Influence of the Chemical Composition, Structure and Heat Treatment on the Topography and Mechanical Properties of Ti5Al4V and Ti6Al4V after Electron Beam Surface Treatment

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Abstract. In order to obtain a proper and accelerated osseointegration process, continuous efforts for improving the surface of the implants have been made. The physical texture, structure and mechanical properties of the implant surface are known to be an important factor in bone-implant interaction. Trying to find a solution for weak osseointegration, new modification techniques should be used and examined. In the particular study, the Ti5Al4V and Ti6Al4V alloys with different initial structure and composition were vacuum heat treated at different technological parameters in order to obtain maximum strengthening. One and the same electron beam surface modified (EBSM) by scanning electron beam was subsequently carried out for both alloys and their surface characteristics and mechanical properties were revealed by metallographic analysis, roughness, XRD and hardness measurements. The results revealed that under the selected conditions of treatment, a specific wave-like topography was obtained. The mean grains’ sizes, depth of the structural changes after the surface modification and hardness and crystal lattices’ changes of both alloys was assessed depending on the differences in the composition, initial structural and mechanical characteristics of the alloys in the different heat-treated conditions.

1. Introduction
Titanium is a bioinert material because it does not connect to bone or induces bone growth [1]. In recent years, there are many surface modifications methods such as plasma assisted thermochemical treatment, laser etching techniques, sandblasting, anodic chemical treatment, ion implantation that are used for improving the surface properties of implant materials [2]. These are applied to increase the surface roughness and wettability and thus to enhance effectively the mechanical performance and bone-implant anchorage. Among the surface modifications, the electron beam surface modified (EBSM) by scanning electron beam was subsequently carried out for both alloys and their surface characteristics and mechanical properties were revealed by metallographic analysis, roughness, XRD and hardness measurements. The results revealed that under the selected conditions of treatment, a specific wave-like topography was obtained. The mean grains’ sizes, depth of the structural changes after the surface modification and hardness and crystal lattices’ changes of both alloys was assessed depending on the differences in the composition, initial structural and mechanical characteristics of the alloys in the different heat-treated conditions.
Ti tends to increase with increasing Al content and increasing the volume fracture of α [4] while the β-transus temperature increase. On the other hand, the presence of β-stabilizing elements like V, Mo, and Nb are known to increase the strength, reduce the elastic modulus and improves the passivation leading to higher resistance to corrosion [5]. This study aims at determining the response of two α+β titanium alloys with small variations in the chemical composition in as-received and heat treated conditions to the EBSM with scanning electron beam.

2. Experimental procedures
The chemical compositions of both materials used for the experiment, determined by JEOL JXCA-733 Microprobe scanning electron microscope (SEM) equipped with wavelength dispersive spectrometers (WDS), were shown in Table 1. Samples with dimensions 14×14×4 and 15×15×4 mm were cut out using the electro-erosion cutting method. The as-received (AR) samples were single solution treated (ST) for 30 min at 920 °C and 950 °C for the Ti54 and Ti64, respectively and water quenched. Half of the specimens were precipitated (P) for 4 hours at 500 °C and 540 °C for Ti54 and Ti64, respectively and air cooled. All treatments were carried out in ≤ 1 Pa vacuum. The surfaces of the samples were grounded and polished before the EBSM. To study the effect of the surface treatment, the EBSM was applied to AR, ST, and ST and precipitated (ST+P) samples.

| Table 1. Chemical composition (wt. %) of the substrate material. |
|------------------------|---|---|---|---|---|---|---|---|---|
| Element | Al | V | Fe | Mn | Co | Mo | Pd | Nb | Hf | Ti |
| Ti54  | 5.21 | 4.40 | 0.14 | 0.11 | 0.06 | 0.17 | 0.15 | 0.36 | 0.04 | Bal. |
| Ti64  | 5.80 | 4.67 | 0.16 | - | 0.09 | 0.07 | 0.02 | - | 0.14 | Bal. |

The electron beam surface modification (EBSM) was carried out by electron beam installation Leybold Heraeus (EWS 300/15–60). The following technological parameters were applied: electron beam current – I = 30 mA, accelerated voltage – U = 52 kV, speed of the samples motion – v = 1 cm/s, electron beam frequency – f = 1 kHz, electron beam diameter - d = 0.5 mm and linear manner of scanning.

The samples were evaluated quantitatively with respect to R_s (average roughness) and R_max (maximum roughness height) after ten times scanning with a cut-off value of 0.8 mm in a direction perpendicular to grooves caused by the local melting by using a contact profilometer (Mitutoyo SJ 201 P). The light optical microscopy was performed on the top surface and cross-section of the samples using a Nikon microscope. The 14-megapixel digital camera was adapted to the microscope and used for the image acquisition after Kroll’s reagent etching. Some of the micrographs were processed by Mountains Map premium v.7 software for grain size assessment.

