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INFLUENCE OF NITROGEN FLOW RATE IN REDUCING TIN MICRODROPLETS ON BIOMEDICAL TI-13ZR-13NB ALLOY

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Abstract

Cathodic arc physical vapor deposition (CAPVD) is one of the promising techniques that have a potential to coat titanium nitride (TiN) on biomedical implants due to its good adhesion and high evaporation rate. However, this method emits microdroplets which have the possible detrimental effect on the coating performance. Past studies indicated that micro droplets can be controlled through proper deposition parameters. In the present work, an attempt was made to study the effect of nitrogen gas flow rates (100 to 300 sccm) on TiN coating of the Ti-13Zr-13Nb biomedical alloy. Scanning electron microscopy (SEM) was used to evaluate surface morphology and coating thickness while crystal phase of the coated substrates was determined using X-Ray Diffraction (XRD). Image analysis software was employed to quantify microdroplets counts. Results show that higher nitrogen gas flow rate able to decrease a significant amount of microdroplets and concurrently increase the thickness of TiN coating. A mixed crystal planes of (111) and (220) are obtained on the coated substrates at this setting which exhibits denser structure with higher adhesion strength as compared to substrates coated at the lower N2 gas flow rate.

Keywords: Microdroplets, CAPVD, TiN, Ti-13Zr-13Nb, N_2 gas flow rate

Abstrak

Cathodic arc physical vapor deposition (CAPVD) merupakan salah satu teknik yang berpotensi untuk menyalut titanium nitrida (TiN) ke atas implant bioperubatan disebabkan kekuatan lekatan yang baik dan kadar sejatan yang tinggi. Walaubagaimanapun, kaedah ini menghasilkan titisan mikro yang mempunyai kesan yang buruk ke atas salutan. Kajian lepas menunjukkan bahawa titisan mikro boleh dikawal melalui parameter salutan yang sesuai. Dalam kajian ini satu percubaan telah dibuat untuk mengkaji kesan kadar aliran gas nitrogen (100-300 SCCM) pada salutan TiN ke atas aloi bioperubatan Ti-13Zr-13Nb. Mikroskop imbasan elektron (SEM) telah digunakan untuk menilai morfologi permukaan dan ketebalan salutan manakala fasa kristal salut sub strat telah diuji dengan menggunakan X-Ray Diffraction (XRD). Perisian analisis imej telah digunakan untuk mengukur bilangan dan saiz titisan mikro. Hasil kajian menunjukkan bahawa kadar aliran gas nitrogen yang tinggi dapat mengurangkan sejumlah besar titisan mikro dan dapat meningkatkan ketebalan salutan TiN. Permukaan Kristal campuran (111) dan (220) diperolehi pada salutan substrat yang dihasilkan pada aliran N_2 yang tinggi yang mana mempamerkan struktur yang padat dengan kekuatan lekatan yang lebih tinggi berbanding dengan substrat bersalut yang dihasilkan pada kadar aliran gas N_2 yang lebih rendah.

Kata kunci: Microdroplets, CAPVD, TiN, Ti-13Zr-13Nb, Kadar aliran gas N_2

1.0 INTRODUCTION

Titanium alloys are broadly used in the biomedical implant for knee, shoulder and hip replacement as compared to the conventional biomedical alloys such as AISI 316L stainless steel, cobalt and chromium alloys. The advantages of titanium alloys are high strength to weight ratio, excellence corrosion resistance, superior biocompatibility and low elastic modulus[1-3]. One drawback of these alloys is poor tribological properties. Rubbing actions as a result of relative motion in articulation joints would remove TiO protective layer and expose the bare material to corrosion attack. Wear in biomedical devices also generates debris which causes toxic in the body environment[4]. This issue becomes a major concern in biomedical research communities which has prompted to look for alternatives to reduce or eliminate completely this problem.

