

# Thermochemical Modification of Ti-6Al-4V alloy for Biomedical Applications

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## ABSTRACT

In an attempt to increase the bioactivity and corrosion resistance of a Ti-6Al-4V alloy, the thermochemical process for surface modification was utilized. Ti6Al4V substrates were pretreated with a sodium hydroxide (10 M of NaOH aqueous solution at 60°C for 24 h.). After NaOH pretreatment, a three-dimensional porous network of hydrogel layer made of sodium titanate was observed on the Ti6Al4V surface. The gel can then be converted to Ti-OH groups during hydrothermal treatment, which will contribute to the formation of hydroxyapatite when immersing them in a simulated body fluid (SBF) solution for 30 days. Characterization was performed by means of X-ray diffraction (XRD), attenuated total Reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), Scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX). The resultant apatite layer formed on titanium metal in SBF could enhance the bonding strength between living tissue and the implant.

**Keywords:** Ti6Al4V, Hydroxyapatite, Alkali Pretreatment, Thermochemical - Methods, Sodium Titanate, SBF.

## I. INTRODUCTION

Titanium and titanium alloys are widely used for dental and orthopedic implants, due to their high mechanical strength and good biocompatibility. In addition to these characteristics, it is also crucial to ensure good osteointegration [1]. Besides titanium itself, Ti-6Al-4V is one of the most commonly used materials for medical implants because of its suitable mechanical properties, its corrosion resistance and relative inertia toward living tissues. Despite that, there are some uncertainties concerning the release of Al and V ions under certain conditions [2].

Nevertheless, the essential requirements for any artificial implanted material, especially metallic ones, are demonstrated to possess not only biocompatibility, but also bioactivity with the host. Indeed, several months are required to get a sufficient osteointegration, and in numerous cases, the osteointegration is incomplete [3].

Thus, considerable work has been done to achieve suitable bone-bonding is to deposit a hydroxyapatite (HA) layer, with a composition like the mineral part of

the bone, at the implant surface. Different methodologies have been executed to modify the surface of titanium-based implants and enhance bone development and initial stability of bone-contacting implants.

One common way is immobilization of biologically active peptides on titanium surfaces. Coating hydroxyapatite on titanium is another surface modification method [4]. An electrochemical method, called as anodization or anodic oxidation is an advanced surface modification technique for titanium to produce protective films, which are useful to improve bone growth [5].

Now we present here another approach Thermochemical modification technique, to surface engineer titanium film. This method is based on the chemical activation of the titanium surface during immersion in an NaOH solution and subsequent heat-treatment [6], [7]. On the basis of scanning electron microscopy (SEM) observations and X-rays diffraction (XRD) analyses, these authors proposed the following sequence of transformations. First, the NaOH treatment generates an amorphous sodium titanate hydrogel layer, which

subsequently transforms into fully crystallized sodium titanate (indexed as  $\text{Na}_2\text{Ti}_5\text{O}_{11}$ ) and rutile through heat treatments. During in vitro bioactivity tests of the pretreated titanium in simulated body fluid (SBF),  $\text{Na}^+$  ions from the surface were observed to be released, followed by the growth of a hydroxyl carbonated apatite (HCA) layer.

The aim of this study was to fabricate and characterize surface modified titanium films with Thermochemical technique. We hope the biochemical surface modification of titanium surface can improve the cell biocompatibility of titanium. So, the influence of surface modification of titanium films on osteoblast growth behaviour was observed in vitro as well.

