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Titanium-Base Nanostructure Coatings for AISI M52 Tool Steel by Gas-Phase Mix Process

Abstract- *Deposition of Multicomponent hard coatings (Ti-B-N-C) on the molybdenum high-speed tool steel (AISI M52) has been achieved by mixed vapor deposition technique to improve the mechanical properties of the surface. In this technique the coating materials that were supplied in the gas phase were produced from powders that vaporized by thermal energy (that is, PVD-Reactive Evaporation Process), while the reactor that used to deposit Ti-Base coatings is hot-wall chemical vapor deposition (HWCVD) system equipment. This combination results in technical and financial advantages. The structure of deposited Ti-Base hard film was characterized by XRD technique, Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray spectroscopy (EDX). Mechanical characterization of the hard films has been performed by using Vickers micro hardness tester and The Ball-on-disk wear tests. With different reactive gas flow rates that ranged from 500 to 3000Sccm(standard Cubic Centimeter per Minute), the film showed amorphous matrix with crystalline Nano fibers of Ti-B phase which led to achieve higher hardness of 2051HV and better wear resistance with relatively good COF values of 0.61 than the uncoated tools.*

Keywords- *AISI M52, Titanium base coatings, HWCVD, Hybrid gas phase, Mechanical properties.*

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1. Introduction

High-speed tool steels are the toughest materials; however, their relatively low wear resistance limits their application to low-speed machining (Cutting speed may be defined as the relative speed between the cutting tool and the surface of the work piece) [1,2]. There is, however, a tradeoff between wear resistance and toughness that can limit the application of these super hard tools to lighter cutting speed. The wear behavior of steels can be influenced by many factors [3]. Thus, the need for machining with increasingly higher cutting speeds and for machine difficult-to-machine materials is done by improving the properties of the tool material by making them more refractory or generate less heat during machining [2]. Depositions of hard coatings (i.e. TiN, TiAlN, TiC, etc.) have been applied widely by vapor deposition method to improve forming process and considerably enhance tools wear resistance in numerous cases [4]. Nanomaterials display unique, superior and indispensable properties and distinct characteristics that are unavailable in conventional macroscopic materials [5]. Titanium base nanocoatings had been widely used in the coating of tool steels to, increase tool life, improve the surface quality of the product, and to increase the production rate. In reactive evaporation, the difficulties involved in direct evaporation processes due to fragmentation of the vaporized compounds are overcome in reactive evaporation, where a metal is evaporated in the presence of the reactive gas, a partial pressure of reactive gas is used to deposit compounds of the vaporized material by the reaction of deposited atoms with ambient gases [6,7]. The CVD process can be defined as the deposition of a solid on a heated surface via a chemical reaction from the vapor or gas phase [8]. This combination(CVD and PVD) will result in technical and financial advantages that are; 1- The use of pure metal powders will produce a coating film that is free of chlorine content which is a major element in the Ti, B, and Al gases (chlorine will cause the tool hardness to be decrease after few months) [1]. 2- The use of metal powders greatly reduce the coast of using very expensive gases such as $TiCl_3$, $TiCl_4$, BCl_3, and $AlCl_3$. 3- Also this technique has proven great futures to overcome the main limitations that associated with PVD and CVD process, this represented by the not restricted to a line-of-sight deposition which is a general characteristic of sputtering, evaporation and other PVD processes, also the above mentioned gases are consider to be extremely toxic (this is not the case of our precursor) and must be neutralized, which may be a costly operation [2,9]. Finally, this technique

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will result in a high deposition rate and thick coatings that can be readily obtained due to its flexibility that it allows many changes in composition during deposition. This work is based on the Deposition of the Ti-B-C-N multicomponent nanocoating on the surface of the high-speed steel substrate by gas phase process; this was done in an attempt to improve the structural, mechanical, and tribological properties of the working steel surface.

