Fatigue behaviour of the chemically treated titanium grade 4 implant material

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"As-received" and "sand-blasted" commercially pure titanium plates were chemically treated in alkaline and hydrogen peroxide solutions in order to improve osseointegration. Both surface modification methods were carried out under optimum conditions stated in the literature. The samples were subjected to a bending cyclic loading under a stress amplitude of 250 MPa and R=0. The fatigue life of the as-received samples decreased from 4.10^5 to 2.10^5 due to surface roughening effect of the surface treatments. On the other hand, sand blasting increased the fatigue life of the sample significantly, although it also increased the surface roughness. The reason is the blasting induced deformation and in turn compressive stresses in the surface vicinity. Chemical treatments applied did not affect the surface roughness of the sand blasted samples. However the fatigue life of the sand blasted samples decreased drastically after chemical treatment. Chemical surface treatments are generally accompanied by a post heat treatment. The decrease in the fatigue life of the sand blasted plates is stemmed from stress relieving effect of the post heat treatment. As a result surface modification methods applied for bioactivity should be also evaluated with respect to its effects on the fatigue performance of the material. The process parameters of the chemical surface treatment should be optimized taking into the account the fatigue life of the implant.

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1. Introduction

Titanium and its alloys are widely used in orthopaedics and dentistry as artificial bones, joints and dental implants because of their significant biocompatibility, mechanical and corrosion properties. In comparison with stainless steel or cobalt alloys, titanium and its alloys exhibit an advantageous combination of biocompatibility and mechanical properties in direct contact with the tissue. In load bearing applications implant materials are subjected to severe and fluctuating loading conditions in service. Therefore fatigue is the one of the major failure mechanisms in these implants [1-3].

In case of cementless anchoring of the prosthesis directly to the living bone, the structure and composition of the implant surface play an important role for bone-implant interlocking. Rough surfaces, porous coatings and osteoinductive layers have been shown to be good surfaces for osseointegration [4-8]. Therefore several surface modification methods have been introduced in order to improve bone-implant interlocking. These treatments will increase also the performance of the implant. The methods for surface modification can roughly be classified as mechanical, chemical and physical according to the formation mechanism of the modified layer on the substrate [1,2,4-19]. Traditionally hydroxyapatite coatings are used to achieve the promoted bioactivity on a metallic surface [6,19,20]. On the other hand, there has been increasing interest in the formation of a bioactive surface layer directly on titanium substrates by chemical treatments in recent years. Such layers have been reported to induce apatite formation in the living environment or simulated body fluid [4,6-8,17,19].

Since the fatigue behaviour of a material is closely related to the surface structure, the surface modification methods conducted for osseointegration may affect the fatigue performance of the implant. Furthermore, most chemical surface modification methods require post-thermal processes (heat treatment) which may alter the microstructure of the implant material. This microstructural change might affect the fatigue performance in service. Therefore these methods must also be evaluated with respect to their effects on the fatigue performance of the implant material.

In the present work, the effect of the alkali treatment and hydrogenperoxide treatment on the surface structure and fatigue life of titanium implant material has been evaluated. Both methods are well known chemical treatments for the surface modification of titanium and its alloys.

2. Experimental

Material

The material used for evaluation was commercially pure (c.p.) titanium grade 4. The chemical composition of Ti plates is given in the Table 1. As-received plates were in a surface condition of mill finished and they have a thickness of 3 mm. Some of Ti plates were sand-blasted with a jet of SiO_2 particles of 200-300 μm in size at a pressure of 6-8 atm. The samples for characterization and the fatigue specimens were cut from the as-received and sand-blasted plates.

Table 1. Chemical analysis of the Ti grade 4 samples.

C	Fe	H	N	O
0.05	0.1	0.010	0.045	0.30

Surface Treatments

Two different chemical surface treatments have been investigated:

1. Alkaline Treatment: The specimens were ultrasonically washed in distilled water and dried at a temperature of 100 °C, subsequently treated with 5M NaOH solution at 60 °C for 24 h. After the rinsing in water, the specimens were dried and heat-treated at 600 °C for 1 h.

