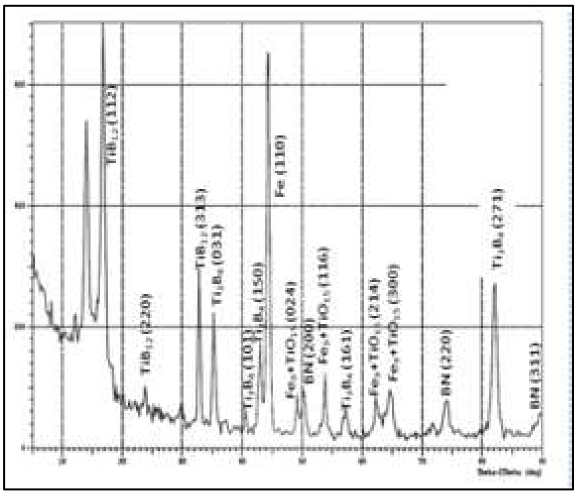


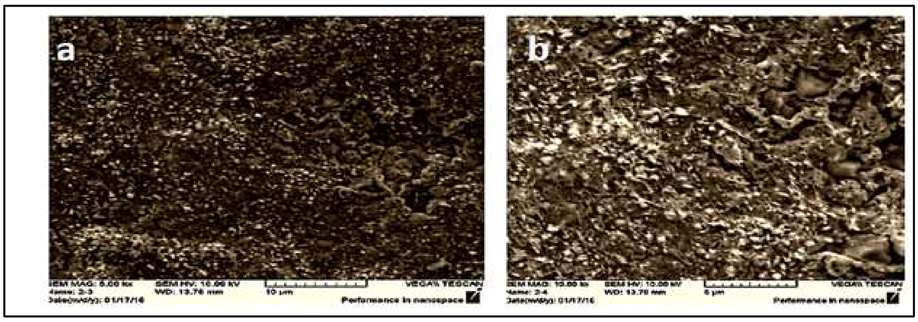
Figure 5: XRD pattern of Ti-B-C-N Film deposited at temperature of 950 °C and with 2.55LPM Ammonia flow rate

II. SEM Images for Ti-B-C-N Gas Phase Coatings

The surface layer morphology was examined by using SEM test for the Ti-B-C-N coating, The coating layer was produced by using deposition temperatures ranging from T_d = 750-950 ° C and the same rate for ammonia flow rate for all samples (2.5SLPM), these images are shown in Figures 6 to 8. In Figure 6 at low deposition temperature (750°C), the surface is characterized by the amorphous structures and the not uniform surface film that resulted from the use of relatively low temperatures for the deposition of these samples, which resulted in low deposition rates.

Table 2: (d) measured and (d) standards for Fe+2TiO$_3$ at 950°C

Intensity	FWHM	d-standard(A)	d-measured(A)	2Θ-masured	2Θ-standered
24	0.611	1.174	1.173	81.974	82.13
11	0.554	1.434	1.437	64.970	64.82
7	0.745	1.50	1.49	61.537	62.130



Figur 6: SEM topography for Ti-B-C-N Film deposited at temperature of 750 °C and with 2.55LPM Ammonia flow rate, with different magnifications

