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# Effect of laser parameters on the microstructure of bonding porcelain layer fused on titanium

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ABSTRACT

Bonding porcelain layer was fused on Ti surface by laser cladding process using a 400 W pulse $CO_2$ laser. The specimens were studied by field-emission scanning electron microscopy, X-ray diffraction and bonding tests. During the laser fusion process, the porcelain powders were heated by laser energy and melted on Ti to form a chemical bond with the substrate. When the laser scanning speed decreased, the sintering temperature and the extent of the oxidation of Ti surface increased accordingly. When the laser scanning speed is 12.5 mm/s, the bonding porcelain layers were still incomplete sintered and there were some micro-cracks in the porcelain. When the laser scanning speed decreased to 7.5 mm/s, vitrified bonding porcelain layers with few pores were synthesized on Ti.

## 1. Introduction

Titanium was an alternative metal substrate for porcelain fused to metal because of its excellent performance, such as good corrosion resistance, biocompatibility, mechanical strength and low cost [1–3]. However, compared to conventional NiCr alloy-porcelain, the poor bonding strength restricted its application [4–6].

Laser cladding is the fusion of a powder on a substrate and the laser energy melts the cladding material forming a metallurgical bond with the substrate [7–10]. More recently, laser cladding technology is a promising way to prepare coatings on Ti due to its limited heat affected zone, low dilution ratio and metallurgical bond between the coating and substrate [11,12]. This process allows for a coating built on titanium substrates to be built layer by layer and may prevent unwanted phase changes in the titanium [13,14]. However, there were no available reports on using laser cladding process to synthesize porcelain layers on Ti.

In addition, the coefficient of thermal expansion of the bonding porcelain ($\alpha = 9.4 \times 10^{-6}$/°C) used in this research is slightly lower than that of titanium ($9.5 \times 10^{-6}$/°C) [15], which will minimize the thermal stress between Ti-porcelain and avoid the formation of crack during high temperature cladding and rapid solidification.

During the laser cladding process, the porcelain powders, which are glassy solid, were heated by laser energy and melted on Ti to form a chemical bond with the substrate. Microstructure of the coating and the interface between the coating and the substrate is of greatest interest [16]. Therefore, laser parameters were optimized to synthesize a crack-free coating on titanium. In addition, acid etching and anodization processes were combined to improve the surface roughness of Ti and chemical bonding between porcelain-Ti.

## 2. Experimental procedures

ASTM grade II CP titanium was cast, ground and polished to prepare plate-shaped specimens ($\Phi$13 mm × 0.5 mm). The specimens without any treatment were used as control.

### 2.1. Anodization of titanium

In a typical anodization process, the electrolyte was prepared by

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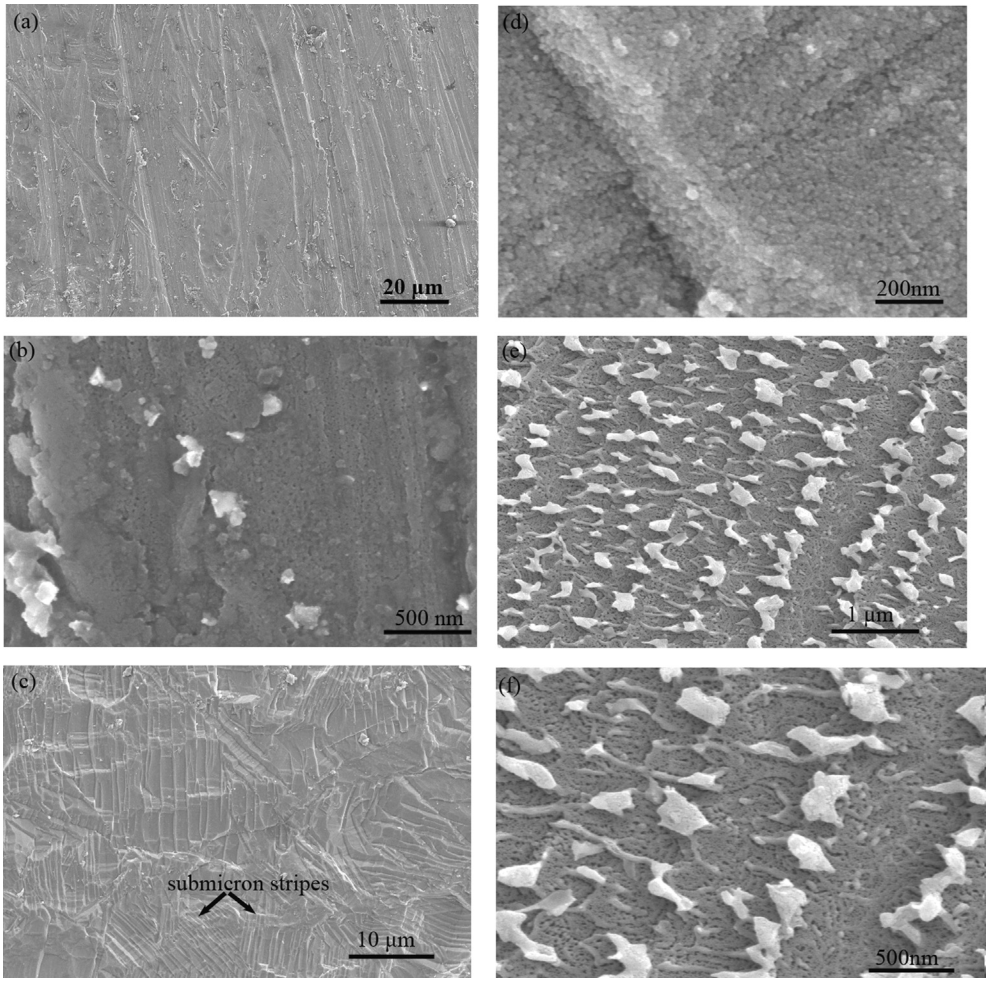

