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# Surface Integrity of TiC Thin Film Produced by RF Magnetron Sputtering

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## Abstract

Surface structure determines the performance of materials in service. Enhancing the surface topography of materials with a refractory ceramic coating such as Titanium carbide has gained unprecedented development of recent due to the increase in applications of these functionally graded materials. Radio frequency (RF) magnetron sputtering exhibits a lot of potential in depositing and growing thin film thin. One of the major advantages of RF magnetron sputtering is the ability to be used to coat both the conducting and insulating target. In this research work, RF magnetron sputtering is used to grown titanium carbide (TiC) on Ti6Al4V alloy. The process parameters varied in this study are deposition time, substrate temperature and deposition Power. Other parameters were kept constant throughout the deposition process. Atomic force microscope and Optical profilometer were used to determine the surface roughness of the thin film and scanning electron microscope is employed to analyze the morphology of the surface structure. Homogenous and dense surface morphology was noticed for sample with mid-process parameters and the surface roughness reduces with increase in process parameters.

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**Keywords:** Magnetron sputtering, Process Parameter, Surface Strcuture, Thin film, Titanium Carbide

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## 1. Introduction

The surface integrity (morphology, topography, structure, roughness, and texture) of material has a substantial impact on the sophisticated surface related properties, such as optical, magnetic, electronic, catalytic, mechanical,

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chemical and tribological properties [1]. The importance of surface integrity lies in their ability to improve performance, create new products and conserve scarce materials by substitution [2]

Several methods of surface treatment have been used for improving and modifying the surface properties [3,4]. These processes include laser cladding, laser additive, weld overlay, heat treatment, implantation, carburizing, nitriding, chemical vapor deposition CVD, physical vapor deposition PVD and electrochemical deposition[5-11] Surface modification of materials by coating with refractory carbides and nitrides is an area that poses viable ways for enhancing the surface properties, require attention and need to be investigated.

Refractory nitrides and carbide are prominent materials with several applications in both industries and research environments. They are being considered to be materials of great interest to the scientific world with attractive promising future and properties. They possessed unique properly such as high strength and rigidity, excellent hardness behaviour, enhanced tribocorrosion resistance, high-temperature stability, resistance to radiation, high thermal conductivity, low coefficient of friction, outstanding biocompatibility and electrical insulation (semiconductor applications) and can take the form of powders, bulk/monolithic shapes, fibres, whiskers, and coatings[12-14].

From the practical applications point of view, carbides form the most important class of inorganic refractory compounds and Titanium carbide (TiC) is one of the major materials of interest in this category. TiC appears to be one of the most important and hardest pure refractory carbides known [14]. TiC is exclusive because of the specific properties such as hard and high strength and outstanding wear resistance. It has a meagre coefficient of friction and moderate modulus of elasticity. It also has good stability at high temperature. For these reasons, it has become a major industrial and research material for many applications [15].

With the enormous coating techniques available, PVD has been one of the most promising technique since it can be easily and readily produced with high repeatability rate, non-thermally activated excellent adhesion bond and good composition control without the high-temperature requirements of CVD. Magnetron sputtering, which is a variant of the PVD process has been an area of interest in the research community of recent. The process involves removal of atoms from the surface of the target material by transfer of sustainable momentum from an atomic-sized energetic bombarding particle usually gaseous ion accelerated from a plasma and condensation of the ejected atom on the surface of the substrate.

Since it has been established that the surface integrity is a determinant factor for enhancing the physio-chemical properties and magnetron sputtering is a viable coating technique for modifying the surface, magnetron sputtering has been explored for numerous research work but optimizing the operating parameters is a limiting barrier encountered in PVD technique. It becomes imperative to investigate the influence of the process parameters of magnetron sputtering on the formation of thin film coating morphology since engineered surface structure can be achieved by optimizing the process parameters. In this study, three independent process parameters namely sputtering power, time and temperature were selected and varied from low to high level.