2. Experimental

Multicomponent hard coatings (Ti-B-N-C) were deposited on molybdenum high-speed tool steels (AISI M52) containing 0.9%C (Table 1). In this work different metal powders were used to synthesize the Ti-B-C-N coating with various reactive gas (NH_3) flow rate at a relatively high deposition temperature (950°C) in the hot-wall chemical vapor deposition (HWCVD) system equipment. A mixed gas phase deposition process technique (PVD and CVD) in Figure 1 were used in this work as a new rote for the hard film deposition. This system mainly consists of four units as follows: 1. The Powder evaporation unit used in this work consist of high temperature vacuum tube furnace type GSL-1600-60X that used to supply the metal gases for the deposition process, 2. Gas delivery system**,** is used to supply all needed gases into the chambers in a controlled manner, (its consists of three feeding lines namely: Ti-Base vapor, N_2 gas and NH_3 gas). 3. Deposition Chamber, is the reactor to deposit Ti-Base coatings, it is tow stage furnace that was constructed from AISI 304L Stainless Steel material as a pipe with 700mm in length and 2" in diameter with Alumina tube which represented the deposition region, and its contain inside a glass tube (1/2 in dia.) that made from quartz for the purpose of obtaining clean surface film, 4. The Exhaust gas system to release all the non-reacted chemical substances and by products of the reaction. different metal powders , a pure Titanium powder with purity of 98.5% that provided by Fluka (Switzerland) with average particle size of 9.989µm, Titanium carbide powder (TiC) provided by High Media (India) with average particle size of 1.263µm, and Boron powder with purity of 98.5% provided by Merck (Germany) with average particle size of 32µm, were supplied in the gas phase was produced from powders that vaporized by thermal energy (that is, PVD- Reactive Evaporation Process), while the deposition route was based on the CVD deposition technique.

3. Results and Discussion

I. XRD Results

Figures 2 to 5 shows the XRD patterns of Ti-B-C-N coatings deposited with different nitrogen flow rates (500-3000Sccm) and at the same deposition temperatures (950°C). It was found that Ti-B-C-N coatings that produced with different nitrogen contents can have significant differences for the presence phases and for the microstructures between different samples. The XRD patterns for Ti-B-C-N coating samples that deposited at 500Sccm for ammonia flow rate is shown in Figure 2, from this Figure the deposited film contain only Ti oxides and Ti oxides mixed with the iron. This poor phases film was formed due to The lack of the reactive gas (ammonia or N_2) which represent the difficulties involved in direct evaporation processes due to fragmentation of the vaporized compounds that caused by the reaction kinetics of the compound formation in this process. [10-12] No significant change was observed in the produced surface film with higher ammonia flow rate until it was reached 1500Sccm. Where in Figures 3 and 4 the increase in the reactive gas flow rate of (1500 and2000Sccm respectively) will cause new hard phases to be detected by the XRD test.

Table1: Chemical composition of the M-52 work substrate

Element	C	Co	Cr	Cu	Mn	Mo	P	W	V	Fe
Percentage (%)	0.90	0.62	3.98	0.11	0.36	1.51	0.198	1.02	2.89	Balance
-/+	0.04	0.09	0.06	0.02	0.04	0.02	0.005	0.04	0.08	-----