The conditions of the alkaline treatment were reported to be optimum for osseointegration in Ref.s 8,11,12 and 13 where the details of the procedure can be found.

2. Hydrogen Peroxide Treatment: The specimens were ultrasonically rinsed in distilled water, dried at a temperature of 100 °C and subsequently dipped into 8.8 M H_2O_2 and 0.1 M HCl mixture at 80 °C for 1 h. After the solution treatment the specimens were heated up to 500 °C for 1 h. The details of the treatment were carried out according to Ref. 14. The conditions applied were referred as optimum for hydrogen peroxide treatment with respect to hydroxiappatite formation of titanium surface in the simulated body fluid [14].

Characterization

For the metallographic evaluation of the chemically treated and non-treated specimens, the samples were cut from the fatigue specimens. The samples were ground, polished and etched with Kroll’s Reagent. The cross-sections were examined by optical microscope.

Glancing angle X ray diffraction (GAXRD) analysis (Cu Kα) was performed in order to identify the phases present in the surface layers. The surface topography and the roughness (R_a and R_t) of the fatigue specimens were determined.

The hardness of the specimens was determined by Vickers Microhardness test. The test load was 196 cN (200 g) in order to achieve a low indentation depth, i.e. to get information from the near-surface of the specimen. After the fatigue test, the fractured surfaces were examined by scanning electron microscope without any further treatments.

Fatigue Test

The fatigue specimens were machined by means of laser cutting from the as-received and sand blasted plates. The form and the dimensions of the fatigue specimens are shown in Fig. 1. The cross section in the centre of the specimen was reduced to amplify the stress amplitude.

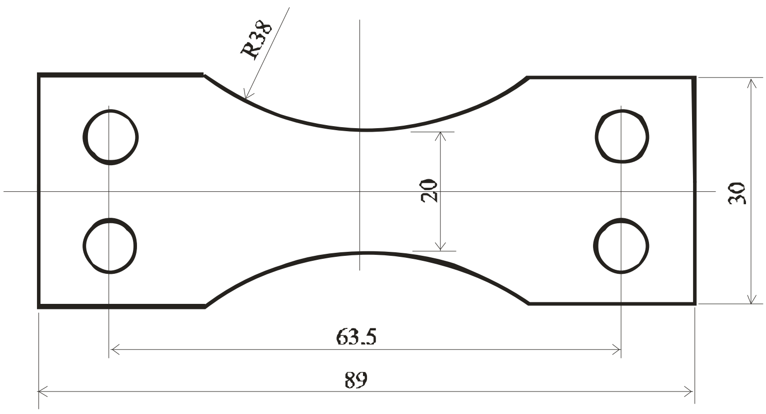

Fig. 1 The schematic drawing of the fatigue test specimen.

Fatigue experiments were performed using "Denison Fatigue Test Apparatus" working at a cycling frequency of approximately 25 Hz. The uniaxial stresses over the cross-section of the specimens were calculated from the bending moment and section modulus. The specimens were flexural loaded so that the upper side of the neutral axis was stressed only in tension (Loading rate R=0). Therefore the skin of the specimen was subjected to a stress fluctuation between 0 and 250 MPa. The specimens were tested with constant deflection until failure or at least for $2x10^6$ cycles if they did not fail.

3. Results and Discussion

Fig. 2 shows the glancing angle x ray patterns of the as-received sample and additionally chemically treated samples. The marked peaks reveal the existence of the sodium titanate ($Na_2Ti_5O_{11}$) phase in the surface layer of the titanium for the alkaline treatment and anatase phase for the hydrogenperoxide treatment. Both phases have been reported to improve osseointegration for titanium and its alloys. Identical peaks exist also on the surface of the sand blasted and chemically treated samples (Fig. 3). Comparing the Fig 2 and Fig. 3, it can also be noticed that the sand blasted titanium plate has a texture in the surface due to the cold deformation. The surface texture endured the post-heat treatment (Fig. 3a and Fig. 3b).

