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Microstructure and Corrosion Properties of Orthodontic Brackets by Laser Treatment

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The austenitic stainless steel AISI 316L has been chosen as the material for orthodontic bracket. This paper reported our studies on the surface of the stainless steel 316L treated by laser heat input. We substantiated the effects of laser heat input including the microstructure, microhardness and corrosion resistance. The results showed that laser surface treatment not only refined grain, but also enhanced microhardness of the 316L orthodontic bracket at certain heat input. Through X-ray diffraction with Cu–Kα radiation, $Cr_{0.19}Fe_{0.7}Ni_{0.11}$ was the main component phase. The corrosive characteristic of 316L orthodontic bracket with E = 0.67 kJ/cm was higher than that of the 316L without heat treatment.

Keywords: Orthodontic bracket, Laser heat input, Microstructure, Corrosion resistance.

1. INTRODUCTION

Austenitic stainless steel (ASS), as a biomedical implant material, is generally used for orthopedic, cardiovascular and dental devices due to its high corrosion resistance, biocompatibility, hardness, and tensile strength [1-5]. Type AISI 316L stainless steel is known as the most commonly used orthodontic bracket material [6], containing approximately 16-18% Cr, 12-15% Ni, 2-3% Mo and small amounts of other elements such as Mn, C, P S and Si. However, orthodontic bracket is exposed to potential damage from the highly complex and dynamic oral environment, resulting in corrosion and unintegrated structure [7, 8]. Thus, resistance to corrosion is a crucial property of metals or metal alloys applied in orthodontic bracket. Previous research has been mainly performed to study the corrosion behavior of AISI 316L stainless steel in the simulated physiological environment [9-12].

The corrosion resistance of ASS is not only affected by the chemical composition, but also related to its phase structure and grain size. Recent strategies designed to address the problem of corrosion properties were primarily aimed at developing the surface modification techniques [13-17] including refinement of grain size, changing surface characteristic and wearing protective coatings. Hao et al. [13] introduced surface mechanical attrition treatment (SMAT) for synthesizing a nanostructured surface layer on the stainless steel AISI 316L. They found that lots of cracks formed by SMAT on the surface caused the degradation in the corrosion resistance of 316 SS; whereas, it had been remarkably improved after annealing. Zhang et al. [14] employed a high-current pulsed electron beam (HCPEB) with different pluses to evaluate corrosion performances of AISI 316L surface, and the best corrosion resistance was found in the sample treated with 20 pulses of HCPEB. In a study conducted by Liu et al. [15], Ti/TiN multi-layered film was formed on the surface of AISI 316L by arc ion plating contributing to increase the corrosion resistance of stainless steel.

Laser surface engineering (LSE) offers several advantages over other surface modification techniques [18-21], such as fast processing time, homogeneity of melting layer, refinement of grain size on metal surface, and low distortion of the components. The most important advantage stems from the fact that it involves rapid heating with melting followed by quenching to modify the near surface microstructure without affecting its chemistry [22, 23]. In according to the surface requirement of the application, the composition and microstructure in the melt layer depends on the process variables. Currently, LSE has been found useful to produce coatings which possess high wear and erosion resistance [24, 25]. Nevertheless, previous investigations were rarely guided on the utilization of this technique to prepare modified layer on the surface of 316 L orthodontic bracket. Therefore, the purpose of this study is to develop several modified layers by the laser surface heat treatment on the surface of AISI 316L orthodontic bracket and to assess their effects on the corrosion property of 316L stainless steel. In particular, microhardness measurements and X-ray analysis were carried out in order to establish better relationship between laser process parameters and characteristics of the modified layer.

2. MATERIALS AND METHODS

Samples were austenitic stainless steel AISI 316L used as the substrate material of orthodontic brackets. The chemical compositions (wt%) of the stainless steel were as follows: C 0.022, Si 0.65, Mn1.94, S 0.03, P 0.041, Cr 18.36, Ni 11.52, Mo2.29 and Fe balance.