**Fig. 1.** F-SEM microphotographs of titanium surface (a), (b) the untreated Ti (c), (d) the Ti just treated in 40 wt% HF, (e) and (f) Ti surface anodized at 20 V for 15 min after pre-treatment in 40 wt% HF.

adding 0.3 wt% of ammonium fluoride ($NH_4F$, Sinopharm Chemical Reagent Co. Ltd., AR) and 1.25 vol% of distilled water into ethylene glycol ($C_2H_6O_2$, Sinopharm Chemical Reagent Co. Ltd., AR). In a typical preparation procedure, the titanium specimens (>99% purity, thickness of 0.5 mm) were pre-treated in 40 wt% HF acid, and then anodized in the electrolyte solution using a graphite counter electrode at 20 V for 15 min at room temperature.

### *2.2. Preparation of titanium–porcelain test specimens*

Then thin layer of bonding porcelain (Ti-bond porcelain, Dentsply, USA) was brushed on Ti surface and the thickness were controlled to about 0.5 mm. Laser cladding was carried out by using a LCY-400 (Wuhan Huagong Laser Technology Co., Ltd, China.) 400 W pulse $CO_2$ laser. The laser was operated by smart MC software with Argon as the feeding gas. The laser cladding parameters were selected as 100–200 W laser power, 120 HZ frequency, 0.3–0.5 mm beam diameter and 7.5–15 mm/s traverse speed.

The surface roughness ($R_a$) of titanium was measured using a JB-4C surface roughness tester. The cross-section of the specimens were ground and polished successively. Microstructural characterization of laser-cladding ceramic layers was observed by using a Jeol JSM6400 scanning electron microscope. Universal testing machine (DSS-25T, Shimadzu, Japan) was used to evaluate the tensile bond strength between coating-Ti. The bond strength was calculated by dividing the force (Newton) to the coating area ($mm^2$).

## 3. Results and discussion

Fig. 1 shows the F-SEM microphotographs of titanium surface (a), (b) the untreated Ti (c), (d) the Ti just treated in 40 wt% HF, (e) and (f) Ti surface anodized at 20 V for 15 min after pre-treatment in 40 wt% HF. Compared with the untreated Ti, a compact oxide layer with hybrid structures consisting of parallel micro-stripes and compact nano-protuberances was obtained after pretreatment in 40 wt% HF, as shown in Fig. 1(c) and (d). The size of the nano-protuberance was about 10 nm, while the spaces between the stripes were about 1 μm. Hybrid structures with submicron rows of leaf-like embossments and nano-pores were synthesized after anodization of titanium at 20 V for 15 min with pre-treatment in 40 wt% HF, as shown in Fig. 1(e) and (f). The spaces between the rows of leaf-like embossments in Fig. 1(e) are the same order of magnitude as the spaces between the micro-stripes in Fig. 1(c). The formation of leaf-like embossment rows and nano-pores attributed to the hybrid effect of HF acid etching and anodization processes [3]. The selective corrosion of the titanium surface resulted in the formation of leaf-like embossment rows.

The surface roughness of titanium was increased from 0.24 ± 0.02 μm to 0.82 ± 0.09 μm after anodization, which was

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