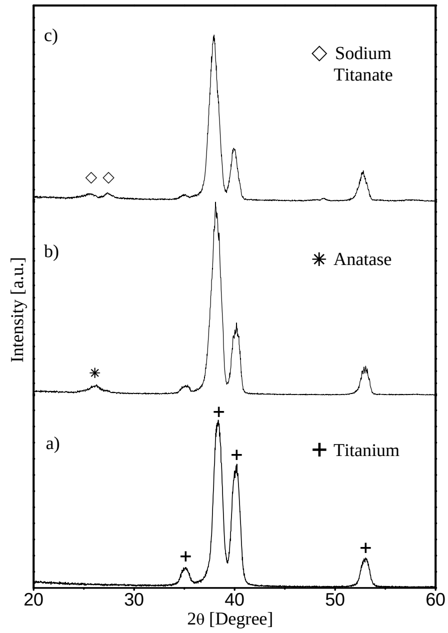

Fig. 2 X-Ray pattern of the as-received samples; (a) non-treated, (b) hydrogen-peroxide-treated and (c) alkaline-treated.

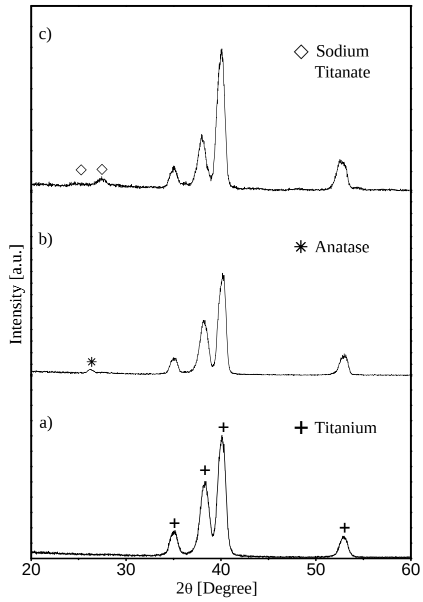

Fig. 3. X-Ray pattern of the sand blasted samples; (a) non-treated, (b) hydrogen-peroxide-treated and (c) alkaline-treated.

Fig. 4 shows the surface topographies of the as-received samples. The figures reveal the existence of the some surface asperities. The chemically treated samples exhibit higher surface irregularities. The detailed surface roughness values are given in Table 2. Surface roughness value R_a is simply the arithmetic average deviation of the profile from the mean line. R_t is, however, the peak-to-valley height value. Apparently, both surface treatments had an effect on the existing surface asperities. They attack the existing surface asperities, and increase the peak to valley height locally. Comparing the R_a and R_t values, it can be estimated that the local surface roughening effect is much more pronounced in case of hydrogen peroxide treatment.

Table 2. Surface roughness values of the samples.

Sample	Chemical Treatment	R_a (µm)	R_t (µm)
As-received	Non treated	1,02	12,34
	Alkaline treated	1,19	12,88
	Hydrogen peroxide treated	1,17	16,03
Sand Blasted	Non treated	1,42	21,62
	Alkaline treated	1,37	19,18
	Hydrogen peroxide treated	1,45	18,65

