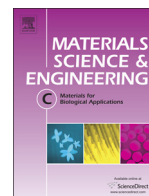




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Laser surface modification of 316 L stainless steel with bioactive hydroxyapatite

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ABSTRACT

Laser-engineered net shaping (LENSTM), a commercial additive manufacturing process, was used to modify the surfaces of 316 L stainless steel with bioactive hydroxyapatite (HAP). The modified surfaces were characterized in terms of their microstructure, hardness and apatite forming ability. The results showed that with increase in laser energy input from 32 J/mm² to 59 J/mm² the thickness of the modified surface increased from 222 ± 12 μm to 355 ± 6 μm, while the average surface hardness decreased marginally from 403 ± 18 HV_{0.3} to 372 ± 8 HV_{0.3}. Microstructural studies showed that the modified surface consisted of austenite dendrites with HAP and some reaction products primarily occurring in the inter-dendritic regions. Finally, the surface-modified 316 L samples immersed in simulated body fluids showed significantly higher apatite precipitation compared to unmodified 316 L samples.

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1. Introduction

Metallic materials such as stainless steels, titanium and its alloys, and cobalt alloys are commonly used as bone implants due to their excellent strength, toughness and relatively low rate of *in vivo* corrosion [1]. Among the various implant materials, austenitic stainless steel AISI 316 L is one of the most popular and economical choices in spite of the potential risks associated with release of toxic nickel and chromium ions in physiological media [2–4]. It is known that the leached metal ions can cause sarcomas, fibrous encapsulation, osteolysis, genotoxicity, carcinogenicity, and metal sensitivity [4]. Moreover, these metallic implants are not bioactive and achieving satisfactory osseointegration is always a concern. Earlier research has shown that these problems can be overcome by depositing bioactive hydroxyapatite (HAP) (Ca₁₀(PO₄)₆(OH)₂) coatings on metallic implants [5–13]. HAP coatings were first reported in the mid-1980s for improving the fixation between the bone and the implant [5]. A variety of techniques have been developed since then for depositing HAP coatings on metallic substrates, including thermal spraying, sputter coating, sol–gel coating, dip coating, electrophoretic deposition, and electrochemical deposition [6–9]. Recently, micro-arc oxidation has also been used to prepare HAP coatings [10–14]. Among the various coating methods, plasma spraying is one of the most widely used

commercial methods for depositing HAP coatings on orthopaedic or dental prostheses [15]. However, plasma-sprayed HAP coatings do not strongly bond to the metallic substrate and are also vulnerable to easy wear and tear, resulting in undesirable debris formation [16].

One way to overcome these problems is to treat the surface of the implant such that a composite layer is produced with HAP. This can be elegantly done by melting the implant surface using a laser and feeding HAP into the melt pool in powder form. While titanium implants have been laser treated to good effect in this way [17–20], whether such a surface treatment can similarly work well for stainless steel implants or not is a question at present. The primary objective of this investigation is to evaluate the feasibility of incorporating HAP to 316 L alloy implant surfaces using Laser-Engineered Net Shaping (LENSTM). LENSTM is a well-known additive manufacturing process, which can be utilized not only for building patient-specific custom implants, but also for modifying their surfaces in different ways [21–26].

2. Experimental work

A LENSTM-MR7 (Optomec Inc. Albuquerque, NM) equipped with a 0.5 kW continuous wave ytterbium-doped fiber laser with a beam size of 0.5 mm was used to modify the surface of 316 L stainless steel substrates (150 × 100 × 3 mm sheets) with laboratory-synthesized crystalline HAP powder (size range: 50 to 150 μm). Several coating samples, with 100 mm² area, were prepared at a powder feed rate of 1.4 g/min with different laser powers and scan velocities. The process parameters used in the present investigation are presented in Table 1. All the experiments were carried out in a glove box filled with high

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Table 1
Laser process parameters used in the present study.