## 2. Experimental Set-up

### 2.1. Sample preparation and Sputtering

Titanium carbide TiC coatings were deposited by radio frequency (RF) magnetron sputtering deposition technique. A solid TiC target of 95.5% purity of 75 mm and 3 mm in diameter and thickness respectively was used as the target source. The substrate-target distance was maintained at 13cm throughout the deposition process. Prior to deposition, the sputtering chamber was first evacuated to a pressure of  $1.13 \times 10^{-5}$  mbar. The reason for the low pressure is to provide a long mean free path for a collision between the target and substrate and allows for the control and minimization of contaminants. The process parameter used is presented in table 1. After thorough evacuation of the chamber, the system was filled with argon to a partial pressure of 0.1-10 Pa.

Table 1. Sputtering process parameter

| Process parameter | Sample1<br>(Low) | Sample2<br>(Medium) | Sample 3 (High) |
|-------------------|------------------|---------------------|-----------------|
|-------------------|------------------|---------------------|-----------------|

|                                    |     |     |     |
|------------------------------------|-----|-----|-----|
| Power (W)                          | 150 | 200 | 250 |
| Time (Hrs.)                        | 2   | 2.5 | 3   |
| Temperature ( $^{\circ}\text{C}$ ) | 80  | 90  | 100 |

The flow rate of argon was kept constant at 12 sccm and the working pressure maintained. Maintaining constant pressure helps to place many argon atoms in the path of the ions and ejected coatings. After the plasma formation, the sputtering of the target is triggered, and the shutter is removed. Pre-sputtering was done on all the samples for 5 mins before the main sputtering deposition. The substrate Ti6Al4V was located directly above the target on a rotating disc to ensure uniform distribution and condensation of the target on the surface of the substrate. Prior to deposition on the substrates, the samples were grinded with Silica carbide papers (#320, #400, #600) and polished to remove surface impurities. The substrates were additionally cleaned with acetone, isopropanol and finally with deionized water for 15mins respectively.

## 2.2. Characterization

### 2.2.1. Atomic force microscopy and Optical profilometer

Atomic force microscopy (Veeco Di2100) AFM was engaged to capture the 2D and 3D surface topographies of the samples. Images were taken at  $5 \times 5 \mu\text{m}^2$  scan size in tapping mode and two areas of the disc were selected for analysis. Optical profilometer was used for further analysis of the surface topography.

### 2.2.2. Field Emission Scanning electron microscopy

Field Emission Scanning Electron Microscope FESEM (ZEISS Gemini\*2 Germany) capable of taking nanoscale images was used to observe the surface morphology evolution. The FESEM can take images at very high magnification and images were taken at 50,000x magnification.

## 3. Result and Discussion

The cross-sectional area of the FESEM image is shown in figure 1. Good adhesion bond between the film (TiC) and the substrate (Ti6Al4V) was noticed with film continuity. The coating is free of structural defects like crack and void

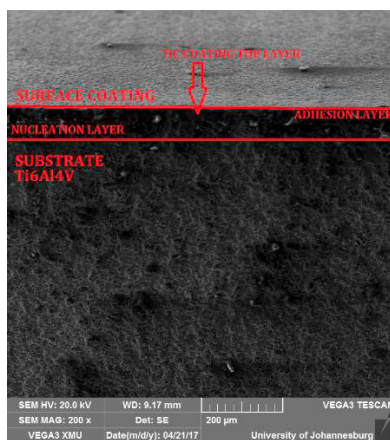


Figure 1. The cross-sectional area of the FESEM image

Figure 2 shows the planar area of the coating at 50,000x magnification. From the surface morphology of the planar view, three different film nucleation and growth were noticeable.