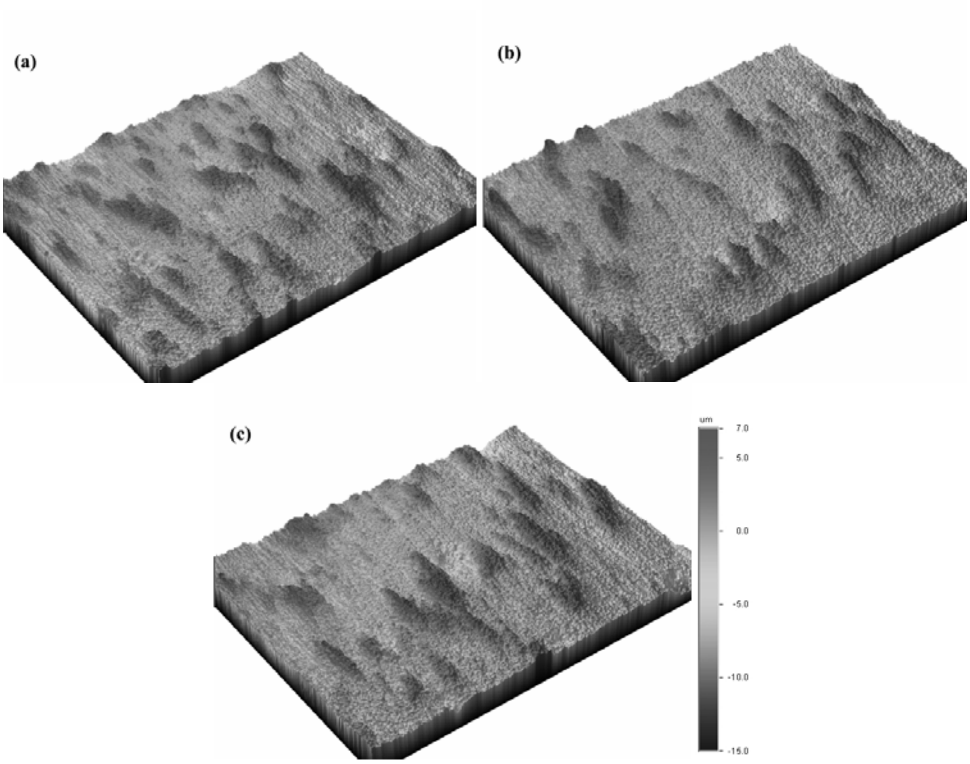

Fig. 4. Surface topographies of the as-received samples a) chemically non-treated, b) alkaline treated, c) hydrogen peroxide treated.

On the other hand, the sand blasted samples have much wavier surfaces (Fig 5) and hence higher surface roughness. As a result of this waviness the surface roughness R_a increased approximately to 0.20-0.25 µm. As R_t values are compared, in contrast to the as-received samples, the both chemical treatments served to reduce the height of peak-to-valley on the sand blasted surfaces. In other words, the chemical treatments acted in favour of surface smoothing on the deformed, wavy surfaces. This is probably resulted from higher dislocation density of the asperities on the sand blasted surface.

