The Effect of Methane Concentration on Micro-textured Ti6Al4V-carbide Hardness and Specimen Weight Gain

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Statement of Purpose: Wear resistance is directly affected by a material's surface hardness. For most total joint replacements, CoCrMo is typically the material of choice at a wear interface. Titanium alloys (Ti) possess excellent biocompatibility; however, they are not as wear resistant as CoCrMo alloys. In the UMBC Laboratory for Implantable Materials and Biomechanics (LIMB) we developed micro-textured, hard carbide surfaces integrated onto a Ti6Al4V implant alloy [1, 2].

In this study, we investigated the effect of methane concentration during microwave plasma-assisted chemical vapor deposition (MPCVD) processing on specimen weight gain, surface hardness and thickness of the LIMB micro-textured Ti-carbide surface.

Methods: An MPCVD protocol was used to create the surfaces on medical grade Ti6Al4V alloy specimens [1,2].

Prior to MPCVD treatment (Table 1), the diameter, thickness, weight and surface roughness of each (polished, cleaned and dried) specimen were measured. The average surface roughness (Ra) of < 0.040µm was verified using a white light interference surface profilometer (WLISP, Zygo New View 100, Zygo, CT) and specimen weight was measured using a digital balance (Model AX205, Mettler Toledo).

Table 1. MPCVD processing parameter matrix

	1016°C	1041°C	1066°C
2 hrs	*(#1&2)*1% CH_4 *(#9)*5% CH_4	*(#3&4)*1% CH_4 *(#10)*5% CH_4	*(#5)*1% CH_4 *(#11)*5% CH_4
4 hrs	*(#6)* 1% CH_4 *(#12)*5% CH_4	*(#7)* 1% CH_4 *(#13)*5% CH_4	*(#8)* 1% CH_4 *(#14)*5% CH_4

Post-processing specimen weight and Ra were measured with the same methods as pre-processing measurements. Vickers micro-hardness (HV) was determined for each Ti sample. A minimum of 9 indentations were located across each specimen surface diameter (MICROMET 1, Buehler Ltd). Specimens (5) with surface HV values >2x the as-received Ti HV were cross-sectioned. One half of each specimen was used for scanning electron microscopy (SEM) imagery of the surface depth. Three specimen halves were used for identification of surface constituents by x-ray photoelectron spectroscopy (XPS) (Anderson Materials Evaluation, Columbia, MD).

Results: All specimens processed with a 5% CH_4 concentration gained less weight (< 0.0151g) than those processed with a 1% CH_4 concentration (> 0.0174g; < 0.0412g), regardless of process temperature or time.

The weight gain of specimens with an improved HV was distinctly lower than the weight gain of specimens with little or no improvement in HV. An increase in weight gain of specimens processed with a 5% CH_4 demonstrated a direct correlation to increased HV values (R^2=0.946, Figure 1), whereas specimens processed with a 1% CH_4 demonstrated a moderate correlation (R^2=0.743) between an increased weight gain and decreased HV.

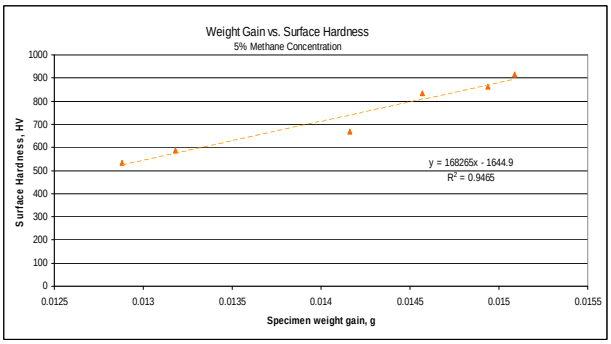

Figure 1. Specimens processed with a 5% CH_4 concentration produced the opposite trend of those specimens processed with a 1% CH_4 concentration.

The HV of specimens processed with a 5% CH_4 concentration also increased with increasing process temperature, whereas specimens processed with a 1% CH_4 concentration had a decreasing HV with increasing process temperature.

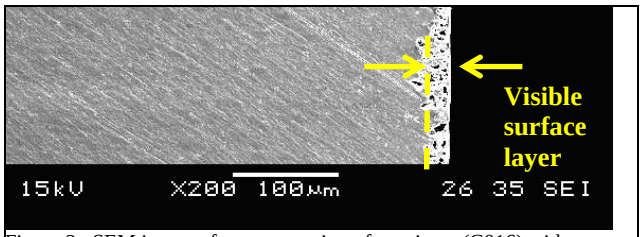

Figure 2. SEM image of a cross-section of specimen (C016) with porous texture of visible surface layer (28.3 µm) just below the top surface.

The visible surface thickness of the 5 cross-sectioned specimens ranged from 14.4µm to 43.3µm (Figure 2) with the 5% CH_4 group all below 28.3µm and the 1% CH_4 group above 34.4µm. TiC was identified as the primary component of all three specimen surfaces analyzed by XPS.

Discussion/Conclusions: Specimens processed with 5% CH_4 had a consistently lower weight gain than specimens processed with 1% CH_4 for the same duration of time at the same temperature. The 5% CH_4 group also produced the highest increases in HV and thinner visible surface layers. It is somewhat counter-intuitive that the greater availability of carbon led to less carbon diffusing into the substrate. In the case of a 5% CH_4, the greater availability of carbon allowed for more TiC initiation sites near the surface and rapid initial coverage of the surface by carbides. The carbide film then slowed the diffusion rate by decreasing the amount of carbon that was able to diffuse through the carbides to the Ti substrate, limiting the amount of weight gained per specimen.

References: 1. Sullivan, S.J.L., SFB Annual Meeting and Exposition, Orlando, FL, April, 2013.
2. Sullivan, S.J.L., 9th World Biomaterials Conference, Chengdu, China, June, 2012.

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