Surface modification in biomedical implant offers better resistance to corrosion and improves tribological behavior.Widely used techniques include Chemical Vapor Deposition (CVD)[5], Physical Vapor Deposition (PVD) [6], Ion Implantation[7]and Plasma Spray coating[8]. PVD becomes the preferred choice because of its low processing temperature (<500 °C) over a wide range of coating thickness as compared to other methods. The problems exist in high processing temperature are detrimental effects on the physical and mechanical properties of the base material which restricts the type of substrates, unexpected phase transitions and excessive residual stresses due to the difference in thermal expansion between the deposited material and substrate.

There are several types of PVD techniques available commercially. However, CAPVD offers better adhesion, high deposition rate, and low voltage power supply as compared to magnetron sputtering and vacuum deposition (evaporation) [9]. Despite these advantages, deposits of microdroplets during CAPVD process has the detrimental effect on the coating performance. It is reported that the micro droplets poorly adhere to the substrate surface and their detachment causes pin holes defect [10]. This is considered as an undesirable phenomenon if occurs in coated biomedical implant where pin holes may act as channels for corrosion attack.

Recently, TiN materials have been investigated widely as an effective coating material to enhance the performance of implants on account of their high hardness, wear resistance, and good corrosion, as well as good biocompatibility. For instance, Vadiraj and Kamaraj [11] studied the performance of TiN coating on fretting wear using plasma spray and PVD. They reported that both methods improve the fretting wear better than untreated samples. Subramanian et al. [12] compared the coated samples of TiN, Titanium Oxynitride (TiON) and Titanium Niobium Nitride (TiNbN) with untreated ones on cytotoxicity effect and platelet adhesion. They noticed that coated samples improve platelet adhesion and becomes non toxic when compared to untreated ones. Pham et al. [13]evaluated the effect of a TiN film on the mechanical properties and endothelial compatibility of a Co–Cr substrate. They claimed that TiN film able to improve the mechanical properties of the Co–Cr significantly and enhances the attachment and proliferation of endothelial cells on the coated substrate.

Most of the previous studies focus on the improvement of TiN coating mechanical properties, cytotoxicity effect and cell attachment. Nevertheless, there is a limited report available in the literature addressing microdroplets issues when implant coated with TiN. It is believed that the presence of massive micro droplets on the coated substrate have a direct effect on the coating performance. Therefore, the aim of this study is to evaluate the effect of N_2 gas flow rate in reducing microdroplets deposits on Ti-13Zr-13Nb biomedical alloy during CAPVD coating.

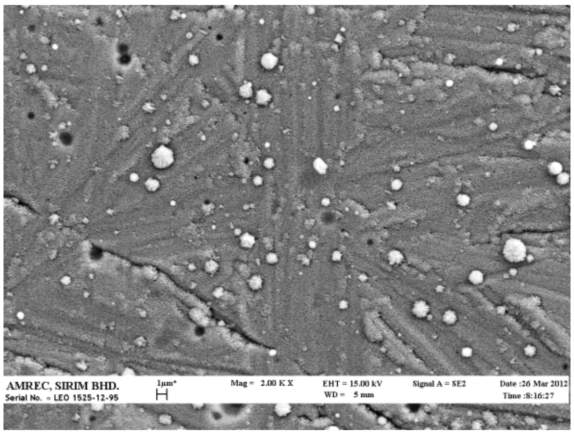
2.0 METHODOLOGY

The work piece material used in this study was biomedical grade Ti-13Zr-13Nb. The chemical compositions of the material in wt. %: are Nb: 14; Zr: 13.5; Fe: 0.05; C: 0.04; N: 0.02; H: 0.002; O: 0.10 and Ti: balance. The received material in rod was cut into disk having a diameter of 10mm x 2mm thick. Prior to TiN coating, the substrates were cleaned ultrasonically in acetone for 30 minutes, followed by a steam cleaning and finally dried using a stream of compressed air. All substrates were prepared to give uniform initial surface roughness, Ra of 0.1μm. Substrate was coated using CAPVD method. Titanium of 99.99% purity was used as the target material. Prior to the deposition, the substrates were subjected to metal ion etching for 5 minutes at -1000V bias voltage. It was followed by the deposition process which was carried out under the following fixed parameters: cathodic current (100A), deposition time (1 hr), substrate temperatures (300 °C), and substrate bias (-200V). The nitrogen gas flow rate was varied from 100 to 300 sccm (stands for standard cc per min). Surface morphology and coating thickness were examined under SEM. An XRD was used to determine the crystalline structure and d-spacing of the TiN coating.The analysis of microdroplets deposits on the coated samples was performed using two different types of commercial image analyzer software.