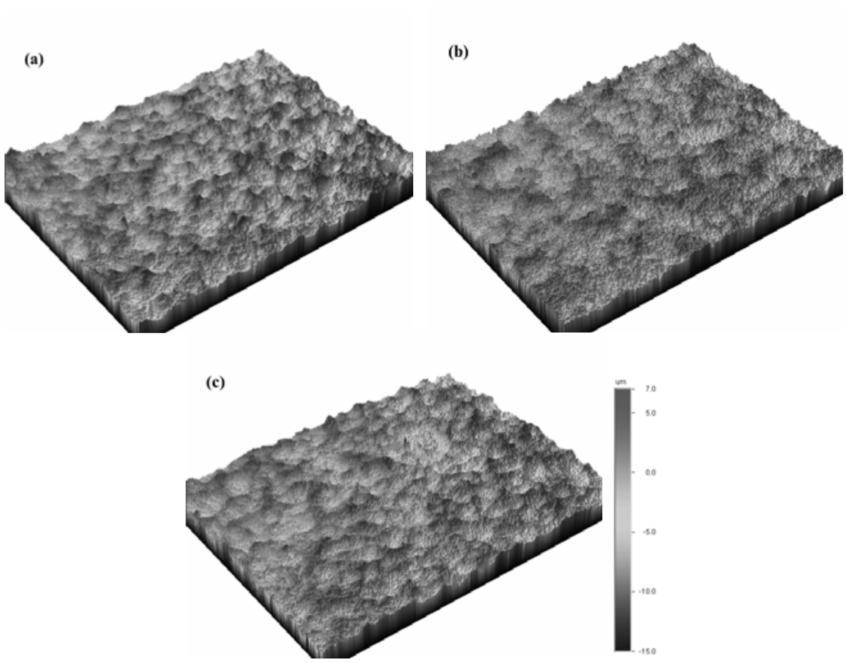

Fig. 5. Surface topographies of the sand blasted samples a) chemically non-treated, b) alkaline treated, c) hydrogen peroxide treated.

Fig. 6 shows the hardness values of the samples. Due to the low measurement load, the hardness values are directly related to the surface of the samples. Nevertheless, the existence of the chemically deposited layers cannot be noticeable in the hardness values, since these layers are very thin.

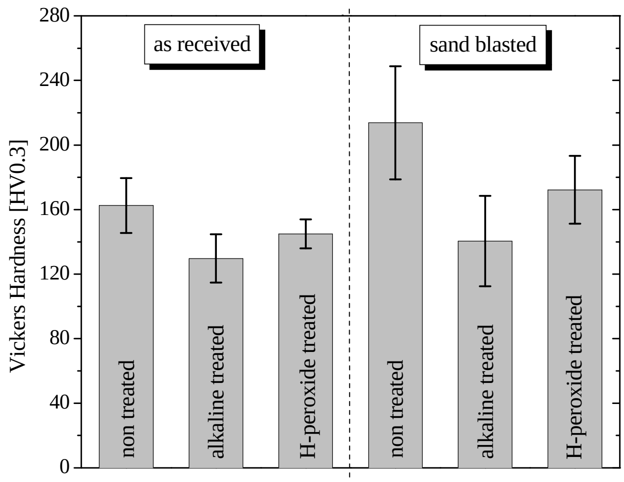

Fig. 6. Hardness values of surface for the chemically treated and non-treated specimens.

In the as-received samples the hardness value slightly decreased with surface modification treatment. The slight decrease was caused by heat treatment after the chemical dipping process. As a matter of fact, the decrease is relatively high in the sample subjected to alkaline treatment, because the temperature of heat treatment was by 100°C higher than that of hydrogen peroxide treatment to obtain an optimum condition. The reason of the decrease should be stress relieving during the heat treatment.

