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Hydrophilicity and Near-Surface Mechanical Response of HF-Etched Titanium after DC Magnetron-Generated Reactive Glow Discharge Plasma Activation

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Introduction

Titanium is widely used in biomedical applications due to its favorable mechanical properties and biocompatibility. However, surface characteristics play a crucial role in determining its interaction with the biological environment. Therefore, surface modification strategies are of great interest to improve the physicochemical properties of titanium and potentially enhance its performance in biomedical applications.

Objectives

The aim of this study was to investigate the effects of HF etching and DC-MS-generated reactive GDP activation on the wettability, surface roughness, indentation response and crystallinity of Grade 1 titanium.

Methodology

Samples: Grade 1 Ti disks (ASTM F67; Ø 8.00 mm, 0.60 mm thick) were prepared in three cumulative conditions: control cleaning (1CC; ultrasonic DI water/detergent, DI water and isopropanol, N_2 drying), HF etching (2AE; 6% (v/v) HF, 40 kHz, 2 min) and reactive plasma activation of the etched disks (3RP; air, 6×10^{-1} Pa, 22 W, ≈ 440 V, 1 min).

Caracterization: Contact angle (ASTM D7334) and profilometry (ISO 4287/4288) used n = 60, 60 and 20 disks (1CC, 2AE, 3RP; Kruskal–Wallis/Dunn); FESEM, representative micrographs. Knoop indentation (1 N, ISO 14577; universal hardness H_U, indentation hardness H_{IT}, indentation modulus E_{IT}) and XRD/GIXRD (1°) were done on one sequentially treated disk (n = 1).

Results and Discussion

Wettability. ϑ decreased progressively from 1CC (intermediate) to 2AE (hydrophilic) and 3RP (superhydrophilic), with all pairwise differences significant (Kruskal–Wallis, $p < 0.0001$; Dunn, $p \leq 0.0008$). Plasma also homogenized wetting (coefficient of variation: 28.5% → 7.2%), and disks with $\vartheta \leq 15°$ rose from 5% to 90%.

Morphology and roughness. HF attacked α-Ti preferentially along grain boundaries ($Ti + 3HF \rightarrow Ti^{3+} + 1.5H_2 + 3F^-$), exposing band-like grooves and raising R_a, R_q and R_z by ≈ 86%. Plasma preserved this morphology (R_a +8.9%; R_q and R_z not significantly different from 2AE); the nanoscale tip blunting seen by FESEM lies below the profilometer bandwidth.

Topography versus chemistry. From 2AE to 3RP, ϑ fell a further 9.6° (+5.7% in cos ϑ) with only minor roughness change, so topography alone is unlikely to explain superhydrophilicity. Plasma-induced cleaning, oxidation and polarity changes are more consistent, but were not probed here. The relative wetting r is an algebraic transform of ϑ.

Near-surface mechanical response. From 1CC to 3RP, H_U, H_{IT} and E_{IT} rose by 23.0%, 23.3% and 25.3%. Etching mainly raised E_{IT} (+13.1%), whereas most of the hardness gain appeared after the plasma step (H_U +18.4%; H_{IT} +20.2%), without relevant roughness change. Hardness dispersion doubled after etching (H_{IT} CV: 5.0% → 10.8%), consistent with a heterogeneous microtexture; mean ± SD ranges of 1CC and 3RP overlap only for E_{IT}.

Crystallinity. Diffraction stayed α-Ti-dominated, with the strongest XRD reflection shifting from (002) in 1CC to (101) in 2AE and 3RP; without texture analysis, and with possible hydride contributions, this is only an intensity redistribution. No anatase/rutile reflections were resolved; the low-angle diffuse rise in 3RP is not evidence of amorphous TiO_2, and a nanometre-scale oxide would escape detection in a substrate-dominated diffracting volume.