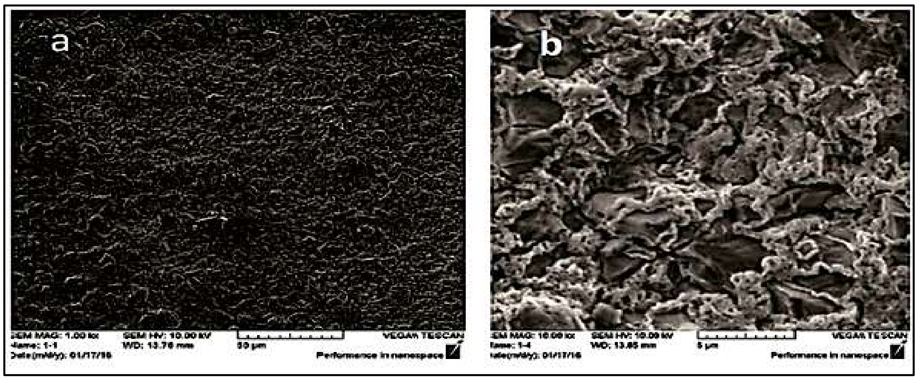


Figure 7: SEM topography for Ti-B-C-N Film deposited at temperature of 850 °C and with 2.55LPM Ammonia flow rate, with different magnifications

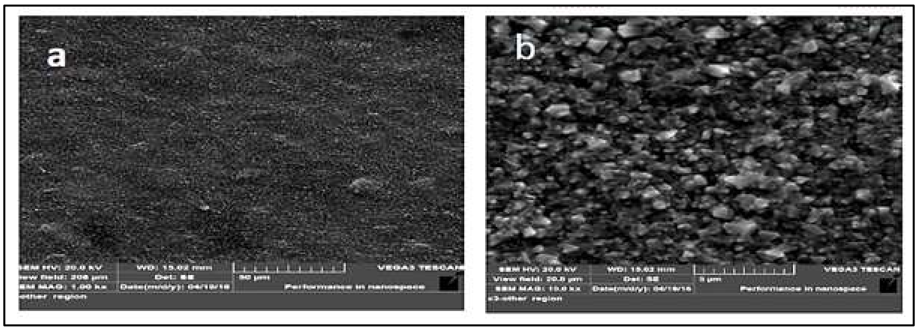


Figure 8: SEM topography for Ti-B-C-N Film deposited at temperature of 950 °C and with 2.55LPM Ammonia flow rate, with different magnifications

This effect can be monitored by the presence of some spots where the thickness is low in this film, which can be identified by heterogeneous coatings in this image. Using higher deposition temperatures (850°C and 950°C), the surface layer of the coating was denser; in addition there was an increase in surface roughness resulting from a relatively large increase in the average particle size [12]. As it was indicated by many researchers, The deposition temperature that was used, can have significant influences on the average grain size, while the effect of N content will be demonstrated by effectively controlling the rates of deposition through the chemical reactions type controlling that will occur in the coating and the interface, which can result in increased coating thickness [12,13].