The laser surface heat treatment was carried out by using a continuous wave CO_2 laser (Model HL-T5000D, China) with a defocused laser beam of 3 mm wide. These parameters were optimized to produce the coating with good bonding. The laser power was 300-700 W and the laser beam scan speed was 2-6 mm/s. A side jet of argon with the gas flux of 15 L/min was used to prevent the sample from oxidation. Multi-track with 25% overlap ratio was made to create the modified layer. In order to analyze the effect of laser processing parameters on the microstructure and properties of modified layer, the laser heat input was calculated using the following formula [26]:

$$E=\eta P/v \tag{1}$$

Where E is heat input (kJ/cm), P laser power (w), v laser scan speed (cm/s), and η the effective absorbing coefficient of laser power for ASS (η=0.8 was adopted in previous publication [27]). According to the calculated results, the values of E were in the range of 0.4-2.8 kJ/cm. Sample S0, S3, S6 and S5 were processed with laser heat input of 0, 0.4, 0.67 and 1 kJ/cm, respectively. Sample S0 was same as Sample Original.

The potentiodynamic measurement and electrochemical impedance spectroscopy measurement were performed by using a Princeton Applied Research 2273 electrochemical workstation at a scan rate of 20 mV s^{-1}. The standard three-electrode cell system comprises of a saturated calomel electrode (SCE) and a platinum foil. They were used as the reference and counter electrodes, respectively. All samples were machined to block with a dimension of 10 mm × 10 mm × 3 mm. 1.0 cm^2 of the surface was exposed to artificial saliva (AS) solution (0.4 g/L NaCl, 0.4 g/L KCl, 0.795 g/L $CaCl_2 \cdot 2H_2O$, 0.780 g/L $NaH_2PO_4 \cdot 2H_2O$, 0.005 g/L $Na_2S \cdot 9H_2O$, 1 g/L urea, and 1L distilled water) at pH = 6.8 and 37 ± 1 °C. Electrochemical impedance spectroscopy measurement was performed in the potentiostatic mode after the stable of open-circuit potential (OCP), and its frequency was subsequently swept from 100 KHz down to 0.01 Hz with the applied AC amplitude of 5 mV (rms).

The structural analysis of different phases present within the coating was carried out on a D/Max-2500PC X-ray diffraction with Cu–Kα radiation (1.54 Å) at 60 kV and 40 mA. Microstructure was observed by using a Keyence VHX-1000 optical microscopy. Microhardness measurements at melting layer of stainless steel surface were performed on a Shimadzu HMV-2000 micro Vickers, and the average value of hardness was obtained from three measurements.

3. RESULTS AND DISCUSSION

A number of studies have shown that laser can be used to alter structure of orthodontic brackets [28]. However, it is rare to report the effect of this technique on the corrosion property of orthodontic bracket. Thus, microstructure of AISI 316L orthodontic bracket treated with laser surface heat was observed to evaluate the corrosion resistance.

Figure 1 (a)-(d) showed a typical microstructure of original, S3, S6 and S5 respectively. Figure 1 (a) exhibited that the microstructure of 316L ASS orthodontic brackets was a single-phase austenite with homogeneous distribution of elements, but the phase was a little coarse. In addition, anneal twinning existed in the matrix. Figure 1 (b)-(d) illustrated the effect of laser heat input on the microstructure of 316L orthodontic brackets. Figure 1 (b) and Figure 1(c) displayed that the orthodontic brackets still had the uniform single-phase microstructure after laser surface treatment. Compared with untreated orthodontic rackets, grain size was refined, which helped to improve corrosion property of the orthodontic bracket. On the contrary, once laser heat input was over 1kJ/cm, the rough dendritic structures were found in the surface of the orthodontic bracket, leading to degradation in corrosion resistance.