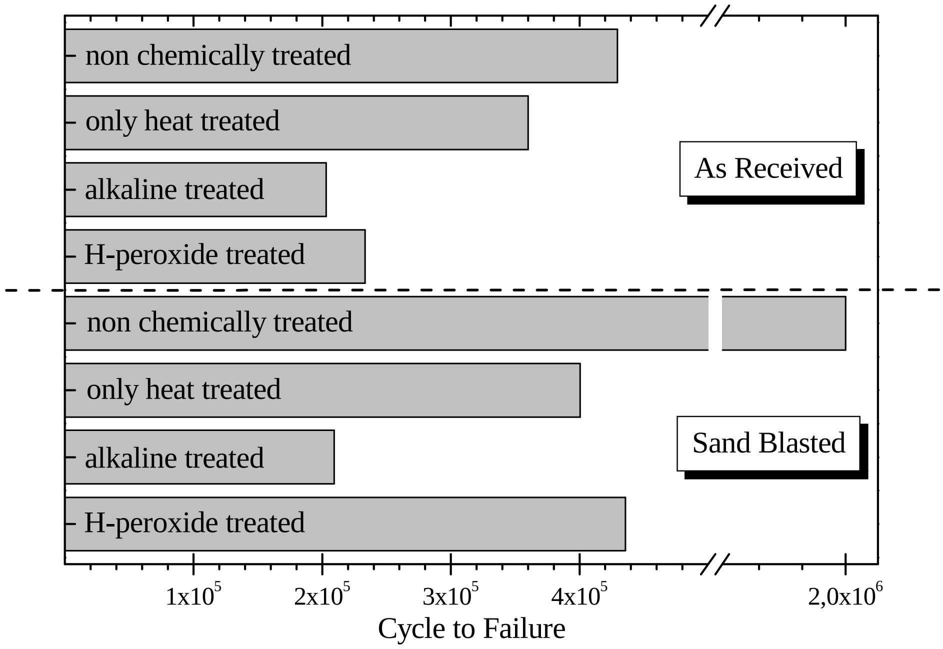

Fig. 7. Cycle to failure values for the chemically treated and non-treated specimens.

The average hardness value of the sand blasted sample was approx. 215 HV; it is significantly higher than the as-received samples. This increase is a normal result of the cold deformation effect of the sand blasting in the vicinity of the surface. The cold deformation texture can be easily noticed from the Ti peaks in the GAXRD patterns (compare Fig. 2 and Fig. 3). However, the hardness values for sand blasted and chemically treated samples dropped nearly to that of as-received sample. As seen in the Figures 2 and 3 ,GAXRD patterns of these samples did not significantly changed. This implies that the cold deformed layer on the sand blasted sample did not recrystallized during the heat treatment, while the decrease in the hardness is implies that the compressive stresses induced by sand blasting was completely relieved.

The number of the cycle to the ultimate failure is given in Fig. 7. The number of cycle to failure for the non-treated titanium is $4.3x10^5$. However, the fatigue life decreased to $2.0x10^5$ and $2.3\ x10^5$ in case of alkaline treatment and hydrogen peroxide treatment, respectively. This decrease occurs as a result of combined effect of the surface roughening of chemical dipping and stress relieving of the post-heat treatment. In order to evaluate these two effects separately, another specimen which was not chemically treated but similarly heat treated at 500°C, was tested. In this case, failure was observed at a cycle of $3.6x10^5$. These results indicate that the decrease in the fatigue life of the as-received samples is mainly due to the surface roughening effect of the chemical treatment.

On the other hand, the sand blasted specimen revealed a fatigue life longer than a cycle of $2.0x10^6$. Although the surface roughness increased, due to compressive stresses induced by blasting, the fatigue performance raise approximately by five times. However, the specimens in sand blasted and chemically treated conditions, the cycle to failure values decreased again down to $2.1x10^5$ and $4.4x10^5$ for alkaline treatment and hydrogen peroxide treatment, respectively. Considering that the chemical treatment did not affect the surface roughness, the reason of the decrease in fatigue performance should be the stress relieving caused by post-heat treatment. As a matter of fact, the failure of the specimen which was sand blasted and heat treated only, was observed also at $4.0x10^5$.