III. Electrochemical test for Ti-B-C-N Gas Phase Coatings

Electrochemical tests were performed to study the anodic polarization curves for both uncoated and the coated AISI 316 stainless steel that was tested in chloride containing electrolytes. The pitting corrosion resistance can be determined by the starting breakdown potential values during the Electrochemical test, were many authors try to developed opinions for what breakdown potentials should be acceptable and what are unacceptable for the stainless steels alloys. The breakdown potential is termed as critical pitting potential when a pitting is present.[14] It was reported by many authors that for the more electronegative Breakdown potential (more than +300 mV) the alloy considered not to be in an optimal corrosion resistant condition.[14,15] The measured anodic polarization curve for the uncoated AISI 316S.S. is shown in Fig.9. In this figure, the uncoated stainless steel has been demonstrated to show a sudden increase in current density during the test at constant potential at about 1500 mV (the starting breakdown potential), this increase in the current density is due to the pitting corrosion occurrence as confirmed by the images of the microscopic examination of these samples after the test. In Figs.10 and 11, the coating that was applied on the stainless steel surfaces results in reducing the current density of the surface within the limits of the anodic region, which leads to the conclusion that there is an improvement in corrosion resistance. It should also be noted that no pitting corrosion was observed after the test in all the coated surfaces with potential test reaches up to 2000 mV (i.e. no breakdown potential), where only general corrosion was generally observed in Fig.9 which can be indicated by the anodic polarization curves. This indicates that the Ti-base coating can improve the pitting corrosion resistance of austenitic stainless steels, but the coated surfaces suffer from relatively high general corrosion rates, whereas lower temperatures often generate the more amorphous form of Ti-O anatase, or a mixture of rutile and anatase, as can be seen from the relatively low potentials for sample that deposited at750°C**.** Also the improve in the pitting resistance can be explained by the existence of the Ti oxide surface film, where the Ti oxide is considered to be highly chemically resistant and is attacked by very few substances. Because the passivity of titanium stems from the formation of a stable oxide film, an understanding of the corrosion behavior of titanium is obtained by recognizing the conditions under which this oxide is thermodynamically stable. Thus, successful use of titanium alloys can be expected in reducing pitting attack in oxidizing environments in which protective Ti-O films form spontaneously and remain stable. For the coated AISI 316 stainless steel that was deposited at 950°C(Fig.11), the anodic polarization curve is shifted towards lower current density by one order of magnitude as compared to those for the uncoated steels or the low temperature deposited Ti-base coatings(at 750°C). This will result in a significant improvement in corrosion resistance, that excellent resistance to corrosion on the surface that has been coated by a hybrid manner, which is to be protected even when using high potentials of up to 2000 mV in the electrolyte testing. Microscopic examination after testing did not reveal any sign of pit formation. The formation of the chemically resistant, highly crystalline form of Ti-Oxide phase known as rutile is usually promote by High-temperature oxidation, whereas lower temperatures often generate the more amorphous form of Ti-O anatase, or a mixture of rutile and anatase. Also a titanium oxide permits electrochemical reduction of ions in an aqueous electrolyte resulting in very high resistance to anodic current flow through the passive oxide film in most aqueous solutions.

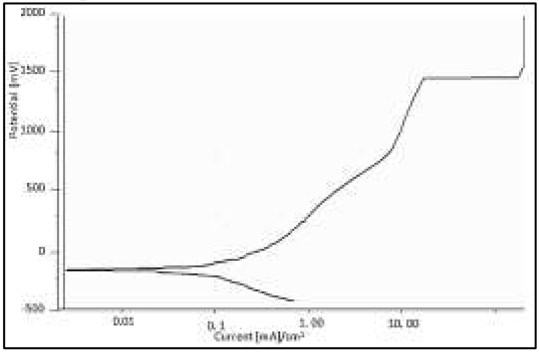


Figure 9: Measured anodic polarization curves by electrochemical test for the uncoated AISI316 St

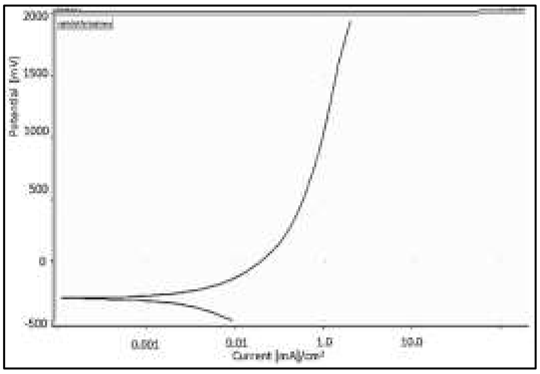


Figure 10: Measured anodic polarization curves by electrochemical test for the TiBNC thin film at 750°C

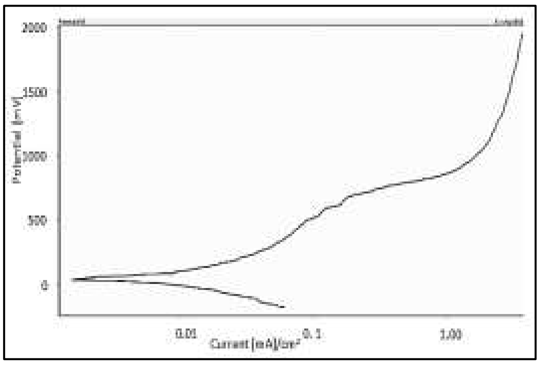


Figure 11: Measured anodic polarization curves by electrochemical test for the TiBNC thin film at 950°C

