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Thermal Oxidation Promotes Growth of Nanocrystalline Diamond on Co-Cr-Mo Alloy

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Abstract:

Diamond coatings are employed to yield significant benefits in applications such as for cutting tools, optical lenses, biomedical components, microelectronics, engineering and thermal management systems. Although there are many research reporting the successful of diamond coating on titanium, tungsten carbide and steel alloys but there are still lacking of research on the cobalt based alloy as the substrate. In order to coat thin film diamond on these metals substrate, chemical vapor deposition (CVD) technique is commonly used. This paper reports on investigations of nano-crystalline diamond (NCD) coating on different carbon content (0.24% and 0.03%) of cobalt based alloys. Emphasis is given to achieve good adhesion of NCD coating on low and highcarbon content of biomedical grade cobalt-chromium-molybdenum (Co-Cr-Mo) alloys using two different processes of surface pretreatment such as mechanical roughening and thermal oxidation. The results revealed that most of the diamond coating was peel-off on the roughened samples. However, there were small portion of diamond coating that still intact on sample that treatedusing thermal oxidation. The thickness diamond coating obtained was approximately 5µm on oxidized samples. Since the adhesion strength of the diamond coatings were very poor and easily delaminated on all samples condition, scratch test could not be performed. Surface morphology and characterization of diamond coatings were investigated by Field Emission Scanning Electron Microscopy (FESEM) and X-ray diffraction respectively.

Keywords: *Co-Cr-Mo alloy, thin film, NCD coating, surface morphology, biomaterial*

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I. INTRODUCTION

Cobalt-chromium-molybdenum (Co-Cr-Mo) alloys have long being used for orthopaedic and dental implants due to their good mechanical and biocompatibility properties [1, 2]. Although this material has been used to produce metal-on-metal artificial joint surfaces, which is said to be extremely good to resist surface wear, it has been shown that the use of these implants over the time result in the release of toxicity metal ions in many patients [3, 4]. To overcome these issues, surface modifications often required[5]. One of the solution that recently been gaining in popularity is by coating the metals with nanocrystalline diamond (NCD) using chemical vapour deposition (CVD).Many researchers agreed that CVD is a perfect technique which allows thin film of diamond coating deposited onto a range of different materials in a cost-effective manner[6, 7]. It is also believed that diamond coatings exhibit good biocompatibility, low friction, low wear rate and good corrosion resistance.

Although there are many research proof that nanocrystalline diamonds (NCD) films grown successfully on other metals such as tungsten carbide[7], titanium [8]and steelalloy [9]with effectively improve the performance of their

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mechanical properties but thereis still few researchhave been done to study NCD coating on Co-Cr-Mo alloy.

In the present work, atwo different processes of surface pretreatment such as mechanical roughened and thermal oxidation were carried out before diamond coatings were depositedon biomedical grade Co-Cr-Mo alloy using hot filament chemical vapour deposition (HFCVD) method.It is expected thatNCD coatings able to anchoring substrate surfaces toreduce corrosion as well as enhance the bone growth.It is also hope that the findings from this research will help scientists and manufactures to produce a moresustainable biomedical implants.

II. EXPERIMETAL DETAILS

The Co-Cr-Mo alloy with two different carbon contents i.e.0.24%Cand 0.03%C were used as the samples. The chemical composition of samples material used in the present study is given in Table 1. These samples are referred as high carbon (HC) and low carbon (LC) respectively. The specification of substrate materials follows the international standards (ASTMF1537) and it is suitable for use as biomedical implant. The rod substrate was cut using a precision cutter into small disk samples with a diameter and thickness of 14 mm and 2 mm respectively. All samples preparation was ultrasonically cleaned with acetone for 30 minutes, followed by steam cleaning and finally were dried using a stream of compressed air before ready for next process [10]. Co-Cr-Mo alloys samples were then prepared using two different processes of surface treatment, i.e. mechanical roughened and thermal oxidation process in order to obtain different sets of surface roughness before underwent diamond coating deposition using HFCVD.

The first batch of HC and LC samples were prepared usingmechanically roughened with wet ground using #500 grit SiC paper and the final average roughness obtained from theroughened samples was 0.10 ± 0.02µm. While, the second batch of HC and LC samples wereundergone thermal oxidation at temperature 1050°Cfor 3 hours directly after the drying process. Their final surface roughness, Ra after oxidationfor HC and LC samples were1.0 ± 0.03µm and 1.52 ± 0.02µm respectively. Surface roughness of all samples condition was measured using Mitutoyo SJ-301surface profilometer.

The purpose of thermal oxidation process was done is to create oxide interlayer (chromium oxide, Cr_2O_3) on the substrate surface, which acts as an intermediate layer between the substrate and diamond coating.Types of oxide/carbide layer formed on the substrate were characterized using XRD and scanning electron microscope.All the prepared samples are then sent to CemeCon AG, Germany for smooth diamond coating in a CC800®/9 Hot Filament Chemical Vapour Deposition unit. The gasses involved were hydrogen, methane and oxygen involving oxygen pulsing every half an hour for 22 hours and 1-hour cooling.Surface morphology and thickness of the diamond coated samples were performed using the Zeiss Supra 35VP field-emission scanning electron microscopy (FESEM)with energy dispersive X-ray (EDX) attachment.