Sample ID	Power, W	Velocity, mm/s	Energy density, J/mm ²
1	250	20	32
2	250	15	42
3	350	20	44
4	350	15	59

purity argon gas. The oxygen content in the glove box was kept below 10 ppm throughout the experiments.

The surface-treated samples were sectioned and metallographically prepared for microstructural examination. Microstructural studies were carried out with a light microscope and a scanning electron microscope (SEM, FEI Quanta 200) equipped with an energy-dispersive spectrometer (EDS). The constituent microstructural phases of the laser surface-modified samples were determined using an X'Pert Pro MPD diffractometer (PANalytical) operating at 45 kV and 40 mA using Ni-filtered CuK α radiation. Vickers hardness measurements were carried out on the modified surface using a microhardness tester (Wolpert Wilson Instruments 402MVD) at a load of 300 g applied for 30 s.

The biocompatibility of unmodified and surface-modified 316 L stainless steel samples was evaluated by immersing them in a simulated body fluid (SBF) with an ionic composition similar to human blood plasma. The samples were immersed in a plastic bottle containing 10 ml of SBF and were kept in a biological thermostat at 37 °C for 3, 7 and 14 days. The media was changed every 2 days during the experiment. After each time period, the samples were washed with distilled water, dried overnight at 100 °C, and examined under SEM for apatite precipitation.

3. Results and discussion

The cross-sectional microstructures of the laser surface-modified samples are shown in Fig. 1. As can be seen, the modified surfaces are free from any gross defects such as porosity or cracks. The modified surfaces exhibited an as-cast microstructure with austenite dendrites and some inter-dendritic phases. In general, the scale of microstructural features in the modified surface was found to increase with increase in the laser energy input from 32 J/mm² (Fig. 1a) to 59 J/mm² (Fig. 1d). The interface between the modified surface layer and the substrate is sound and rather diffuse, as can be seen in Fig. 2. Such diffuse interfaces are characteristic of laser surface-modified materials and laser deposited coatings [21–25]. In contrast, HAP coatings produced using other techniques such as plasma spraying show a sharp interface, which is undesirable for their long-term performance [21].

Fig. 3 shows the influence of laser process parameters on the thickness of modified surface. Among the various samples prepared in this study, the thickness of the modified surface was the lowest ($222 \pm 12 \mu\text{m}$) at a laser power of 250 W and a scan speed of 20 mm/s and the highest at a laser power of 350 W at a scan speed of 15 mm/s. The results show that the thickness of the modified surface can be controlled by controlling the laser energy input. The thickness of the modified surface can be increased by either increasing the laser power or decreasing the scan speed as both would result in a deeper melt pool on the substrate. Similar trends were reported in earlier studies in other material systems such as AISI 410 stainless steel [26]. From the present experimental results, it appears that the incident laser power had stronger influence on the thickness of the modified surface than the scan speed. For example, the increase in the thickness of the modified surface was nearly 50% (from $237 \pm 14 \mu\text{m}$ to $355 \pm 6 \mu\text{m}$) when the laser power was increased from 250 W to 350 W at a scan speed of