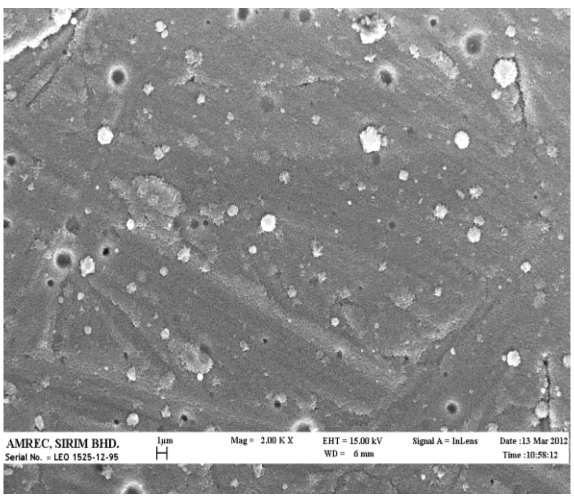
3.0 RESULTS AND DISCUSSION

TiN coating was successfully deposited at different nitrogen gas flow rates on Ti-13Zr-13Nb substrates. Prior to the coating, all substrates were prepared at the uniform surface roughness of 0.1 μm. Figure 1 shows the surface morphology of TiN coating.

Textures of surface roughness with plowing abrasive marks are still clearly visible after coating at both gas flow rate conditions. However, the substrate coated at 300 sccm (Figure 1b) provides a smoother surface than 100sccm (Figure 1b). This indicates that higher N2 gas flow rate promotes thicker coating and initial roughness of the substrate plays vital role to provide a smooth and uniform coating.



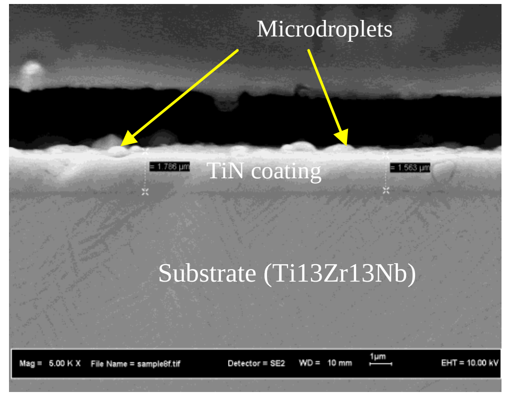
(a)



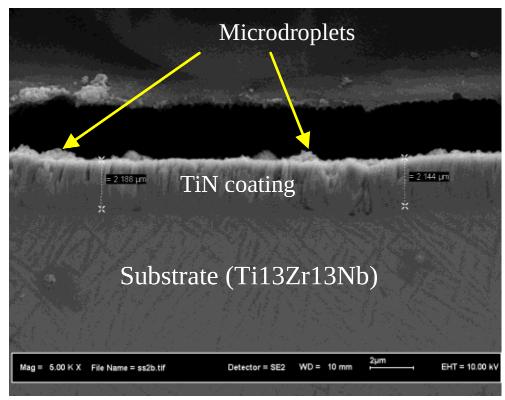
(b)

Figure 1 TiN coating surface morphology obtained at different nitrogen gas flow rate (a) 100 sccm (b) 300 sccm

Figure 2a and 2b show the cross sectional views of the TiN coating on these substrates when coated at 100 sccm and 300 sccm respectively. Both conditions are able to produce a well adhered and uniform coating thickness without any noticeable voids or cracks in between the coating and the substrate. These figures illustrate that 300 sccm N_2 gas flow rate produces 30% thicker coating than 100 sccm gas flow rate. The reason behind this phenomenon can be explained as follows. When nitrogen gas flow rate is increased, more ionize and excitation of Ti metal ion occurs in the vacuum chamber and this gives greater chance for the metal ion to react with nitrogen gas to produce a synthesis of TiN. In contrast, less N2 gas flow rate limits the ionization process of Ti metal ion to take place and hence reduces the synthesis of TiN which finally results in thinner coating deposited on the substrate.