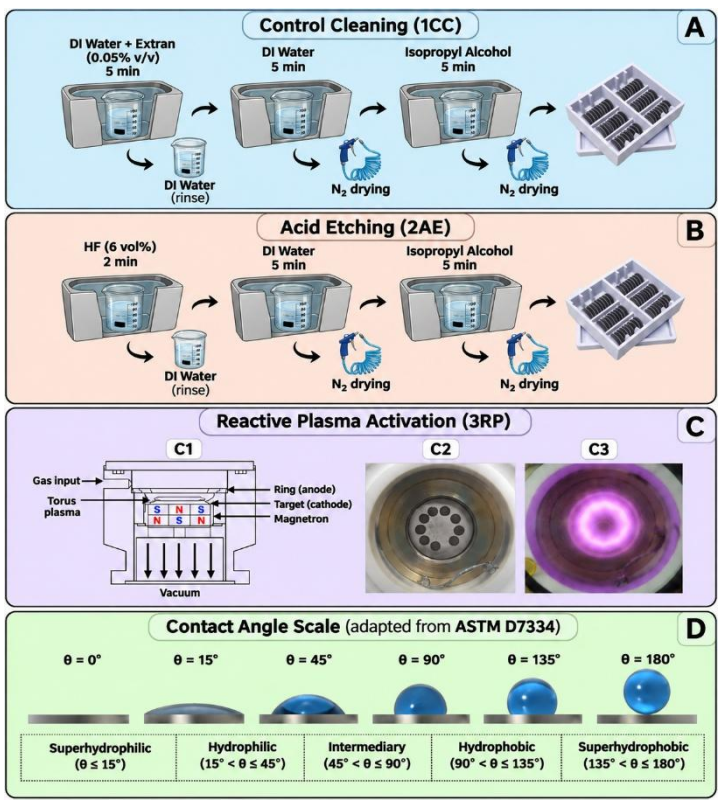


Figure 1. (A) 1CC; (B) 2AE; (C) 3RP in the DC-MS chamber; (D) wettability scale adapted from ASTM D7334.

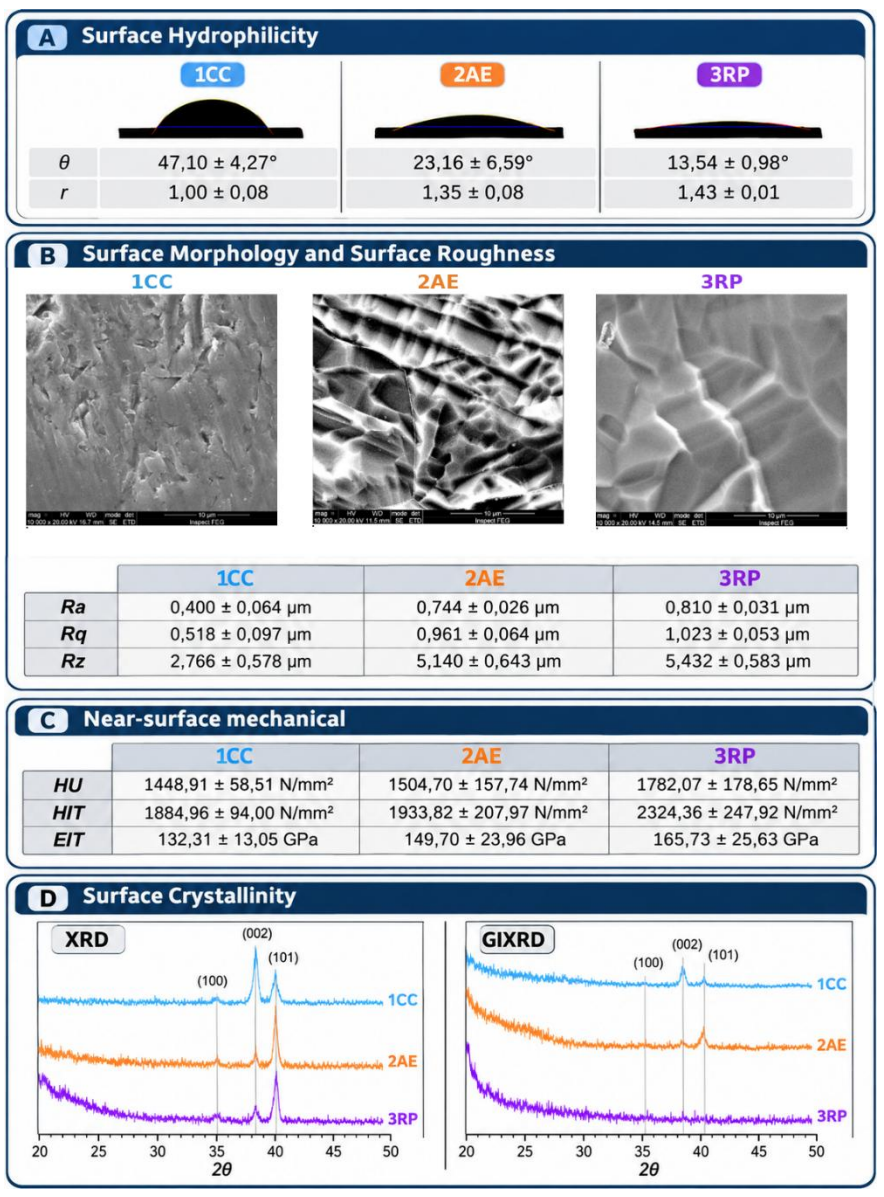


Figure 2. (A) Contact angle and relative wetting; (B) FESEM and roughness; (C) H_U, H_{IT} and E_{IT}; (D) XRD/GIXRD. Mean ± SD.

Conclusions

HF etching produced the principal roughening; DC-MS-generated reactive GDP preserved this topography and yielded a superhydrophilic surface (ϑ = 13.54 ± 0.98°). Indentation values rose by 23–25% with α-Ti-dominated diffraction but, from one sequentially treated disk, cannot be assigned to the surface oxide. Biological performance was not investigated.

References and Acknowledgments

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