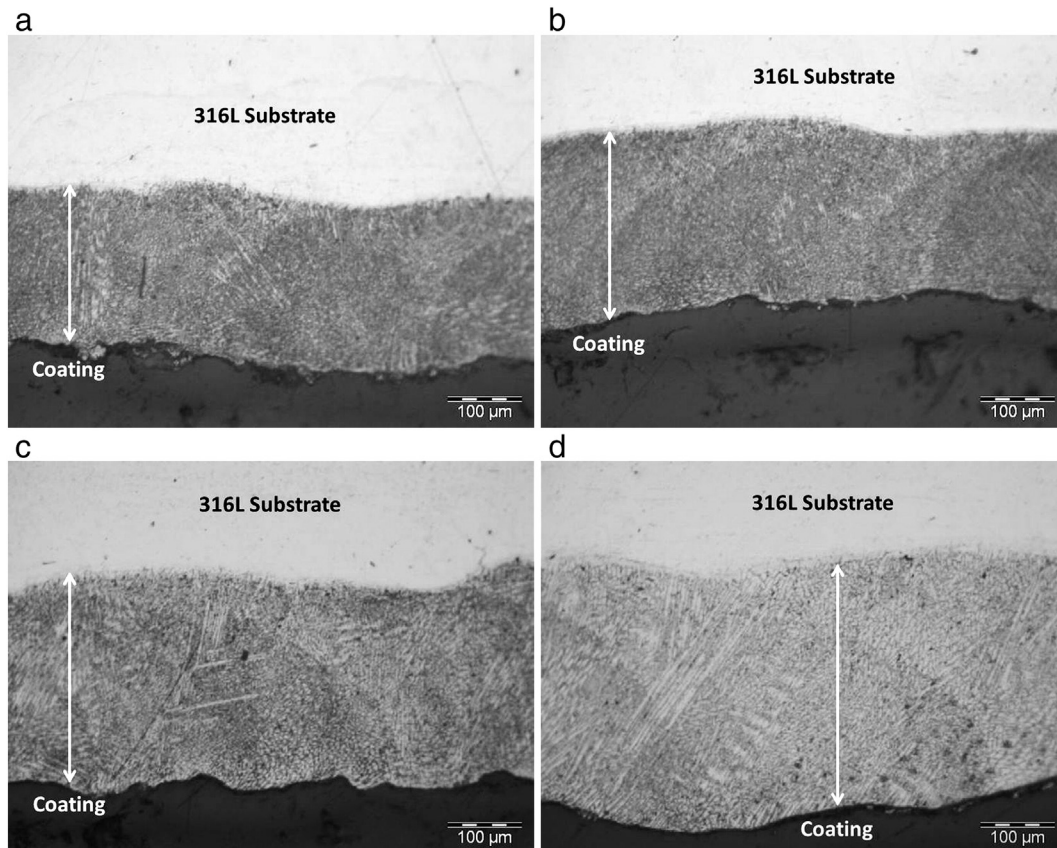


Fig. 1. Optical micrographs of laser surfaced-modified samples. (a) 32 J/mm², 250 W, 20 mm/s, (b) 42 J/mm², 250 W, 15 mm/s, (c) 44 J/mm², 350 W, 20 mm/s, (d) 59 J/mm², 350 W, 15 mm/s.