Table 1. Chemical composition of high carbon (HC) and low carbon (LC) of Co-Cr-Mo alloy as supplied by Carpenter Technology Asia Pacific PTE Ltd in Singapore.

Alloy Designation	**Element wt%**				
	C	**Co**	**Cr**	**Mo**	**Mn Si Ni Fe Cu**
HC	0.24	61.9	29.6	6.5	Residual elements
LC	0.03	65.3	27.5	5.5	Residual elements

III. RESULTS AND DISCUSSION

HFCVD diamond coated on high carbon (0.24%) and low carbon (0.03%) of Co-Cr-Mo alloy are shows in Fig. 1 to 4. It is observed that the diamond film nucleates and grows only on oxidized samples of HC and LC Co-Cr-Mo alloy but not presence in anysamples that treated with mechanical roughened. This is probably due to the high solubility and diffusivity of carbon in cobalt, which acts as a carbon sink (with a formation of solid solution), that promotes the formation of non-diamond carbon (graphite [11] or soot [12]) and thus delays the onset of diamond nucleation on the samples.

Even though it is notable thatthere is the presence of thin film of diamond coating on oxidized LC sample, but the adhesion strength of the diamond film is very poor and easily delaminated from the substrate. Therefore, adhesion test is not able to performed on the samples.

Based on the FESEM images, diamond formed on

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oxidized LC as shown in Fig. 1d. No diamond formation was observed on roughened sample of HC and LC as shown in Fig. 1a and Fig. 1b respectively.

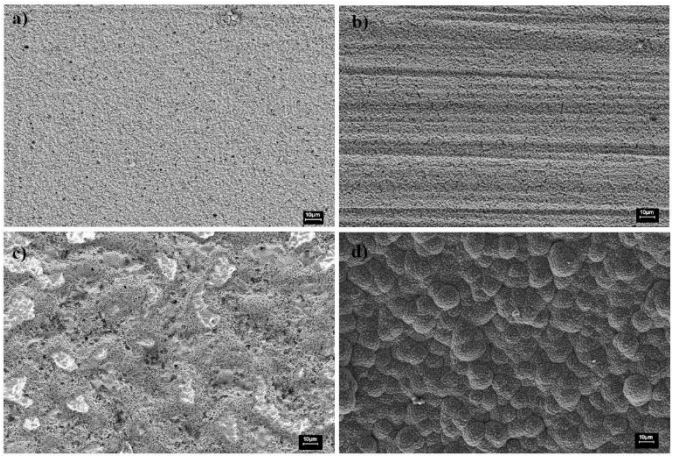

Fig. 1 FESEM surface morphology after diamond deposition at 500x magnification (a) Roughen HC, Ra ≈ 0.3µm. (b) Roughen LC, Ra ≈ 0.3µm. (c) Oxidized 1050°C, 3h HC. (d) Oxidized 1050°C, 3h LC.

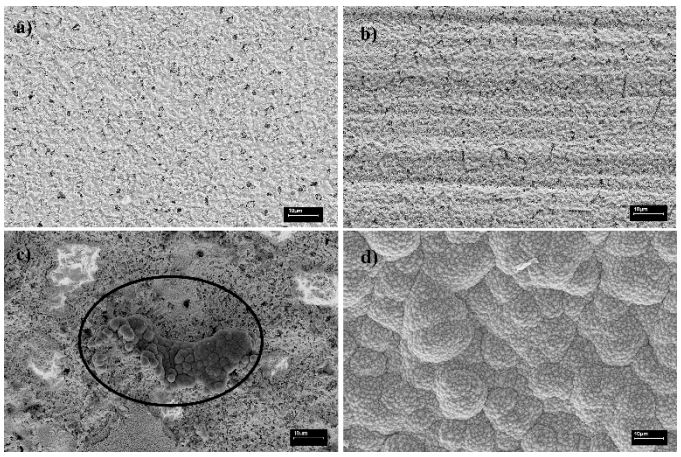

Fig. 2 FESEM surface morphology after diamond deposition at 1000x magnification (a) Roughen HC, Ra ≈ 0.3µm. (b) Roughen LC, Ra ≈ 0.3µm. (c) Oxidized 1050°C, 3h HC. (d) Oxidized 1050°C, 3h LC.

Fig. 2 shows a higher magnification of the diamond coating morphology on HC and LC of Co-Cr-Mo alloy.It is worth to note that in Fig. 2c there is diamondthat nucleate and grow on oxidized HC sampleas highlight in black circle. According to Fig. 2dthe evidence of crystal structure with no facet and ball-like structure known as cauliflower structure was observed[13, 14].Based on FESEM micrographs, the nanocrystalline diamonds (NCD) are grown in ballas or cauliflower morphologythat deposited on oxidized LC substrate of Co-Cr-Mo alloy.The similar results also claimed by other researcher who studied about NCD coating on tungsten carbide samples[15].