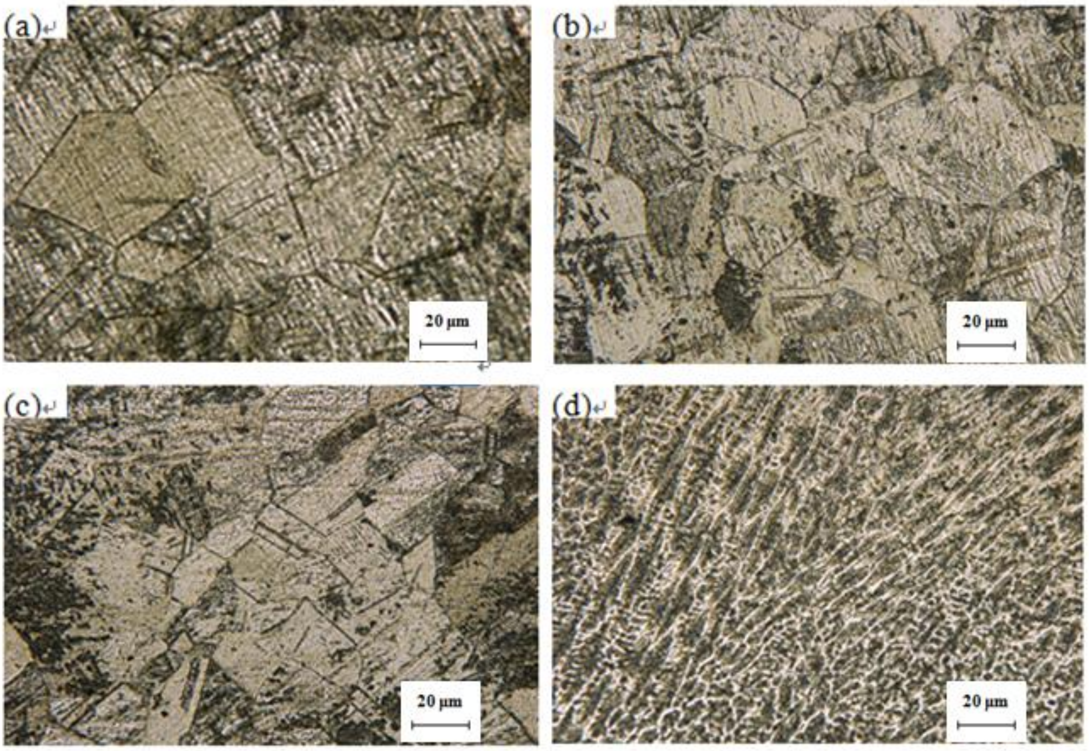

Figure 1. Microstructure of the austenitic stainless steel 316 L orthodontic bracket before and after laser heated: (a) Original; (b) S3; (c) S6; (d) S5.

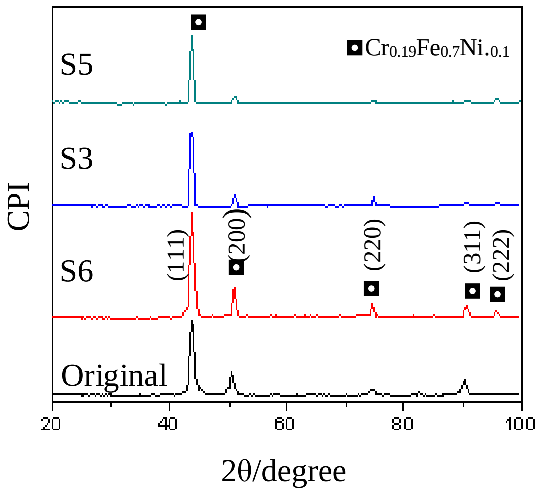

Figure 2. X-ray diffraction patterns obtained using Cu–Kα radiation (wavelength, 1.54 Å) from the 316 L ASS orthodontic bracket: (Original) without laser heat treatment; (S3, S6, S5) with laser heat (power P = 300-700 W and scanning speed v = 2-6 mm/s).

Figure 2 revealed X-ray diffraction pattern of samples before and after laser surface heat treatment. As indicated in Figure 2, the single-phase $Cr_{0.19}Fe_{0.7}Ni_{0.11}$ was the main component in all the conditions. The crystal structure of $Cr_{0.19}Fe_{0.7}Ni_{0.11}$ phase, as a typical ASS phase, was face-centered cubic. Additionally, the laser surface heat treatment did not change the phase structure, but it affected the diffractive strength of the phase. Sample S6 had strongest diffractive strength, which was attributed to the smallest grain size.