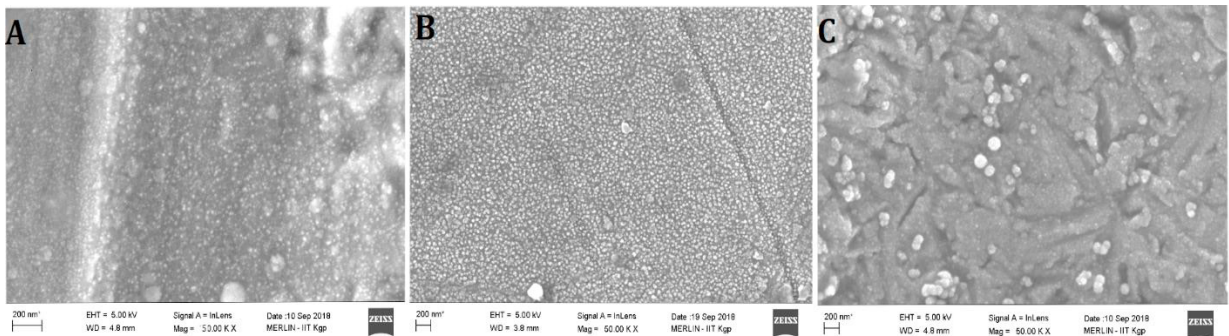


Figure 2. Planar view of the FESEM images (A) Sample A, (B) Sample B, (C) Sample C, at a magnification of 50,000x

For sample A, an island growth mechanism is predominant in film nucleation on the substrate. This growth can be noticed when the adherence between the atom to atom is greater than the bonding between the substrate and the adatoms [16,17]. Two different layers were also present. The bottom layer which is the surface of the substrate and the top layer that shows the initial nucleation and growth of stable adatoms accumulate and coalesce on the surface to form thin film coating. Both columnar and equiaxed grain structure noticeable on the surface.

From the FESEM images, for sample 2 with the mid-process parameters, the surface morphology becomes refined and exhibits a uniformly layered homogenous distribution of TiC film. The high energy associated with the process parameter of sputtered particles improves adhesion, produces a densely packed equiaxed structure and grain recrystallization. The high energy level is also tantamount to the higher deposition rate of ejected atoms from the target to the substrate surface: No visible pores or pits generated on the surface. The columnar structure noticed in sample 1 almost disappeared in sample 2. It has been reported that a columnar structure is inferior to an equiaxed structure [18,19]. At lower temperature, coalescence of atoms is slower and as the temperature increases, the rate of surface diffusion of the atoms also increases. Grain boundary migration takes place not only during coalescence but throughout the film thickening process resulting in a structural change of the film. The growth mechanism in sample 2 is similar to Volmer Weber growth mechanism. For Sample 3, reoccurrence of two layers can be seen. The outer layer which consists of the meager sparingly distributed grain and the inner layer which is made up of compact grain with a crack in between. The first layer becomes a new open substrate area for rapid coalescence which results in the formation of secondary nucleation zone on top of the bottom equiaxed layer. The nucleation mechanism in sample 3 is similar to the Stranski-Krastanov mechanism. The Stranski-Krastanov mechanism combines both island and growth mechanisms. The ejected atoms from the target begin to accumulate and form islands after an initial layer has grown [20,21]. The transformation from a monolayer to bilayer is due to secondary recrystallization of the atoms. The second recrystallization also referred to as abnormal grain growth had been reported to result in much larger in-plane grain size and enhanced degree of surface texture [22]. The film structure of the bottom layer is equiaxed and homogenous while reoccurrence of the columnar structure was noticed on the top layer. The crack formation in the bottom layer may be as a result of extensive plastic deformation of the thin film grain boundary. Crack nucleation by void coalescence and formation of pores has been reported to occur in the amorphous phase of higher ductility [23-27]. Although the crystalline and amorphous phase can only be properly understood by doing in-depth structural analysis like by XRD, there are several studies that have reported on how the process parameter impact the structural phase and columnar grain growths can consist of both nanocrystalline and amorphous structure [28]. Thin film coating consists of two phases: a nanocrystalline phase and an amorphous phase and this can be altered by varying the sputtering time, deposition power and substrate temperature. Structures with columnar and equiaxed grain reveal both phases [1].