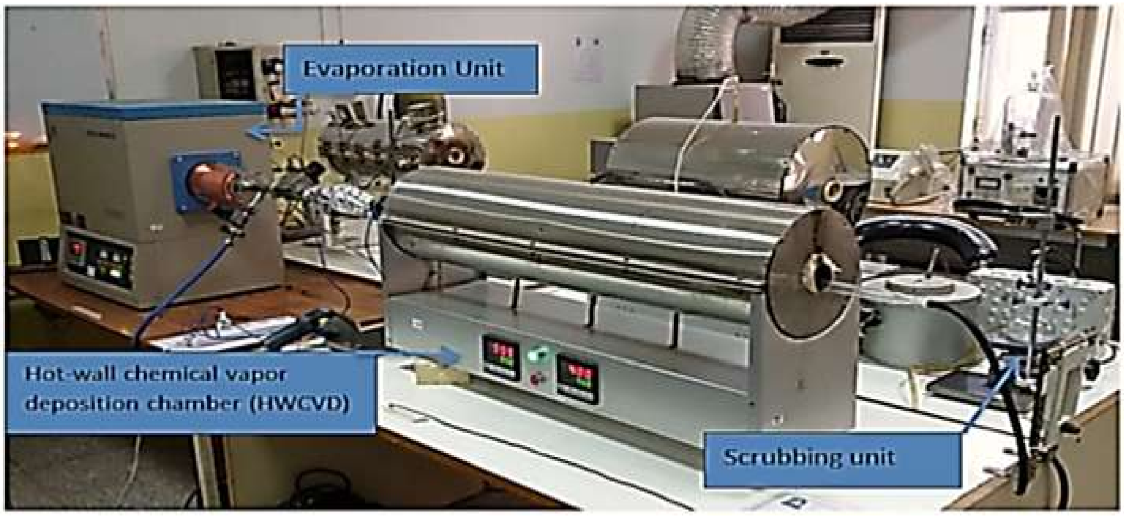

Figure 1: Mixed gas phase system equipment

For Figure 4 at 2000Sccm Titanium–Boron compounds with a chemical formula of Ti_3B_4 that contain 23.14B wt.% and 76.86Ti wt.% of orthorhombic structure, and α-TiB_{12} which contains 73.04B wt.% and 26.96Ti wt.% of Tetragonal structure can be detected in this figure. This pattern also show the present of Ti oxides and Ti oxides mixed with the iron that formed during deposition in air which also lead to low hardness and wear resistance of the coated surface. The diffraction peak intensities corresponding to Ti-B crystal for samples that was produced at 2000Sccm gradually reduced with higher ammonia flow rate and a peak-broadening phenomenon was observed, which indicated that a polycrystalline structure had developed for this sample. With higher ammonia flow rate at 2500Sccm in Figure 5, the produced coatings show the presence of Ti-B type structure with a sufficient amorphous phase (B-N) as a matrix. The substitution of N for B atoms in the Ti(B,C) lattice led to a gradual decrease in the Ti-B phase and an increase in the volume fraction of the Ti oxide and amorphous BN phases, some researchers report this phenomenon at different nitrogen contents when producing the Ti-B-C-N coatings [13]. The diffraction peak intensities corresponding to Ti-B crystal gradually increase and a peak-broadening were reduced which indicated an increase in the amorphous phase.

II. Surface Morphology and EDX Analysis of Ti-B-C-N Gas Phase Coatings

Figures 6 to 10 shows the SEM Surface morphology for Ti-B)-C-N coatings deposited under different nitrogen flow rates and at the same deposition temperature (950˚C). At 500Sccm of ammonia flow rate in Figure 6 the surface is irregular and contains several islands of amorphous structure and micro voids, these voids were arisen in the coating surface due to the not proper deposition process that caused by the lack of the reactive gas (ammonia or N_2) which will produce not dense coating film contain only Ti oxides and Ti oxides mixed with iron as it can be seen from the XRD results.

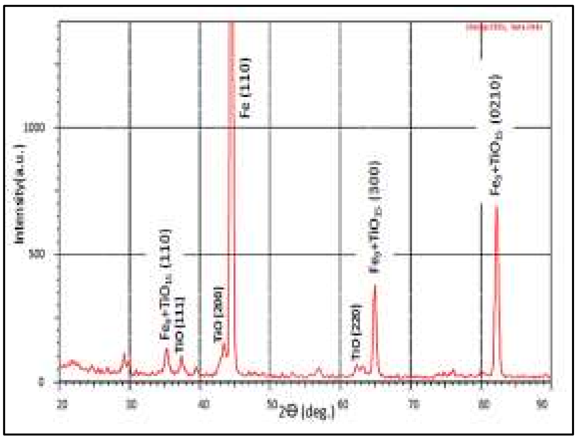

Figure 2: XRD pattern of Ti-B-C-N film for sample deposited with 500Sccm ammonia flow rate and at temperature. of 950˚C