The X-ray phase identification was performed with URD-6 diffractometer, applying Bragg-Brentano geometry and Cu-Kα radiation and working at 30 kV and 20 mA. The diffraction angle range scanned was 2θ = 30-100° with a step size of 0.05° and counting time of 2.5 s/step. The qualitative and quantitative phase analysis was held using Match3 software.

A Vickers Hardness tester 432 SVD by Wilson-Wilpert was used for the hardness measurements of the alloy according to the standard ISO 6507-1. In order to compare the hardness changes, the researchers were made on the top of each sample with a load of 10 kg and dwell time of 10 s. Ten sequential measurements by increments of 500 μm between the imprints were made.

3. Results
The micrographs of both alloy – Ti54 and Ti64 in as-received and heat treated (ST) condition are shown in Figure 1. Because of the sub-micron size of the phases separated after the precipitation, no changes in the optical micrographs of the ST+P were detected as opposed to the ST specimens. In contrast to the coarse lamellar structure of AR Ti54, the Ti64 alloy displayed smaller lamellar colonies within the α+β grains (Figure 1a). The micrographs of the ST alloys show that the heat treatment was conducted from the α-β-range of both alloys despite the difference of 30 °C in the process temperature (Figure 1b).
Although the higher solutionizing temperature, the microstructure of the Ti64 displayed finer martensite lathes among the primary α-grains because of the fine initial structure instead of gross acicular martensite laths that were found in the ST Ti54 alloy. In order to compare quantitatively the amount of the undissolved α-grains, both ST micrographs of the bimodal structures were software processed and shown in Figure 1c. It is clearly seen that the amount of the primary α-phase is higher for the 950° C ST Ti64 than that of the 920° C water quenched Ti54 alloy.

![Figure 1](image_url)

**Figure 1.** Optical micrographs of the AR (a), heat-treated (ST) (b) samples and software processed micrographs of the heated treated alloys (c). The numbers (1) and (2) indicates the Ti54 and Ti64 alloy respectively.

As shown in Figure 2a the higher Al content in the alloy increased not only the AS sample hardness but also straighten the material after the heat treatment process. Except for the ST+P Ti54 samples, after the EBSM treatment, the surface hardness values increased. The EBSM surface strengthening is the highest for the ST Ti64, followed by the AR Ti54 alloy. The lower temperature of α-phase precipitation hardening led to decreased surface hardness values of the ST+P Ti54 alloy. After the EBSM the depth of the structural changes was higher for the heat treated samples (Figure 2b) related to the AS materials for both alloys. The largest was the in-depth influence of the electron beam for the ST+P Ti64 allow and the smallest for the AS Ti64.
Figure 2. Comparison of: a) the hardness values of the heat treated and EBSM Ti54 and Ti64 samples and b) depth of the structural changes occurring after the EBSM.

Figure 3. Micrographs of the cross-sections of the EBSM Ti54 (a) and Ti64 (b) alloys: (1) AR; (2) ST; (3) ST+P.

The structural changes occurring after the EBSM in cross-section, seen in Figure 3, indicates that the lamellar microstructure of the alloys with distorted Widmanstatten α-plates concentrated the energy of the electron beam nearer to the surface thus changing substantially the surface hardness. After the heat treatment, a tendency of an increase in the depth of the structural changes was displayed from the bimodal structure especially by the ST+P samples. Despite that similarity, the Ti64 alloy showed the greater ability for surface strengthening in ST and ST+P condition.
Figure 4. Topographic micrographs of the EBSM samples: a) AR Ti54; b) AR Ti64; c) ST Ti54; d) ST Ti64; e) ST+P Ti54; f) ST+P Ti64. The numbers and (3) used indicates the micro-roughening of the surface at small magnification (1), the grains in the re-melted zone (2) and software processes images determining some grains’ parameters.
The topographic view of the surface response of the alloys (Figure 4) shows a morphology of wave-like patterning which is more pronounced for the Ti54 alloy and sensitive to the initial heat treatment of the material. The changes in the surface roughness values, as opposed to the polished samples with roughness values of \( R_a 0.11\pm0.02 \) and \( R_z 0.81\pm0.16 \), are presented in Table 2. The roughness values of the ST Ti54 alloy were the highest followed by AR material which tendency was also seen from the topographic micrographs (Figure 4-1). The form and size of the grains in the surface re-melted zone extensively differed for both alloys (Figure 4-2 and 4-3). Depending on the grains’ size, smaller or coarser martensite laths were found at the surface of all examined samples. Despite the close mean values of the area, diameter and perimeter, the Ti54 top grains of the AR EBSM samples showed a wide disparity among the diameters compared to the AR Ti64 alloy (Figure 5-1). A tendency of grains’ refinement was observed for both ST Ti54 and Ti64 alloys as opposed to the AS EBSM samples (Figure 4 c and d), but in contrast to Ti64 alloy, the variations in the mean diameter of the Ti54 grains were the highest (Figure 5-2). Similar to the ST Ti54, the microstructure of the ST+P EBSM alloy (Figure 4e) demonstrated a variety of grain sizes (Figure 5a-3) that followed an asymmetric normal distribution. The surface grains of the ST+P EBSM Ti64 alloy had slightly larger mean values of the area, perimeter and diameter (Figure 4f) than the ST sample from the same alloy (Figure 4d) and both of them showed nearly normal distributed mean diameters (Figure 5-2 and 3).