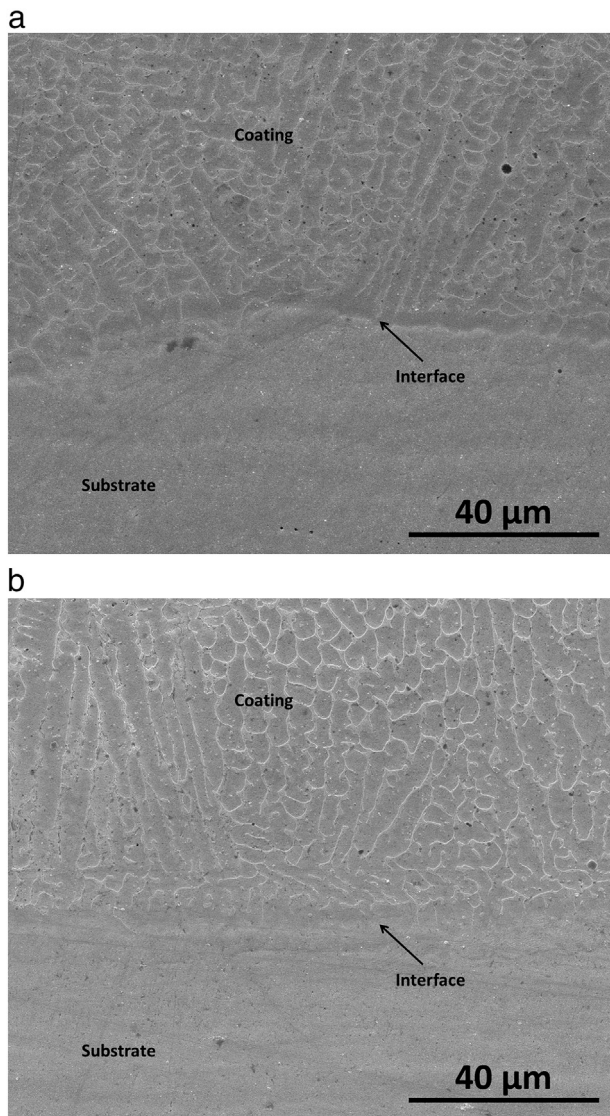


Fig. 2. Interface microstructures of surface-modified samples. (a) 32 J/mm², 250 W, 20 mm/s, (b) 59 J/mm², 350 W, 15 mm/s.

15 mm/s. On the other hand, the increase in the thickness of the modified surface was only 16% when the scan speed was decreased from 20 mm/s to 15 mm/s at a laser power of 350 W. Overall, the results show that it is possible to modify the implant surface to desired depth by judiciously selecting the laser parameters.

Typical SEM microstructures of the various laser surface-modified samples are shown in Fig. 4. The austenite dendrites and the inter-dendritic phases can be more clearly seen in these pictures. The

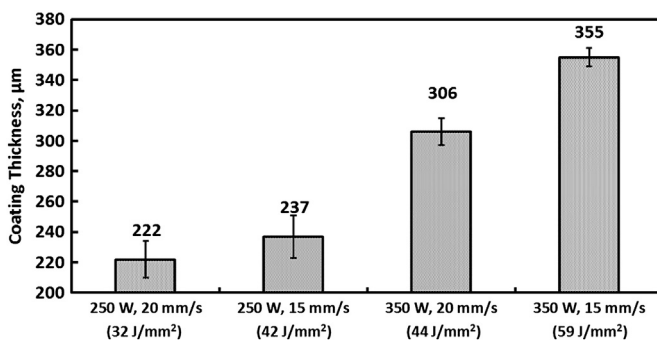


Fig. 3. Influence of laser parameters on the depth of modified surface.