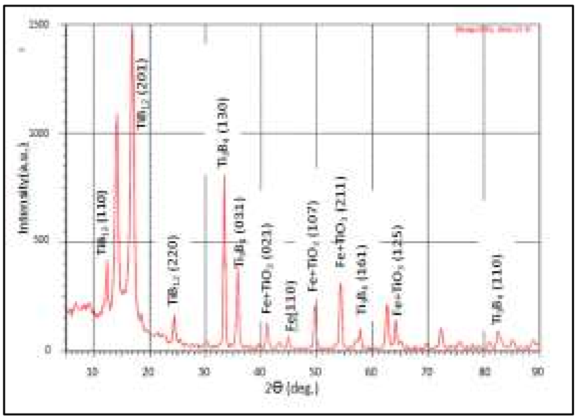

Figure 3: XRD pattern of Ti-B-C-N film for sample deposited with 1500Sccm ammonia flow rate and at temperature

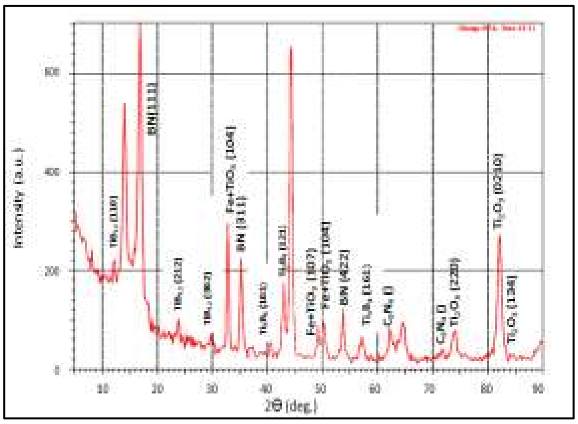

Figure 4: XRD pattern of Ti-B-C-N film for sample deposited with 2000Sccm ammonia flow rate and at temperature of 950°C.

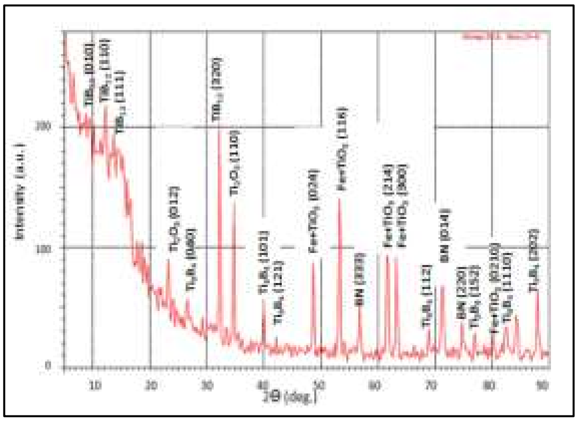

Figure 5: XRD pattern of Ti-B-C-N film for sample deposited with 2500Sccm ammonia flow rate and at temperature of 950°C.

