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Controllable hierarchical micro/nano patterns on biomaterial surfaces fabricated by ultrasonic nanocrystalline surface modification

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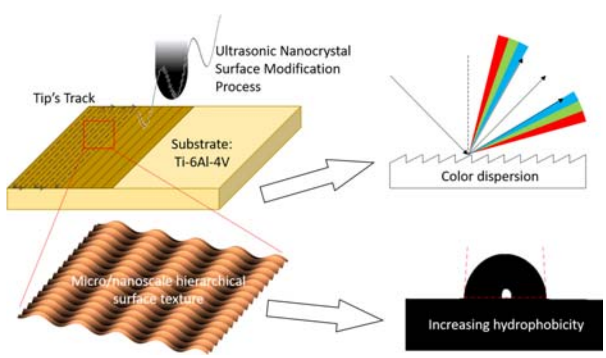
HIGHLIGHTS

- Improved biocompatibility, which has been revealed in literature.
- A diffraction grating, a new optical property
- Modulate the wettability of the treated surface

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we have shown that Ultrasonic Nanocrystal Surface Modification (UNSM) cannot only improve the mechanical properties of Ti-based biomaterials but also produce surface texture with hierarchical micro/nano-scale patterns due to its high controllability. After UNSM-treatment the surface texture of Ti-based biomaterial consists of a major microscale structure with widths ranging from 4 μm to 200 μm, and an embedded nanoscale structure with widths as small as 120 nm. With a customized cylinder tip, the average surface roughness (R_a) can be reduced to 0.03 μm, comparable to the superfinishing surface. The embedded nanoscale structure originates from the formation of the pile-up, which is determined by the elastic-plastic property of materials. Such hierarchical patterns enable new functions for the treated surface. It is demonstrated that light dispersion and the alteration of wettability can be achieved by controlling surface patterns using UNSM. The capacity of improving mechanical properties, biocompatibility, and hydrophobicity simultaneously, in conjunction with its low-cost and easy-to-operate features, makes it a promising surface engineering technique for biomaterial treatment.

1. Introduction

The demand for biomaterial implantation and replacement continuously grows due to the increasing aging population worldwide [1,2]. Ti-based alloys win its popularity as implants for their excellent mechanical

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properties, such as high corrosion resistance, low Young's modulus, and low density/strength ratio [3]. The high corrosion resistance reduces the release of toxic ions to the human body. The low Young's modulus of Ti-based alloys ranging from 50 GPa to 110 GPa is comparable to that of human bones [4]. The closer modulus induces less stress shielding, and the host or patient, therefore, can heal faster [5]. In addition, the low density/strength ratio of Ti-based materials alleviates body's burden. These excellent mechanical properties pave the way for Ti-based alloys to be the most promising biomaterials for implants.

The poor wear resistance of Ti-based alloys, however, decreases the lifetime of bioimplants. Surface modifications (for example, chemical method, physical method, and mechanical method) are routinely applied to increase their surface hardness, wear resistance and fatigue performance [6–9]. Meanwhile, biocompatibility can also be improved by altering the surface structure of bioimplants. Biocompatibility is the ability of a biomaterial to generate positive cellular or tissue response, and few rejections during therapy [10]. It has been revealed that specific micro/nanoscale patterns on biomaterial surface can positively affect cell behaviors including adhesion, growth, proliferation, differentiation, and shaping [11]. For instance, Hasan et al. developed randomly oriented anisotropic nanostructures on titanium surface using chlorine-based reactive ion etching to enhance the attachment and proliferation of human mesenchymal stem cells in vitro [12]. Huang et al. created a hierarchical micro/nano-topographies, resembling the structure of natural bone with micro-arc oxidization, to improve the biological performance of commercial pure (CP) titanium [13]. Zhao et al. and Navarrete et al. produced hierarchical Ti-based surfaces by the means of sandblasting and acid etching to enhance the multiple cell functions and accelerate bone maturation around the implants [14,15]. Nevertheless, few methods mentioned above can simultaneously improve the mechanical properties of metallic biomaterials and fabricate regular hierarchical surface textures without changing the chemical components of the metal surface.

Ultrasonic Nanocrystal Surface Modification (UNSM) is one kind of surface engineering technique to impart surface severe plastic deformation (SSPD) into metallic materials by a tough tip strikes at an ultrasonic frequency (20 kHz) which induces high strain rate up to 10^3–10^5 s^{-1} [16,17]. The impact can introduce plastic strain and residual stress in the surface. More importantly, because high strain rate impact suppresses thermal activation and thus recrystallization and dislocation mobility, it generates more refined grains and more uniform dislocation distribution compared with low-strain rate impact [18,19]. After UNSM treatment, metal surface plastically deformed and a gradient nanostructure layer with an affected depth up to a few hundred of micrometers will be formed [20]. Compared with the undeformed regions, this grain refinement layer contains more grain boundaries and dislocations that can significantly impede further plastic deformation and prevent both crack initiation and propagation [21–23]. Therefore, the wear resistance, which is proportional to hardness, together with the fatigue performance can be enhanced by UNSM.