4. Conclusions

A hybrid vapor deposition process (HDP) multicomponent coating (Ti-B-N-C) was successfully deposited on the austenitic stainless steels (AISI 316). The effect of increasing the deposition temperature on the resulting chemical composition and the precise composition of the finished coating leads to the formation of new phases that are formed in this coating system. With increasing the deposition temperature (850 and 950°C) the surface of the resulting coatings was found to be more dense but with increased roughness of the coated surface which was due to the increase in average grain size with increasing the deposition temperature. Also the increase in the deposition temperature this improved resistance to corrosion of the treated surface resulted in a coated surface that is protected against pitting corrosion even when using high voltage up to 2000 mV for the electrolyte test.

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References

[1] R.L. Klueh “Properties and Selection: Irons, Steels, and High Performance Alloys,” ASM Handbook, Volume 1, Metals and Ceramics Division, Oak Ridge National Laboratory, 2005.

[2] S.D. Washko and G. Aggen, “Properties and Selection: Irons,Steels, and High Performance Alloys,” ASM Handbook, Volume 1, 2005.

[3] J.G. Sánchez, L.D. Pérez, E.G. Ochoa, G. Canto, and M.S. Baz, “Corrosion pit growth on austenitic stainless steels in chloride containing solution: a quantitative approach,” Anti-Corrosion Methods and Materials,Vol. 59 Iss: 5, 2012.

[4] R.M. Davisonvol, “Corrosion of Stainless Steels: Effects of Processing, Design, Fabrication, and External Treatments,” ASM Handbook, Volume 13, 2005.

[5] R.F. Bunshah, “Friction, Lubrication, and Wear Technology,” ASM Metals Handbook, Vol-18, 1708-1730, 2000.

[6] Y.Z. Lee, and K. Jeong, “Wear-Life Diagram of TiN-Coated Steels,” Journal of Wear 217, 1998.

[7] P.H. Mayrhofer, C. Mitterer, L. Hultman, and H. Clemens, “Microstructural design of hard coatings,” Progress in Materials Science 51, 2006.

[8] D.G. Hasko, H. Ahmed, and G.A.J. Amaratunga, “Plasma Enhanced Chemical Vapor Deposition Carbon Nanotubes/Nanofibre,” Institute of physics publishing nanotechnology 14, 2003.

[9] F.Q. Mohammed, “Enhancement of High Speed Steel Surface Properties by PVD/CVD Vapor Deposition,” A thesis Submitted To Department of Production Engineering and Metallurgy University of Technology, 2017.

[10] J.H. SHIN, K.S. CHO, and T. WANG, “Microstructure Evolution and Mechanical Properties of Ti−B−N Coatings Deposited by Plasma-Enhanced Chemical Vapor Deposition", Trans. Nonferrous Met. Soc. China 22(2012).

[11] A. Agarwal and N. B. Dahotre, “Pulse Electrode Deposition of Superhard Boride Coatings on Ferrous Alloy,” Journal of Surface and Coatings Technology 106, 1998.

[12] R.V. Ben, M.O. Jarligo, T. Steinke, D.E. Mack, and D. Stover, “Overview on Advanced Thermal Barrier Coatings,” Journal of Surface & Coatings Technology 205, 2010.

[13] P.H. Mayrhofera_ and C. Mitterer, “Thermally Induced Self-Hardening of Nano crystalline Ti–B–N Thin Films,” Journal of applied physics 100, 044301, 2006.

[14] R.A. Corbett, “Laboratory Corrosion Testing of Medical Implants,” Corrosion Testing Laboratories, Inc., Newark, Delaware, USA, published by ASM International, 2004.

[15] J. Pan, C. Karlén, and C. Ulfvin, “Electrochemical Study of Resistance to Localized Corrosion of Stainless Steels for Biomaterial Applications,” Journal of the Electrochemical Society, 147, 3, 2000.

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