With a gradual increasing in the ammonia gas flow rate, a uniform coating with no apparent micro voids and high surface roughness with a splash-like appearance can be seen clearly at 1500Sccm in Figure 7 and at 2000Sccm in Figure 8. The best deposition conditions for the Ti-B-C-N coatings are represented in Figure 9 at 2500Sccm for ammonia flow rate. A change of morphology is noticed towards a more dense featureless structure, the more uniform coting with no apparent cracks and less surface roughness can be seen clearly in this figure. This can be explained by the formation of the new film microstructure that produced with the increase in the ammonia flow rate. Also fine fiber structure is visible by SEM in this figure. This Nano crystal fibers do not exhibit any preferred orientation and their size is in the order of several nanometers, This could be explained by the formation of some crystalline phases of Ti_3B_4 or BN but their d-spacing are very close and it is not possible to distinguish them accurately as can be seen from the XRD beaks for this coatings. As the ammonia flow rate increase to 3000Sccm, the coating surface was found to be dens as in the case with the former coating surface but with higher surface roughness that can be a result of the globular shape islands. In the present work, the gas phase deposition process is performed in air and this deposition technique was found to support the globular mass-transfer mechanism, as shown in Figure 10. Although the Globular mass transfer can provide high deposition rates that result in the deposition of high thickness coatings, a decrease in the crystallinity was observed, which can be correlated with an increase of the carbon amorphous phase (as evidenced in the XRD test) for this coatings which lead to the reduction in the amount of hard Nano fibers that formed in the coating surfaces for the former coating at2500Sccm.

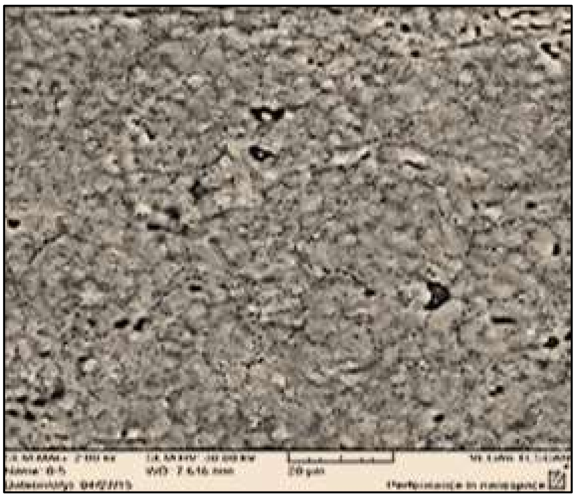

Figure 6: SEM micrograph for Ti-B-C-N thin film with 500Sccm flow rate of ammonia

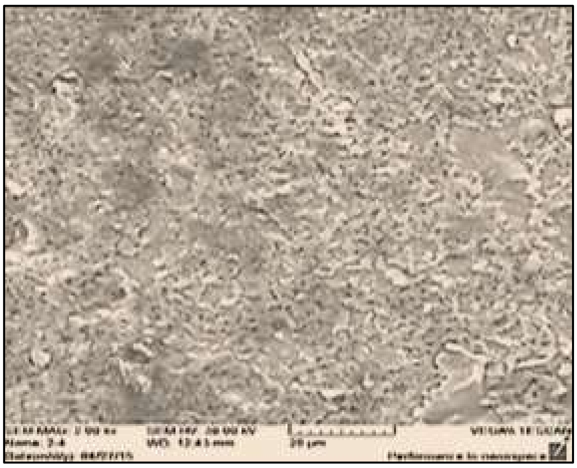

Figure 7: SEM micrograph for Ti-B-C-N thin film with 1500Sccm flow rate of ammonia

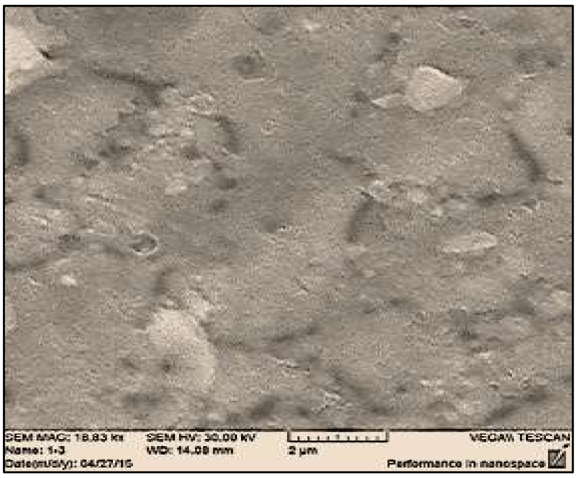

Figure 8: SEM micrograph for Ti-B-C-N thin film with 2000Sccm flow rate of ammonia