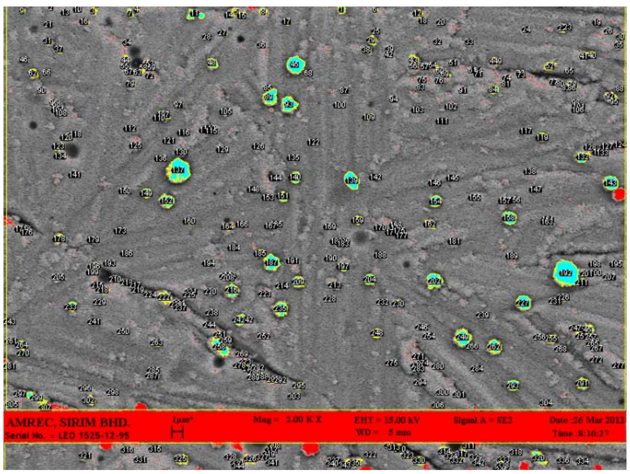
(a)



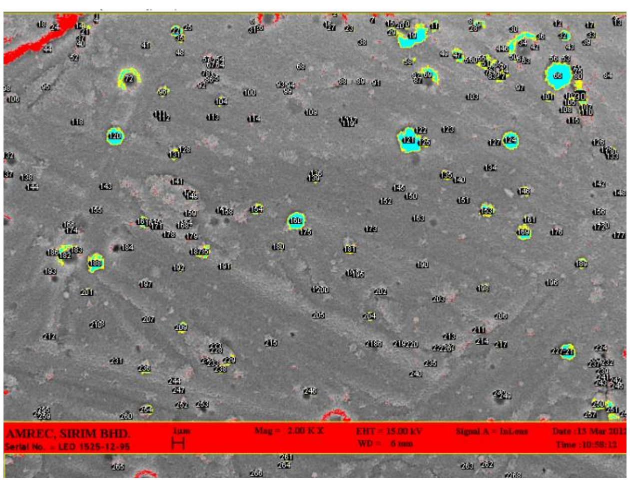
(b)

Figure. 2 Cross sectional views of TiN coating thickness at different nitrogen gas flow rate (a) 100 sccm (b) 300 sccm

Despite smooth TiN coating observed on the substrates in Figure 1, there are also traces of microdroplets which appear in white color spots. It seems that a number of microdroplets have an inverse relationship with N_2 gas flow rate. The massive presence of microdroplets in Figure 1a can be attributed to the incomplete ionization process at lower N_2 gas pressure. Image analysis software was used to verify the amount of microdroplets on the TiN coating surface under both gas flow rate conditions. Prior to the microdroplets counting analysis, both images in Figure 1 were enhanced using Photoshop software for improving the edge quality. This action helps to provide better contrast between microdroplets border and the TiN coating matrix. It was achieved through the application of sharpening edge filter. Second image analysis software was employed to quantify and classify microdroplets features into average ferret diameter and groups. This was done through five steps operations, i.e. i) image calibration, ii) selection region of interest, iii) image thresholding, iv) roundness adjustment and v) quantification and grouping of microdroplets size. In the final step, only microdroplets size of above 0.2 µm was considered into grouping. Any microdroplets size below 0.2 µm is regarded as noise. Figure 3 shows the completed output from this analysis. Different color in the image represents a similar group of microdroplets size. Table 1 summarizes the counts in each range under different N_2 gas flow rates. Specifically, substrates coated at 300 sccm have a lower microdroplets count compared to 100 sccm. This result proves that higher N_2 gas flow rate able to reduce microdroplets deposition during coating.