The 3D surface images and the height profile of the AFM results are presented in figure 3. The 3D AFM structure for sample 1 exhibits extended columnar grain growth which agrees with the result of the FESEM images. The AFM morphology of samples 2 shows evenly distributed coating and for sample 3, the surface becomes coarse

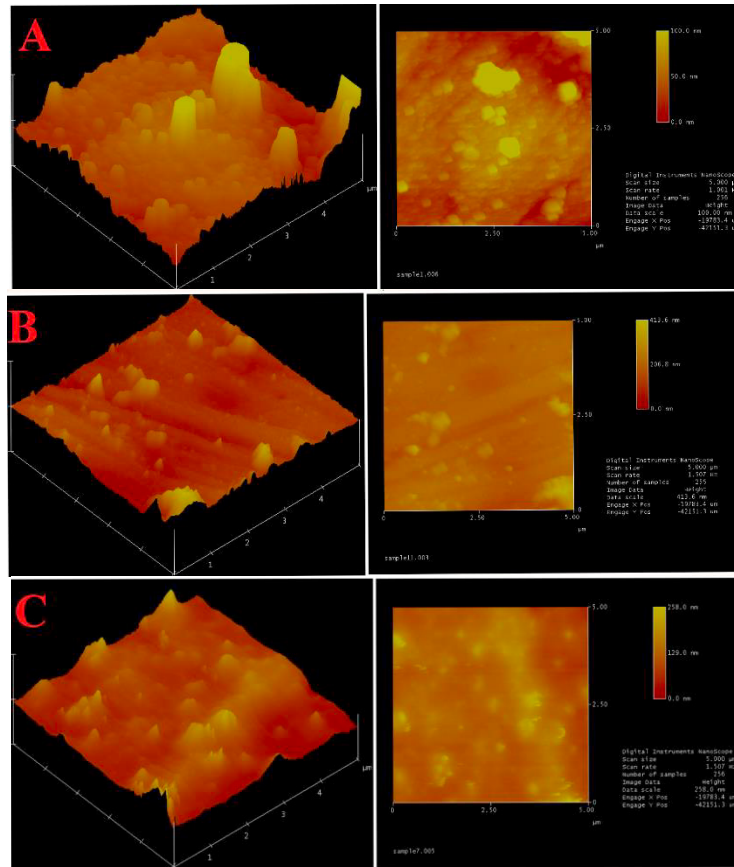


Figure 3: AFM images (A) Sample A, (B) Sample b and (C) Sample C

The surface roughness of the coating is 3.429 nm, 1.358 nm, and 1.541 nm respectively. The variation in the process parameters influences the final morphology of the surface coating. The level of discrepancies noticed for the surface roughness between sample 2 and 3 is small compare to sample 1 and 2. The reason for the high anomalies from sample 1 to 2 is the change of surface structure to from columnar to equiaxed nanocrystalline film. The nanocrystalline film shows a smaller grain size and better adhesion properties. The 3D-surface profile from the optical profilometer is shown in figure 4. The low height variation for the sample is an evidence for uniform and homogenous coating. High peaks are noticeable for the other samples.

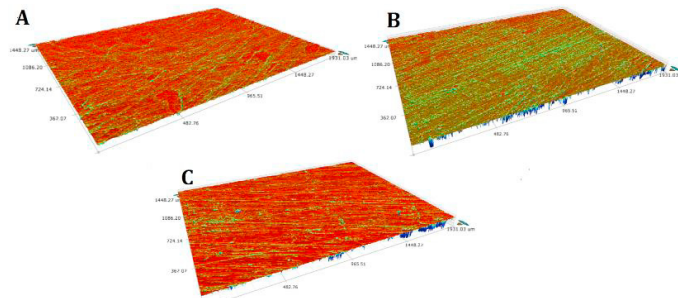


Figure 4: Optical surface profilometer 3D images of the samples

## 4. Conclusion

The observation from the surface characterizations shows promising results that can stand as an argument for further characterization. The variation in the morphology and structures of the FESEM and AFM images will be a motivating factor for future analyses on the sample to better understand the film nucleation and growth process. It has been established that the process parameters influence the surface integrity and the process parameters used in this study can be used in designing complex experimental setup and design of the experiment matrix.

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