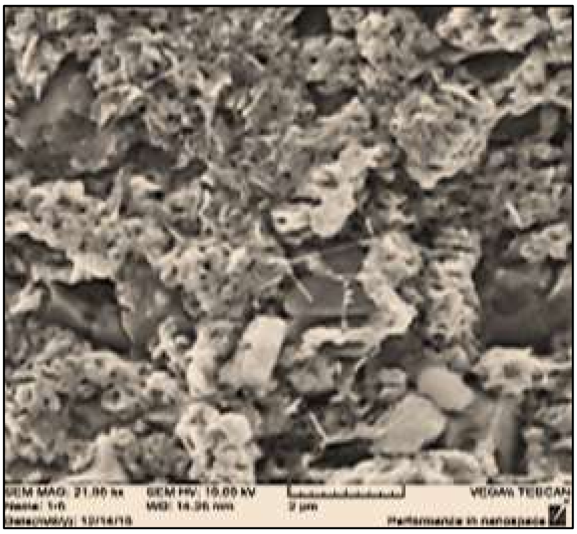

Figure 9: SEM micrograph for Ti-B-C-N thin film with 2500Sccm flow rate of ammonia

Figure 10: SEM micrograph for Ti-B-C-N thin film with 3000Sccm flow rate of ammonia

The chemical composition of the interphases between Ti-B-C-N coatings and HSS were analyzed by using energy dispersive X-ray spectroscopy (EDX). The EDX analysis of the interphase that showing in Figures 11 and 12 suggests that there is some diffusion that has occurred between Fe and Ti-base coating. The presence of Ti, N, C and O at the interphase region in the ratio of, 11.55: 1.66: 10.98: 13.4 in atom percent respectively 2500Sccm and 13.53: 2.64: 10.33: 11.6 respectively at 3000Sccm samples can be seen in these patterns. However, there is a reduction in the concentration of Fe in the interphase region (73 and 78 wt.% at 2500 and 3000Sccm respectively) which is lower than that of the substrate Fe concentration (~89.31wt%). This provides evidence that Fe has migrated into the Ti-B layer, which can explains the metallurgical bond formation between Ti-B coating and steel. Were the intermixing that occurs between Fe and Ti-B will provide evidence that Fe has migrated into the Ti-B layer, which will result in the formation of a metallurgical bond between Ti-B and steel [13-15].

III. Mechanical Characterizations

Mechanical characterization of hard metal samples has been performed using a micro hardness tester to measure the hardness of the coating. The hard metal substrate (High Speed Steel sample) hardness before coating was found to be equal to 1057 HV under testing load of 0.98N. The sequence of hardness test result after deposition process (coating) were summarized in Table 2.

From Table 2, the very low hardness of the samples that was produced under 500 and 1500Sccm was a result of the very low thickness of the Ti-base coating for these samples (1-3µm), and the softening of High Speed Steels when subjected to high deposition temperatures (over 600°C) [16,17]. Because of thermodynamic and kinetic reasons, high temperatures are needed for thermal chemical vapor deposition (CVD) in this materials system. Therefore, no hardness enhancement was reported for which the hardness typically decrease during annealing due to decrease the defect density and compressive stresses relief [11].