(a)



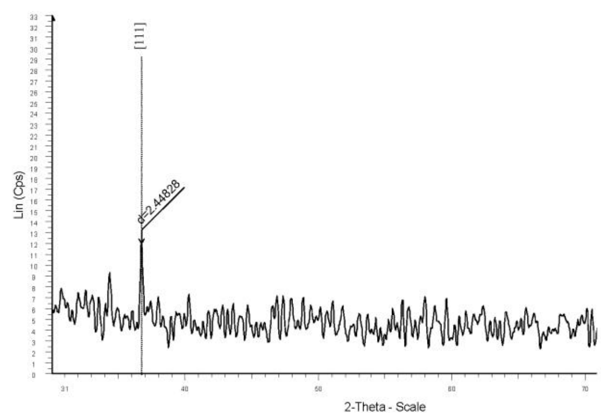
(b)

Figure 3 Output images of macrodroplets counting using image analyzer at (a) 100sccm, (b) 300sccm N_2 gas flow rate

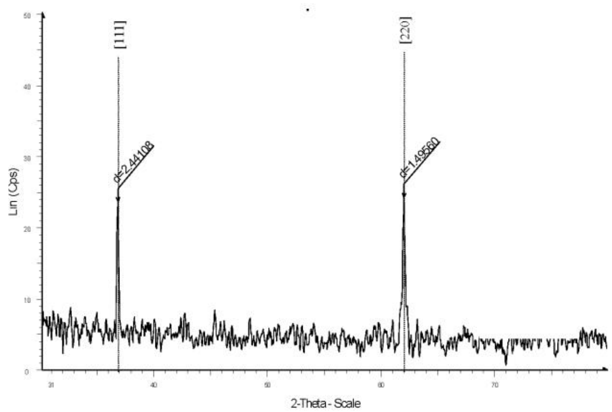
Table 1 Summary of macrodroplets counts

Microdroplets diameter, µm	N_2 gas flow rate	
	100sccm	300sccm
0.200 - 0.500	3	3
0.501 - 1.000	180	154
1.001 - 1.500	110	69
1.501 - 2.000	35	26
2.001 - 2.500	13	9
More	4	7
Total counts	345	268

XRD patterns shown in Figure 4 provide information on the crystalline plane and d-spacing of TiN film deposited on Ti-13Zr-13Nb at different nitrogen gas flow rates. TiN coating at low N_2 gas flow rate exhibits single crystal plane (111) while a mixed crystal plane (111) and (220) is obtained at a higher gas flow rate. This suggests that a highly crystalline TiN phase was able to be deposited on the substrate at this range of coating parameters. N_2 gas flow rate seems to have a direct influence on the kinetic energy of incident particles onto the substrate surface. The competition between the surface and strain energies in TiN film becomes larger at the higher N_2 gas flow rates which finally affect the change in the growth orientation. It is also noticed that the d-spacing value in (111) crystal plane becomes smaller when N_2 gas flow rate was increased from 100 sccm to 300 sccm. This suggests that higher N2 gas flow rate produces denser structure and more compact.



(a)



(b)

Figure. 4 XRD patterns of TiN coating deposited at different N_2 gas flow rate (a) 100sccm (b) 300sccm

4.0 CONCLUSION

TiN coating was successfully deposited on Ti-13Zr-13Nb alloy using CAPVD technique at two different nitrogen gas flow rates. The main results obtained from this study can be summarized as follows:

I. Nitrogen gas flow rate has an inverse relationship to the formation of TiN micro droplets on the Ti-13Zr-13Nb alloy. As N_2 gas flow rate increases the number of microdroplets decreases significantly. Reduction in the microdroplets count on the coating surface has the potential to reduce a risk of corrosion attack when implants in the body fluid.

II. A dense, smooth and well adhered TiN coating without noticeable voids or cracks are successfully deposited on the Ti-13Zr-13Nb substrate. A low N_2 gas flow rate provides thinner coating thickness and vice versa.

III. XRD patterns show that a highly crystalline TiN phase ((111) and (220)) is feasible to be deposited on the Ti-13Zr-13Nb substrate within the range of studied coating parameters. Higher N_2 gas flow rate produces mixed crystal phases with dense and higher adhesion coating strength.

IV. Initial surface roughness of the substrate has a direct influence on the smoothness of the TiN coating on the titanium-zirconium alloy. Surface finish of less than 0.1 μm is recommended for preparing titanium substrate for TiN deposition.

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