![Figure 5](image)

**Figure 5.** Histograms of the mean diameter of the grains from the motif analysis study of Ti54 (a) and Ti64 (b). The numbers indicate (1) AR; (2) ST; (3) ST+P conditions.

| Sample       | AR \( R_a [\mu m] \) | \( R_z [\mu m] \) | ST \( R_a [\mu m] \) | \( R_z [\mu m] \) | ST+P \( R_a [\mu m] \) | \( R_z [\mu m] \) |
|--------------|-----------------------|------------------|----------------------|------------------|------------------------|------------------|
| Ti54 EBSM    | 1.21±0.2              | 5.97±0.9         | 1.28±0.3             | 6.89±1.5         | 1.07±0.3               | 5.32±0.9         |
| Ti64 EBSM    | 0.23±0.2              | 1.5±0.14         | 0.22±0.2             | 1.3±0.13         | 0.24±0.3               | 1.4±0.19         |
Figure 6. XRD patterns of the Ti54 (a) and Ti64 (b) alloy in AR, ST, and ST+P condition before and after the EBSM.

The difference in the chemical composition of the alloy influence mainly the “c” cell parameter of the α-phase of the alloys (Tables 3 and 4). In contrast to Ti64, after the EBSM of the AR Ti54, the “c” parameter was increased for the account of “a” decrease due to the dissolution of β into α phase which explained the substantial hardness change of this sample. Similar to the treated AR Ti64 alloy, the EBSM rose up the (101) and (002) intensity of the Ti64 samples. The ST samples of both alloys showed increased inter-planar spacing due to phase pre-saturation and enhanced (101) intensity as opposed to the AR samples (Figure 6). The (101) and (002) peaks’ intensity was increased for the ST-EBSM Ti54.
alloy at the expense of a decrease of (110) intensity. After the EBSM, both “a” and “c” parameters of the ST Ti64 alloys were simultaneously raised. The ST+P samples showed decreased parameters of the α-cells compared to the ST (Table 3 and 4) because of the alloy elements’ partitioning effect. These changes tended to affect mainly the “c” cell parameter, which was afterward increased by the subsequent EBSM.

| parameter | AR | AR EBSM | ST | ST EBSM | ST+P | ST+P EBSM |
|-----------|----|---------|----|---------|------|---------|
| a, Å      | 2.907 | 2.904  | 2.914 | 2.902 | 2.893 | 2.900  |
| c, Å      | 4.659 | 4.668  | 4.689 | 4.667 | 4.629 | 4.690  |

| parameter | AR | AR EBSM | ST | ST EBSM | ST+P | ST+P EBSM |
|-----------|----|---------|----|---------|------|---------|
| a, Å      | 2.901 | 2.905  | 2.907 | 2.902 | 2.906 | 2.901  |
| c, Å      | 4.668 | 4.652  | 4.660 | 4.676 | 4.643 | 4.674  |

4. Conclusions
The heat treatment of the Ti64 alloy results in higher hardness values because of the obtained fine martensite laths and higher content of primary α-grains containing more Al that is a α-solution strengthening. After EBSM of both alloys, the heat treated bimodal structures are more susceptible to in-depth morphological changes than those of the AR materials, where larger surface grains are detected. The increased Al content in the α+β-alloy allows further surface hardness increase by EBSM not only in ST but in ST+P condition. The finer initial and heat treated structures of the Ti64 alloy form more homogenous in size surface grains after the EBSM while the coarse lamellar and bimodal structures of Ti54 alloy give rise to higher surface roughness values and grains that differ extensively in size. For both alloys, the heat treatment decreases the size of the re-melted grains at the surface after the modification. The EBSM have a similar effect on the crystallographic orientation of the grains predominantly increasing the (101) reflection despite the different initial grains’ morphology. The higher overall content of the β-stabilizing elements enhances significantly the hardness of AR Ti54 as opposed to the AR material while the higher Al content in Ti64 contributes to the thermal stability and therefore the straightening response of the alloy to heat treatment and concentrated energy flux modification. However, these differences will have different consequences for the elastic modulus values of both alloys that is very important for the implant materials.

5. References
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