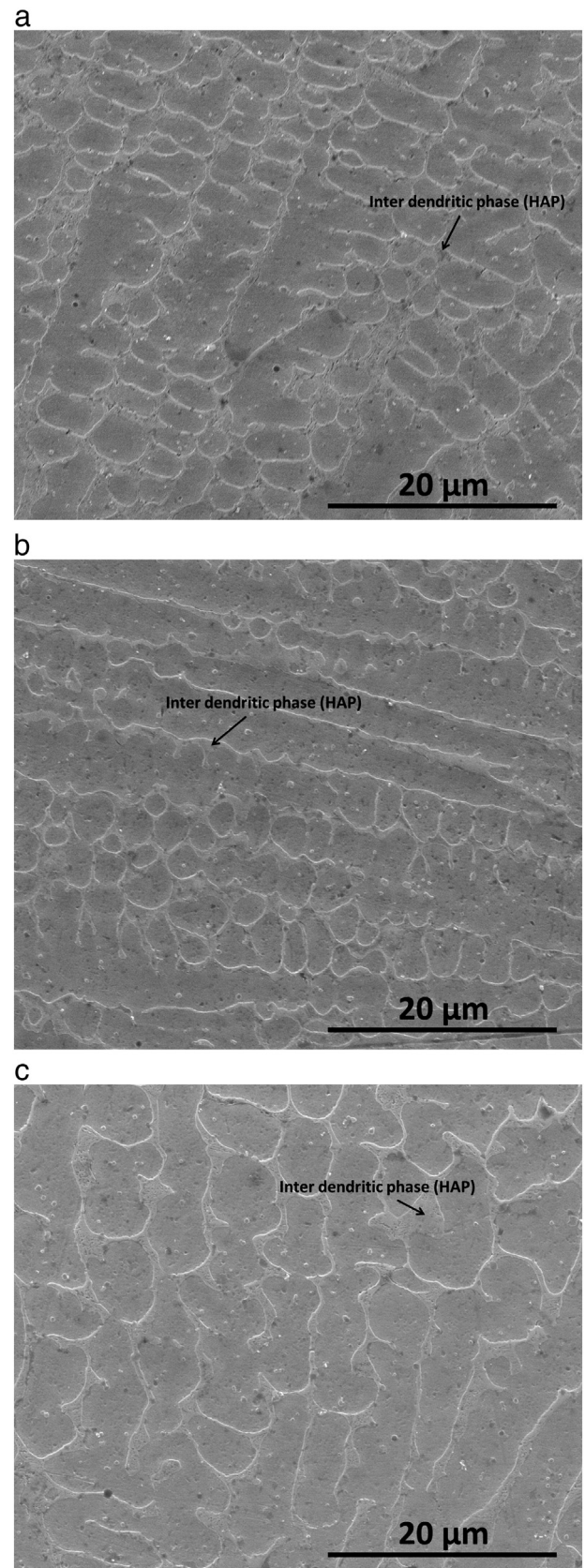


Fig. 4. SEM microstructures of surface-modified samples. (a) 42 J/mm², 250 W, 15 mm/s, (b) 44 J/mm², 350 W, 20 mm/s, (c) 59 J/mm², 350 W, 15 mm/s.

size of the austenite dendrites was measured using image analysis. The results showed that the dendrite size increased from $2.92 \pm 1.19 \mu\text{m}$ to $7.96 \pm 3.73 \mu\text{m}$ as the laser energy increased from 32 J/mm^2 to 59 J/mm^2 . The samples produced at 32 J/mm^2 (250 W, 20 mm/s), 42 J/mm^2 (250 W, 15 mm/s), 44 J/mm^2 (350 W, 20 mm/s) and 59 J/mm^2 (350 W, 15 mm/s) showed a dendrite size of $2.92 \pm 1.19 \mu\text{m}$, $3.84 \pm 1.83 \mu\text{m}$, $3.92 \pm 1.06 \mu\text{m}$ and $7.96 \pm 3.73 \mu\text{m}$, respectively. It is known that the scale of the solidification structure has an inverse relationship with the cooling rate experienced by the solidifying melt [27–29]. As the laser energy input is reduced (by decreasing the laser power and/or increasing the scan speed), the cooling rate increases (due to increased thermal gradients), resulting in a finer solidification structure.

Fig. 5 shows typical x-ray diffractograms of the laser surface-modified samples along with those of the HAP powder and the 316 L substrate. The results showed that the surface-modified samples contained HAP in crystalline form along with a small amount of Fe_3P . From Fig. 4, it can be seen that these phases mainly present in the inter-dendritic regions. These observations suggest that the current surface modification process involved complete melting of the HAP powder along with the substrate material. During cooling, the melt begins to solidify in dendritic mode with the formation of austenite. In this process, because of the low solubility of calcium and phosphorous in austenite, the liquid gets richer and richer in these elements as more and more austenite forms. The process of solidification proceeds to completion with the formation of HAP and some amount of Fe_3P in the inter-dendritic regions. This is just a conjecture at this stage and further studies are necessary to fully understand the microstructure evolution during laser surfaced modification of alloy 316 L with HAP. Interestingly, the surface-modified samples showed no delta ferrite (as per XRD data), which is normally seen in alloy 316 L in as-cast condition. This can be attributed to the rapid cooling rates, of the order of 10^5 K/s , involved in laser surface modification [27]. It is known that in austenitic stainless steels such as alloy 316 L, rapid cooling rates can result in a change in solidification mode from primary ferrite to primary austenite [30]. When austenitic stainless steels solidify in the later mode, no delta ferrite shows up in their room temperature microstructure. While such a change in solidification mode is known to result in hot cracking during laser or electron beam welding of austenitic stainless steels, in the present study, however, none of the laser surface-modified samples showed any hot cracks. This is all the more surprising in the present case given the high phosphorous content in the solidifying melt (due to melting of the HAP powder). It may be that the volume of the liquid metal undergoing solidification at any given instance during laser surface modification is too small for hot cracking to occur. Also, it may be that the amount of HAP fed to the melt pool in the current study is not high enough to result in any undesirable effects. Further