Although UNSM has been successfully applied to improve the mechanical properties of metals [24–29], it has not been used to its full potential, especially in the manipulation of surface roughness and texture. Unlike conventional SSPD techniques, e.g., shot peening and laser shock peening [30–32], which often suffer from surface deterioration after treatment, UNSM is equipped with a high precision Computer Numeric Control (CNC) machine which has three translational degrees of freedom with a resolution of 1 μm. Such unprecedented controllability makes it is possible to produce regular surface textures with micro/nanoscale patterns. In addition to the controllability, there are three more advantages inherent in UNSM. Firstly, the processing tip of UNSM can be economically manufactured in various shapes and the programmable nature of CNC machine enables UNSM to creatively process surfaces with complex geometry. Secondly, UNSM has been proved very effective in improving mechanical properties of biomaterials. In one of our previous studies [26], we have demonstrated that UNSM has increased the surface hardness by 86% and decreased the wear rate by 20% of NiTi. Thirdly, it will not add any new material on sample surface during treatment.

To unleash the potential of using UMSM to achieve both superior mechanical properties and the added values, we will have a systematic study of using UNSM to generate surface textures on Ti64. We will firstly explain why the micro/nano surface patterns can be generated, and discuss the relation between UNSM parameters and the surface hardness enhancement of Ti-based alloys. We will then establish a quantitative relation between processing parameters and resultant surface patterns, in which the length of the primary micro structure can go up to a few hundred of micrometers, and the secondary, embedded nano structure has the dimension of a few hundred of nanometers. We further extend the principle for the generation of hierarchical structure derived from Ti64 to Ti and NiTi aiming at deriving a generalized knowledge for other metallic materials. Eventually, two potential applications of wettability and optics enabled by controllable surface texture will be discussed.

2. Materials and methods

2.1. Materials

Ti-6Al-4V (Ti64) sheets are manufactured by McMaster-Carr Supply Company and the composition is listed in Table 1. Samples were cut into plates of 15 mm × 15 mm × 1.5 mm and ground by 320, 600, 800, and 1200 grit SiC abrasive papers with water as the cooling solvent and followed by polishing with 3 μm and 1 μm diamond suspension, and 60 nm colloidal silica solution to obtain the mirror-like surface finish. Then, sonication was applied, and acetone, ethanol, and DI water were used to clean sample after polishing. To observe the cross-section, the Ti-based alloys were etched by Kroll's Reagent (H_2O:HNO_3:HF = 92 ml:6 ml:2 ml) with 10 s.

2.2. UNSM treatment and the resultant plastic deformation

Fig. 1(a) schematically shows the UNSM process. The sample is vertically mounted and impact by a tip in the Z direction at a frequency of 20 kHz and the displacement amplitude of the ultrasonic oscillation (input amplitude, L) ranges from 8 μm to 40 μm. Meanwhile, the tip scans the sample surface along the square-wave-like track, from left to right (X direction), up and down (Y direction). UNSM is a displacement-controlled process with the input incremental interval in the X direction, δ_x, varies from 1 μm to 200 μm and the theoretical scanning velocity (v_y) in the Y direction ranges from 1 mm/s to 9.999 m/s. Via this LM-520 UNSM system, a severe plastic deformation zone consists of a grain refinement layer will be induced and the topography of the sample will be altered by the high-speed impact as shown in Fig. 1(b). To intensify the impact, extra static load (F_{st}) can be applied to the ultrasonic unit. Typically, the static load ranges from 5 N to 50 N with an increment of 5 N. Two tips were used for the experiment, as shown in Fig. 1(c) and (d). Spherical tip *a* is made of tungsten carbide and the diameter is 2.4 mm. The bulk of tip *b* is made of stainless steel and its top surface has an embedded cylindrical diamond rod with a diameter of 0.5 mm and a length of 4 mm. In general, a number of UNSM parameters, such as v_y, δ_x, tip size, F_{st}, and L, can be adjusted to generate the desired effect on different metals.

Table 1
Composition (wt%) of Ti-6Al-4V.

Material	Ti	Al	V	Fe	C	Other
Ti64	88.10–90.92	5.50–6.75	3.5–4.5	0.04 max.	0.08	0–0.30