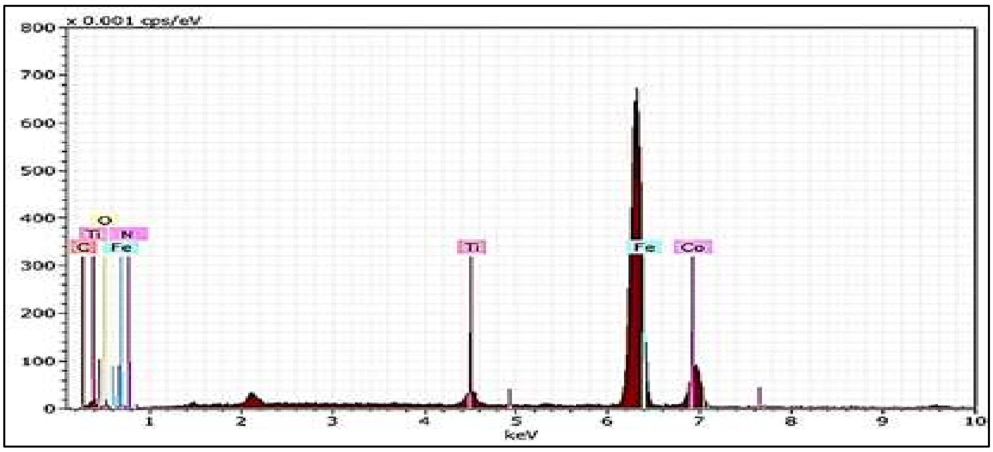

Figure 11: EDX test of the interphases between Ti-B-C-N coatings and HSS at 2500Sccm NH_3.

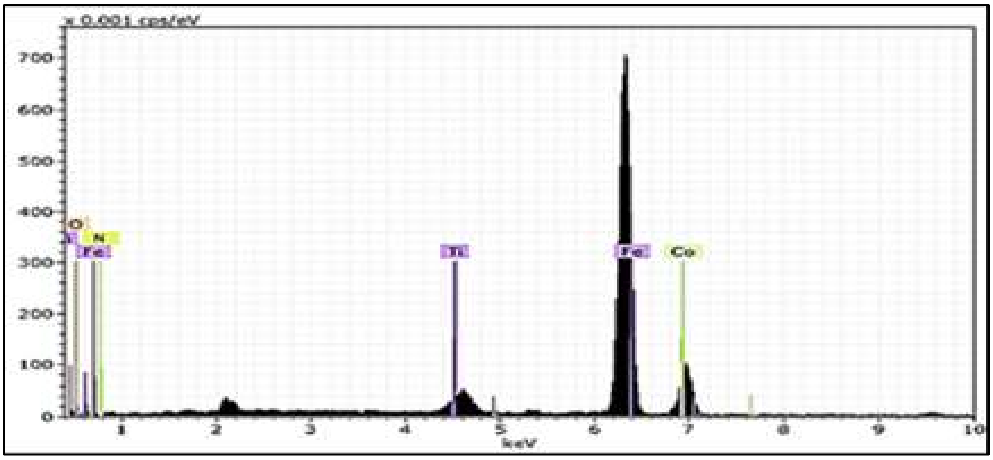

Figure 12: EDX test of the interphases between Ti-B-C-N coatings and HSS at 3000Sccm NH_3.

The maximum hardness achieved for the Ti-B-C-N thin film was recorded for the sample that was deposited under 2500Sccm of Ammonia flow rate (2051 HV), this records can be resulted from the higher thickness that achieved by the formation of the new film microstructure which contain fine fiber structure as a strengthening second phase in the Ti-B type structure with a sufficient amorphous phase (B-N) as a matrix which is visible in XRD patterns, and SEM topography in Figures 5, and 9 respectively. The Ball-on-disk test was performed on the coated and the uncoated samples to calculate the Coefficient of Friction (COF) and wear resistance of the tool surface by using a Microtribometer testing machine with sliding lubricant-free conditions. The testing was carried out in according to the standard test method for wear testing of ASTM G99-04. All samples were tested at room temperature (22 ± 2 °C) with a relative humidity of 20–70%. The applied normal load on the surface of samples was 10N by using a load suspension system. The test counterpart was a 6 mm diameter of martensitic steel ball (AISI 52 100), a circular sliding path with a radius of 3 mm and a velocity of 250 rpm was also used. The average COF of the High Speed Steel substrate is shown in Figure 13a. The process of the wear test will cause the temperature of metal surface to increase; this will result in an increase in the COF for the HSS tools, which will lead to high wear rate for this material. This phenomena is the main parameter that limit the use of HSS tools for not to be used in high speed machining for high strength materials. The Ti-B-C-N coatings generally have average COF that range between (0.7-0.9) as reported by many researchers. [9] The Ti-B-C-N coatings that deposited under low ammonia flow rate for samples that deposited under 2000Sccm show relatively high COF values (0.72–0.86), although they offer better thermal stability than the HSS tools as can be seen in Figure 13b. These