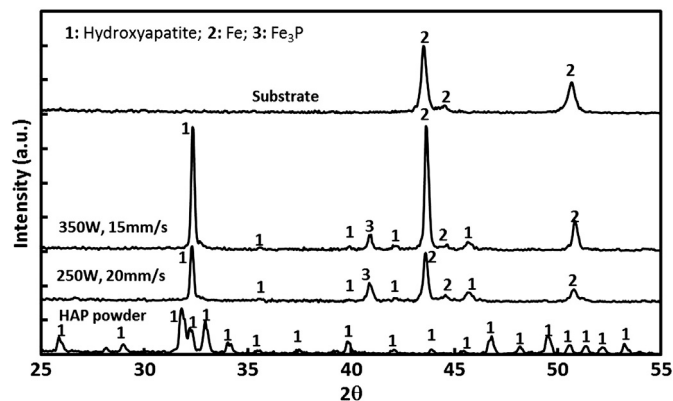


Fig. 5. X-ray diffraction results of 316 L substrate, HAP powder and laser surface-modified samples.

studies are necessary to determine how of much more of HAP can be safely incorporated to alloy 316 L implant surfaces.

The results of hardness testing on laser surface-modified samples are presented in Fig. 6. The hardness of the modified surfaces varied between $372 \pm 8 \text{ HV}$ and $434 \pm 20 \text{ HV}$, which is significantly higher than the hardness of the unmodified alloy 316 L ($265 \pm 7 \text{ HV}$). The composite microstructure of the modified surfaces is responsible for their higher hardness. The increase in hardness is, of course, beneficial for the wear resistance of the implants. Among the various surface-modified samples, the samples produced using the highest laser energy input showed the lowest hardness. The scale of the solidification structure thus has a measurable influence on the surface hardness.

The biocompatibility of alloy 316 L samples with and without HAP surface modification was assessed by immersing the samples in a SBF for 3, 7 and 14 days. Fig. 7 shows the surface morphologies of the samples after 3 days of immersion. In general, the apatite precipitates, if any, appear as particles with bright contrast on the surface of the samples immersed in SBF. As can be seen, the surface-modified samples showed a strikingly better apatite formation compared to the unmodified samples. Further, these precipitates were analyzed using EDS attached to the SEM and found to contain Ca and P as major constituents demonstrating the apatite precipitation. Similar observations were made on the samples immersed for 7 and 14 days, except the amount of precipitation was more on these samples. These results clearly show that addition of HAP to alloy 316 L implant surfaces results in significantly enhanced and early bioactivity, leading to better osseointegration.

Overall, the current study shows that incorporation of HAP in the matrix material of 316 L implant is a very useful strategy. It overcomes the problems associated with plasma sprayed HAP coatings, such as poor coating/substrate bonding and vulnerability to easy wear and tear. The benefits of HAP incorporation can be maximized by increasing its volume fraction. However, further work is necessary to fully understand the process of laser surface modification of alloy 316 L with HAP and to optimize the amount of HAP addition. Also, how well the current approach can address the problem of nickel leaching in stainless steel implants needs to be considered in future work.

