Mesoporous Rutile-Rich TiO_2 Coatings Engineered by Plasma Electrolytic Oxidation for Enhanced Mechanical Performance

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Abstract: In this study, we report the successful deposition of highly crystalline, defect-free, mesoporous pure TiO_2 coatings using a phosphate- and silicate-free electrolyte through the plasma electrolytic oxidation method. The results demonstrate a significant improvement in coating hardness, making it well-suited for external fixator pins that must withstand drilling forces during implantation.

1. Introduction

Titanium (Ti) and its alloys are widely used for orthopedic and dental implants due to their excellent mechanical and biocompatible properties [1]. However, their bioinert nature results in poor osteointegration and implants loosening [2], while chemical interactions with body fluids can release metal ions, potentially causing toxicity or allergic reactions [1]. Previous studies have shown that plasma electrolytic oxidation (PEO) can produce microporous TiO_2 coatings to enhance cell adhesion [3], though conventional electrolytes often result in unwanted ion incorporation, adversely affecting coating crystallinity and mechanical properties.

To address this, we explore ammonium acetate as an alternative PEO electrolyte to engineer rutile-rich, ion-free TiO_2 coatings with improved mechanical performance.

2. Methods

Commercially pure grade 2 titanium discs were coated using 0.8 M ammonium acetate as an electrolyte. The PEO process was performed at 250 V positive pulses with duty cycles of 10–60%, 500–2000 Hz frequencies, and 1–5 minutes in a water-cooled stainless steel vessel (~20 °C). After PEO treatment, the samples were rinsed with deionized water, air-dried, and analyzed using SEM/EDS, XRD (5° grazing angle, 2θ range: 20 – 60°, Cu Kα radiation), and Vickers hardness testing (500 g load, 10 s).

3. Results and Discussion

Figure 1A shows the mesoporous morphology of the coatings, with pore sizes ranging 0.5–5.0 µm. Most pores are approximately round, though some merge into linear or groove-like structures. Oxide growth at pore edges forms columnar, tube-like structures. Fine-tuning deposition parameters achieved a balance between melt-like and ceramic deposits, strengthening the tubes and enhancing mechanical properties. Figure 1B confirms the formation of pure TiO_2 with an oxygen-to-titanium atomic ratio of almost 2 under all deposition conditions. Trace carbon, likely from the environment incorporated during the plasma discharge process, does not significantly affect this ratio. XRD spectra (Figure 1C) reveal sharp peaks, indicating high crystallinity and a rutile-rich (76.4 %) TiO_2 phase, known for superior stability and mechanical properties compared to the anatase phase [4]. Figure 1D demonstrates a significant improvement in surface hardness of coated titanium compared to the bare sample.

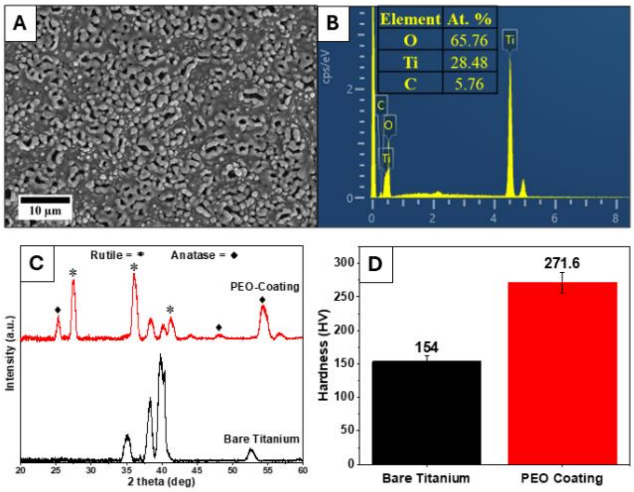

Fig 1. (A) SEM micrograph and (B) EDS elemental composition of the optimized coating, (C) XRD patterns, and (D) surface hardness of the bare and coated substrate.

4. Conclusion

This work successfully developed rutile-rich TiO_2 coatings using a non-conventional electrolyte, featuring a mesoporous structure with tubular growth and optimized integration of ceramic-like and melt-like phases. XRD and hardness analyses confirm the formation of pure TiO_2 with enhanced stability and mechanical strength, highlighting the coating's potential for load-bearing applications such as external fixator pins, by offering improved hardness and resistance to unwanted ionic inclusions.

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