Figure 3 presented the effect of laser heat input on the microhardness of orthodontic bracket. The appropriate laser power was found to improve the corrosion resistance of ASS. In accordance with such studies [29, 30], all the samples were irradiated with 300-700 W power. In the case of less than 0.67 kJ/cm of *E*, microhardness of 316L orthodontic bracket increased with the increasing laser heat input, resulting from the refinement of the grain sizes. The highest microhardness value within laser modified orthodontic bracket were shown at *E* = 0.67 kJ/cm. However, when *E* was higher than 1 kJ/cm, microhardness of the laser heated bracket was lower than that of original bracket. Thus, laser heat input should be controlled within 1 kJ/cm.

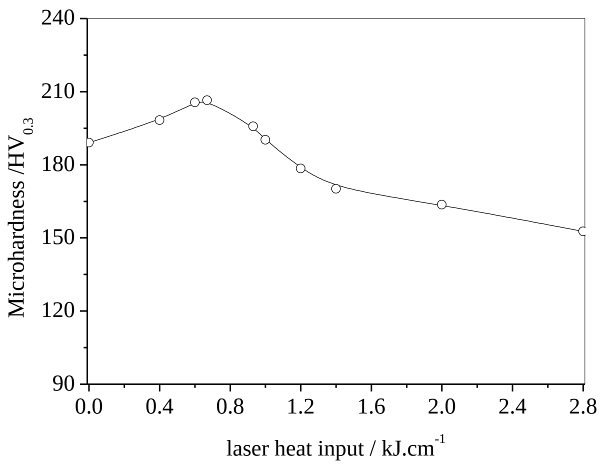

Figure 3. Variation of microhardness (HV) as a function of laser heat input on the cross-sectional plane of samples subjected to laser surface heat treatment with power 300-700 W.

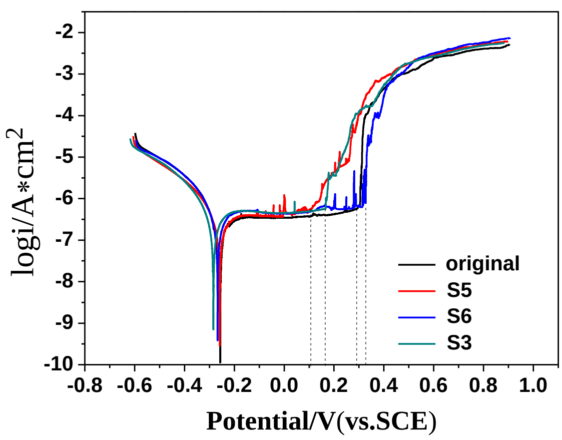

Figure 4. Polarization curves for the effects of laser surface treatment on the potentiodynamic behaviour of 316 L orthodontic bracket samples in artificial saliva. The corrosion potential (*Ecorr*) and breakdown potential (*Eb*) were calculated from the polarization curves via Tafel extrapolation method.

In the presence of artificial saliva solution, potentiodynamic polarization curves of orthodontic brackets in initial state and after laser heat treatments were described in Figure 4. The *E* values for original, S5, S6 and S3 were 0, 0.4, 0.67, and 1 kJ/cm respectively. The result indicated the laser heat treatment influenced the polarization and passivation behaviors of the materials. The corrosion potential (*Ecorr*) was -0.26 V (SCE) for the initial orthodontic bracket in AS. Following the Tafel region, the alloy exhibited a broad range of passivation. The breakdown potential (E_b) was 0.29 V (SCE) for the initial orthodontic bracket in AS. However, the E_{corr} value for laser modified orthodontic bracket was higher than that for initial 316 L in AS. In the case of 316 L at E = 0.67 kJ/cm, E_{corr} and E_b were -0.28 and 0.35 V (SCE) respectively. Compared with the initial 316 L, the range of passivation of S6 was slightly broadened. However, the ranges of passivation of other samples were significantly narrowed, and the E_b values of other samples were less than that of original 316L. It implied that corrosion resistance of the orthodontic bracket was improved by using a given laser heat input. In general, corrosion resistance of ASS is related to chemical composition, phase structure, grain size, and the type and amount of corrosive medium [31]. The high corrosion resistance of ASS roots in the formation of a chromium-enriched passive film [27], which is different with that formed on stainless steel in H2SO4 [32]. For fine-grained ASS, the high density of grain boundary could promote the diffusion of Cr to the surface, thus forming a passive film containing richer Cr that may strengthen its corrosion resistance. Indeed, sample S6 had the high density of grain boundaries, resulting in forming a more uniform passive film containing more Cr. On the contrary, sample S5 showed the poor mechanical behavior of passive film in the polarization test. After test, its surface was covered with lots of large and shallow pits, which could be explained by sensitization due to the high heat input. The microstructure of S5 showed coarse-gained dendrites. Furthermore, some chromium-rich compounds were precipitated to the grain boundary causing uneven distribution of Cr on the surface. Hence, corrosion resistance of sample S5 was inferior to that of the initial 316L.