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relatively high COF measured values are possibly resulted from the large volume fractions of the Ti-B crystal phases in the coatings that characterized by the high hardness (which degraded due to the presence of oxides) and high COF with low toughness flow rate in Figure 13c exhibit relatively good COF values (0.61–0.73), also they offer better thermal stability than the HSS tools. This good result can be attributed to the effect of the more dense featureless structure and the uniform coating with no apparent cracks and less surface roughness that can be seen clearly from the SEM images in Figure 9 for this sample [18].

Table 2: The measured hardness and coating thickness for the Ti-base coating samples

Sample	Thickness of Ti-base coating (µm)	Hardness(Hv) of fixed Points on sample surfaces	Average of Hardness, HV (Kg/mm^2)
500Sccm	1-3	648,993,419,604,692,	671
1500Sccm	3	1273,1096,637,902,674	916
2000Sccm	6	1467,1431,1189,1395,1402,	1376
2500Sccm	19	2038,2068,2064,2036,2053	2051
3000Sccm	12	1206,1240,1243,1279,1248,	1243

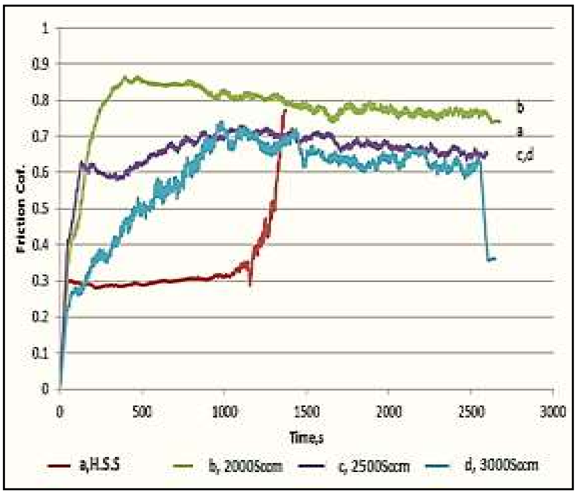

Figure 13: COF charts for H.S.S. and Ti-B-C-N coatings a. uncoated H.S.S., b.2000Sccm, c.2500Sccm, d.3000Sccm

4. Conclusions

The Ti-B-C-N coatings have been deposited on the H.S.S tools by using a mixed gas phase deposition process technique (PVD and CVD) as a new rote for the hard film deposition. Ti-based coatings were deposited with different nitrogen flow rates (500-3000Sccm) and at the same deposition temperatures (950°C). The deposition rate of the Ti-base coatings increases slightly with the nitrogen flow rate and it presents a maximum (20 µm thickness) for ammonia flow rate of 2500Sccm. The deposited thickness decrease for nitrogen flow rates higher than 2500Sccm (at 3000Sccm) is probably due to the formation of a nitride layer leading to a decrease of the deposition rate. Also, the presence of a continuous interface explains the formation of a metallurgical bond between Ti-B and steel. The maximum hardness achieved for the Ti-B-C-N thin film was recorded for the sample that was deposited under 2500Sccm of ammonia flow rate (2051 HV), this records can be resulted from the higher thickness that achieved by the formation of the new film microstructure which contain fine fiber structure as a strengthening second phase in the Ti-B type structure with a sufficient amorphous phase (B-N) as a matrix which is visible by XRD patterns, and SEM topography.

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Author(s) biography

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