4. Conclusions

In the current study, an attempt is made to modify the surfaces of 316 L stainless steel implants with bioactive HAP using a commercial additive manufacturing process, LENSTM. Experiments were conducted over a wide range of laser powers and scan speeds. The modified surfaces showed a composite microstructure with austenite dendrites and inter-dendritic HAP with a small amount of Fe_3P phase. The thickness of the modified surface can be controlled by controlling the laser parameters. An increase in laser energy input results in a thicker modified surface, but with a coarser microstructure and reduced surface hardness. After immersion for three days in a SBF, the laser surface-modified samples showed significantly enhanced apatite formation

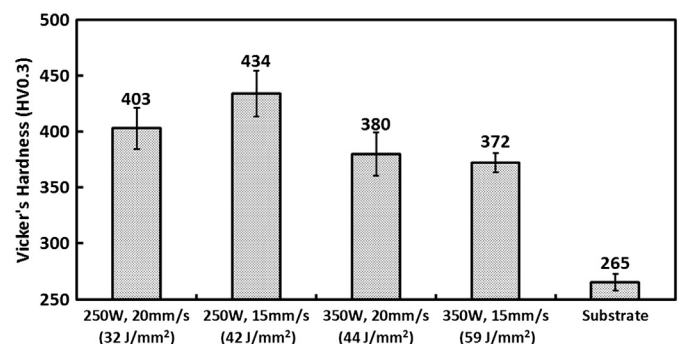


Fig. 6. Average hardness of laser surface-modified samples and 316 L substrate (based on ten measurements).

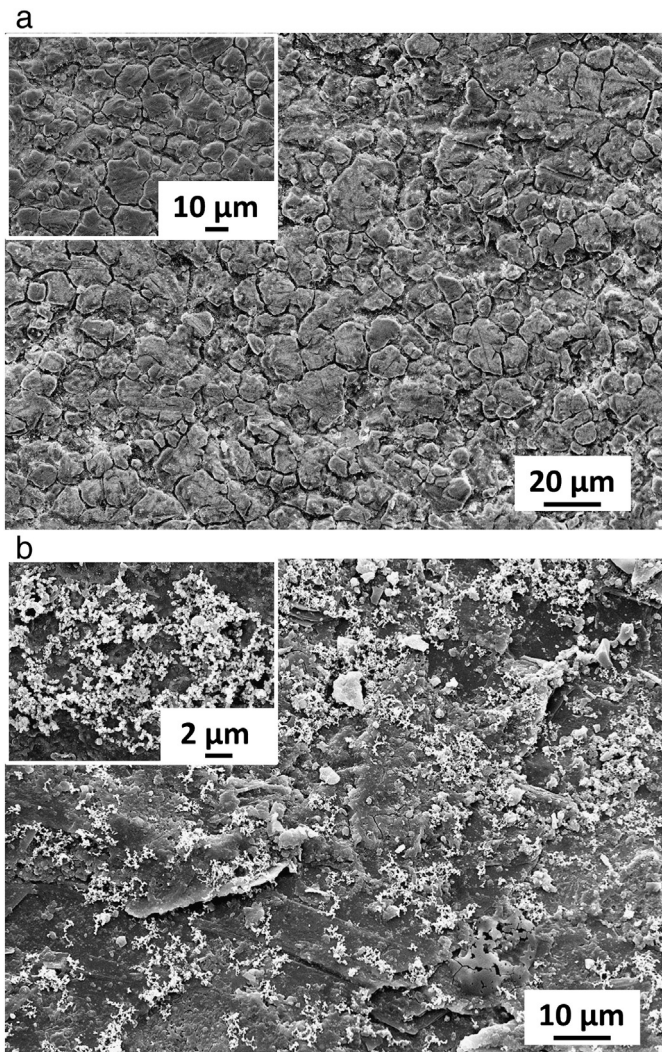


Fig. 7. Comparison of apatite precipitation after 3 days of immersion in a simulated body fluid. (a) Unmodified 316 L samples. (b) Laser surface-modified 316 L samples (59 J/mm², 350 W, 15 mm/s). Note significantly enhanced apatite precipitation in laser surface-modified 316 L samples.

compared to the unmodified samples. The present work demonstrates that it is feasible to modify the 316 L stainless steel implant surfaces with HAP employing lasers.

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