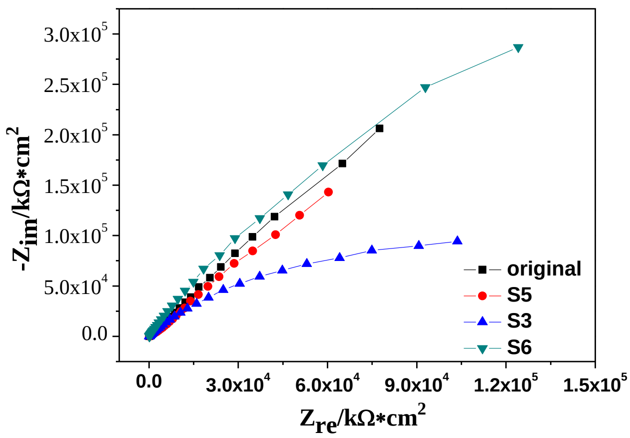

Figure 5. Nyquist plots for Electrochemical Impedance Spectrum (EIS) of 316L ASS samples at 240 h immersion before and after laser surface modification.

Some inclusions on the surface of ASS, such as MnS, damage the uniformity of passive film. After specimens being immersed in AS solution, Cl^- will vitiate passive film. The concentration of Cl^- reaches a certain value on the surface, followed by the formation of soluble saline compounds or complex ions, resulting in anodic dissolution at the partial surface of ASS. That is reason why the passive film exhibits pitting corrosion. For sample S6, due to appropriate laser heat input, most inclusions were melted and then evaporated, which reduced the number of inclusions. In addition, grain refinement increased the density of grain boundary, ameliorating the distribution of inclusions. These protect the surface of ASS from damage. However, owing to low heat input for sample S3, the inclusions cannot be melted completely, and laser surface treatment caused physical damage for ASS. Therefore, the corrosion resistance is not improved by laser surface treatment with low heat input.

The open-circuit impedances of the 316L orthodontic bracket were traced over 240 h from the electrode immersion into AS solution before and after laser surface treatment. Electrochemical impedance spectrum (EIS) of the samples was presented in Figure 5 as a Nyquist diagram. The impedance spectra consisted of a high-frequency intercept with the abscise axis ascribed to the electrolyte's bulk resistance. At lower frequencies, a main arc appeared, due to interfacial processes at the metal/electrolyte interface. As indicated in Figure 5, the curves showed an approximately straight line, which demonstrated that mass transfer involved in the corrosion process. The mass-transfer process contains the diffusion of reactants and products, such as oxygen and Cl^-. For stainless steel electrode, the radius of impedance arc is connected with film resistance and charge-transfer resistance. The material possesses higher corrosion resistance, resulting from radius of impedance arc. From Figure 5, sample S6 had the longest radius of impedance arc, which revealed that it possessed the highest corrosion resistance. Nonetheless, the radius of impedance arc of samples S3 was shorter than that of S0. Thus, sample S3 had more active potential. We hypothesized that the active shift of the OCP of sample S3 arises from the uneven distribution of Cr on the surface.

4. CONCLUSION

(1) $Cr_{0.19}Fe_{0.7}N_{i0.11}$ phase, as the structure of the 316L orthodontic bracket, was analyzed before and after laser surface treatment. However, laser surface treatment caused different grain sizes, due to the different laser heat input. Once E < 1 kJ/cm, the microhardness of the 316L orthodontic bracket increased with the increasing laser heat input.

(2) Corrosion resistance of 316L orthodontic bracket was improved by being treated with laser heat input at E = 0.67 kJ/cm in the artificial saliva solution, which was evidenced from a wider passive range, a lower density of corrosion current, and a higher protection potential.

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