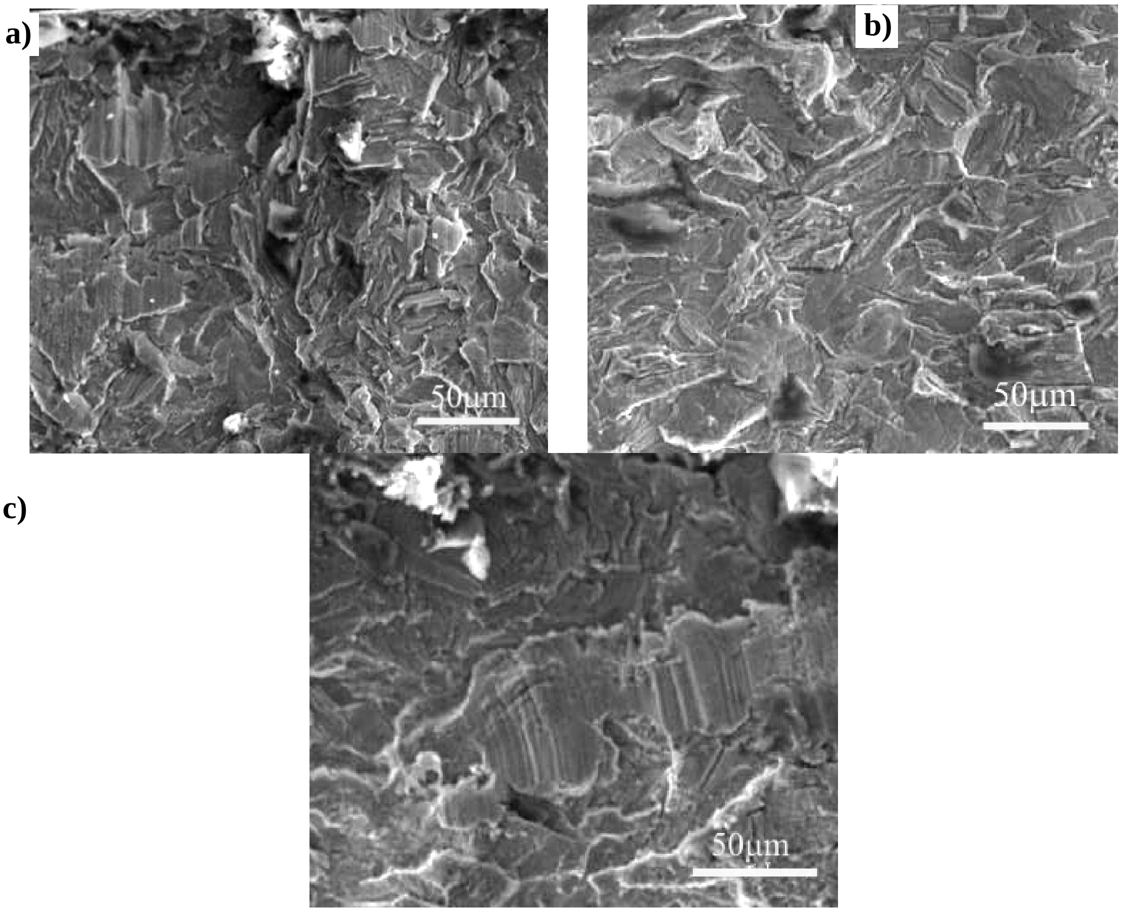

Fig. 8. Fracture cross sections of the chemically treated and non treated samples. (a) non-treated, (b) alkaline treated, (c) peroxide treated.

Fig. 8 shows the fracture surface of the fatigue samples. All trated samples reveal analogous fatigue fracture behaviour with brittle features likewise non treated sample. In all samples, the appearance of the fracture surfaces are a mixed fatigue fracture modus with often intergranular crack growth with pronounced crystallographic cleavage.

4. Conclusions

The alkaline and hydroxyperoxide surface treatments applied to titanium and titanium alloys for osseointegration have a strong effect on the fatigue performance of the material. Both chemical treatments have surface roughening effect on the finished titanium surface. Additionally the complementary post heat treatment affects the microstructure of material. The work has revealed that both chemical treatments reduce fatigue life chiefly due to surface roughening.

On the other hand, sand blasting is a well known process to enhance the fatigue life of materials. Therefore it has been widely used for biomedical implants as a surface treatment [21]. It also increases osseointegration. In case of combination of sand blasting and chemical surface treatment, it has been well established that the post heat treatment affected the fatigue life of the material negatively. In this second case the main reason of the decrease in the fatigue performance is the metallurgical stress relieving effect of the post heat treatment rather than surface roughening.

The results clearly show that the chemical surface treatments and their paramters should be evaluated with respect to their effects on the fatigue performance of the implant material. When the chemical surface treatment is applied to a sand blasted surface, the post heat treatment should be achieved so that a compromise should be obtained between osseointegration and fatigue life of the material.

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