Microarc Oxidized TiO_2 coating on Porous Titanium for Improved Biological Performance

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Statement of Purpose: Surface modification by anodizing process has recently been acknowledged to enhance osseointegration in the orthopedic and dental field. Microarc oxidation (MAO) provides microporous pits, thick oxide layers, and the incorporation of calcium and phosphorus into the coating layer which results in improved osteoblast cell responses [1]. However, this surface modification was not applicable to porous materials because of low interconnectivity and small pore size. Therefore, we herein demonstrate that the combination of the modified freeze casting method and MAO process can create sufficiently large pores to improve cell infiltration and bioactivity. Furthermore, the porous TiO_2 coating layer can enhance the biocompatibility [2].

Methods: Ti/camphene slurries with Ti contents of 15 vol% were prepared by ball-milling at 60 °C. The prepared slurry was poured into cylindrical molds and dynamically frozen for various periods (1~5 days) to allow an excessive growth of camphene dendrites. After casting, the samples were freeze dried to remove the frozen camphene crystals. Thereafter, the samples were sintered at 1300 °C for 2 h. The specimen was microarc oxidized in an aqueous electrolyte containing calcium acetate monohydrate and calcium glycerophosphate at 350 V under a pulsed DC field. The porous structures and morphology of the samples were characterized using SEM. The *in vitro* biological properties were determined by observing the MC3T3-E1 pre-osteoblast cell attachment and proliferation.

Results: Regardless of the casting time, all of the fabricated samples showed a highly porous structure with large spherical-like pores (Fig. 1 (A)–(C)). This suggests that camphene crystals are likely to grow isostatically during the freezing process in rotation, which differs from the conventional freeze casting. All of the fabricated samples showed a similar porosity of 70% and the pore size increased from 302 to 469 μm with increasing freezing time from 1 to 5 days. The microporous TiO2 layer was successfully formed on the surfaces of the Ti walls throughout the sample due to excellent interconnections between the macrochannels, as shown in Fig. 2 (A). The EDS for the MAO treated specimen showed high peaks of calcium and phosphate compared to the bare porous Ti (Fig. 2 (B)). The cells on bare porous Ti showed round morphologies with minimal spreading (Fig. 3(A)). By contrast, the cells adhered and spread well on porous Ti coated with microporous TiO_2 surfaces as shown in Fig. 3 (B). Significantly higher cell density was observed on porous Ti coated with microporous TiO_2 compared to that of porous Ti suggesting that TiO_2 coating enhances the biocompatibility (Fig. 3 (C)).

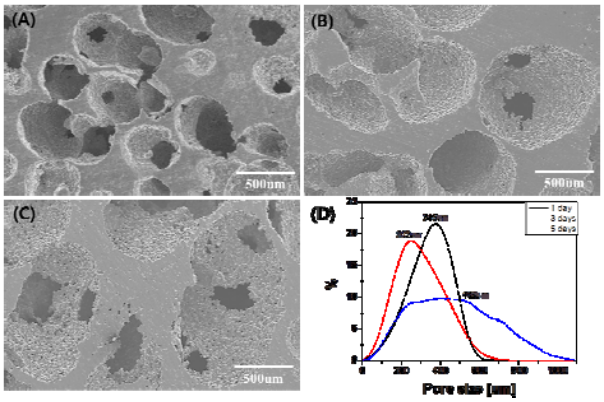

Fig 1. SEM image of porous Ti with freezing time of (A) 1day, (B) 3days, (C) 5days, and (D) pore size distribution.

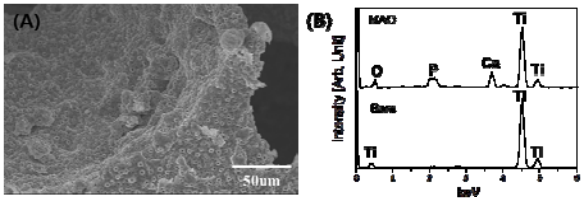

Fig 2. (A) Cell attachment (after 3 h of culturing), and (B) EDS spectrum of before and after MAO treatment

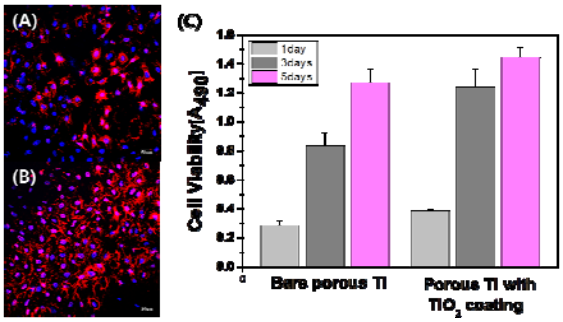

Fig 3. CLSM images of cell attachment after 3 h of culturing on (A) before and (B) after MAO treatment, and (C) proliferation of the MC3T3-E1 cells cultured on porous Ti

Conclusions: Porous Ti scaffolds with large pore were produced by dynamic freeze casting. As the casting time increased from 1 to 5 days, the pore size increased from 302 to 469 μm. Microporous TiO_2 layer was well-fabricated on the pores after forming sufficient large pores. Our results show that cell behavior was better when the microporous TiO2 coating layer was formed on macroporous Ti.

References:

[1] Jung HD et al. Materials Chemistry and Physics 2012;135:897-902
[2] Jung HD et al. Materials Science and Engineering C 2012; 63; 1545-1547