However, only oxidized LC samples were able to measure the thickness of diamond coating in this research study. As mentioned earlier, a small site of diamond was nucleated on oxidized HC samples which is impossible to be measured. The average thickness of thin diamond film obtained on oxidized LC substrate is 4.92µm (Fig. 3).While in Fig. 4, the cross-section of diamond coating on oxidized samples HC and LCare shown.

Based on the FESEM observations, it is clearly shows that diamond formation growth below the oxide layer in oxidized HC sample. While, the opposite manner was observed in oxidized LC sample as diamond formation growth on top of oxide layer with thickness about 4µm (Fig. 4d). Since the preparation samples of HC and LC prior to diamond deposition is similar, therefore this phenomenon can be explained by the different carbon content in Co-Cr-Mo alloy. Due to high carbon content in HC Co-Cr-Mo alloy (0.24%C) somehow have suppress diamond from growth outward as shown in Fig. 4c. Additionally, it is also known that nucleation of diamond ballas tends to prefer certain sites enhancing accumulation of ballas. Thus, oxidized LC sample possess higher surface roughness (1.52 ± 0.02µm vs. 1.0 ± 0.03µm), it isexpected to obtain diamond film on this sample.

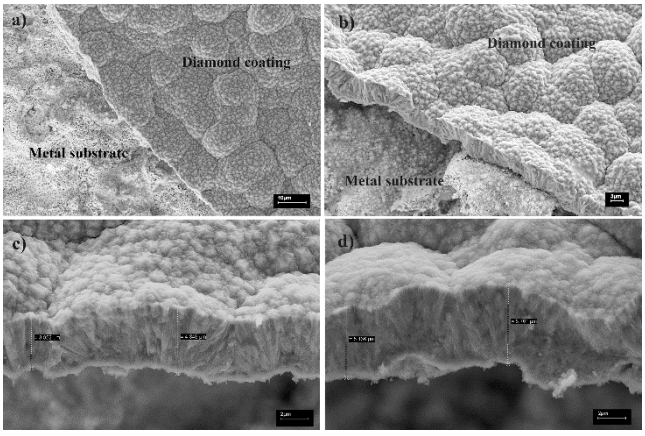

Fig. 3 (a) and (b) FESEM imageshowed that NCD coating peel-off from the oxidized LC substratedue to poor adhesion. (c) and (d) Thickness measurements of NCD coating on oxidized LC Co-Cr-Mo alloy at 5000x magnification.

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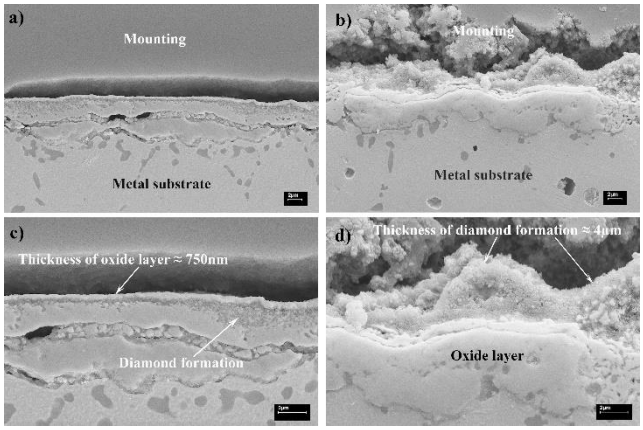

Fig. 4 The cross-section images of diamond coating on oxidized sample (a) Oxidized HC sample. (b) Oxidized LC sample. (c) The diamond growth below the oxide layer in oxidized HC sample. (d) The thickness of diamond coating on oxidized LC Co-Cr-Mo alloy about 4μm. Observation showed formation of oxide layer beneath the diamond coating.

IV. CONCLUSION

The following conclusions can be drawn from the above discussion;

1. Diamond coating were obtained on oxidized high carbon (HC) and low carbon (LC) Co-Cr-Mo alloys. However, the adhesion is very poor due to delamination occurred and left small portion of diamond coating on the both samples. Therefore, cobalt removal is necessary in order to obtain a good diamond nucleation and better quality diamond coating on Co-Cr-Mo alloys.

2. Although the mismatch of coefficient thermal expansion could be the cause of poor adhesion in diamond coating, but in not the major issues this study. Diamond coating of Co-Cr-Mo alloy seems to be un-achievable due to high content of cobalt in this alloy (~60%).

3. Creating oxide as interlayer on the substrate showed possibility of diamond nucleation to form and crystal growth but resulted in poor adhesion strength of diamond coating. Optimization of parameter used during diamond coating using HFCVD should be focused more in order to obtain good adhesion of diamond coating.

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