## II. METHODS AND MATERIAL

### A. Materials

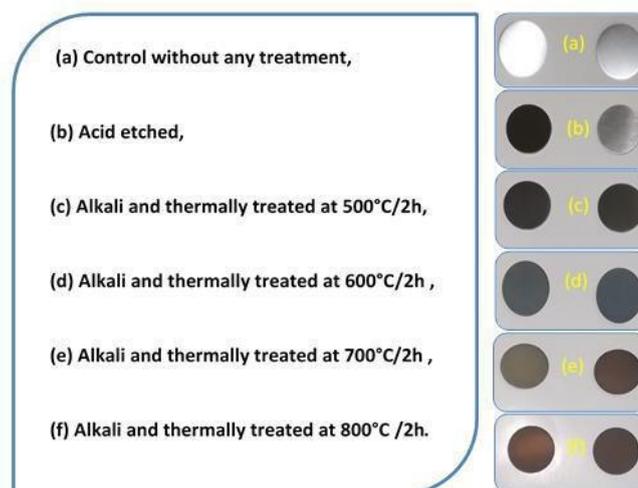
Ti6Al4V discs (2.5 cm diameter and 0.4 cm thickness) used in the present study were mechanically polished using silicon carbide grit paper starting from # 400 to # 2000 to remove macro-level surface defects. Then, they were ultrasonically cleaned in acetone (15 min), and rinsed three times with deionized water and dried by air drier.

### B. Surface pretreatment

The cleaned and polished Ti6Al4V discs were then etched by immersion in a mixture of  $\text{H}_2\text{SO}_4$ :  $\text{HCl}$ :  $\text{H}_2\text{O}$  (3:3:9) ml by volume, for 15 min, and washed in distilled water. Acid treatment is often used to remove oxide and contamination to obtain clean and uniform surface finishes. A combination of acids is frequently used to pre-treat titanium.

The samples were then soaked in 50 ml of a 10 M NaOH solution at  $60^\circ\text{C}$  for 24 h. Careful rinsing (after the soaking in the NaOH solution), washing them gently with distilled water, and dried at  $40^\circ\text{C}$  for 24h.

The samples were heated to several temperatures in the range  $500\text{--}800^\circ\text{C}$  at a rate of  $5^\circ\text{C}/\text{min}$  for 2 h, in a Ni–Cr electrical furnace in air and then allowed to cool at the natural rate of the furnace to room temperature. Fig. (1).



**Figure 1:** Digital camera of As-polished, Acid etched and thermo-chemically modified Ti-6Al-4V alloys.

### C. Examination of the apatite-forming ability in an SBF

The samples subjected to acid, alkali, and heat treatments were soaked in 50 ml of an acellular SBF with ion concentrations nearly equal to those of human blood plasma (Table 1) under static conditions at  $37^\circ\text{C}$  for 2 weeks, in order to obtain a homogeneous apatite layer. SBF solutions were prepared by adding concentrated solutions of KCl, NaCl,  $\text{NaHCO}_3$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{KH}_2\text{PO}_4$ , to double-distilled water buffered with tris(hydroxymethyl)aminomethane and HCl to pH 7.4 at  $37^\circ\text{C}$  [8].

**Table I:** Comparison of the Ionic Concentrations in Blood Plasma and the Theoretical One in SBF ( $\text{Mmol L}^{-1}$ )

	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{HCO}_3^-$	$\text{HPO}_4^{2-}$	$\text{SO}_4^{2-}$
Blood plasma	142.0	3.6–5.5	1.0	2.1–2.6	96.0–107.0	27.0	0.65–1.45	1.0
SBF	142.0	5.0	1.0	2.5	126.0	10.0	1.0	1.0

The samples were removed from the SBF after 30 days, gently washed with ultrapure water, and dried in an oven at  $40^\circ\text{C}$ . The formation of apatite on the surface of the samples was examined using scanning electron microscopy (SEM) and thin film X-ray diffraction (TF-XRD) using the methods described in the next section.

### D. Surface analysis of treated Ti metals

The surface of the Ti metals subjected to acid, alkali, and heat treatments, and those subsequently soaked in an SBF for several periods were analyzed using TF-XRD with a copper target ( $\text{Cu } \alpha = 1.54060 \text{ \AA}$ ) and Nickel filter with a conventional Bragg–Brentano  $\theta$ - $2\theta$  geometry was used. The current and the voltage of the X-ray tube were 25 mA and 40 kV, respectively. The

samples were measured in the continuous mode at a rate of 1.0°/min, with 2θ-angles ranging from 10° to 60°.

The surface morphology of the samples after various surface pretreatments was examined by scanning electron microscopy (SEM) model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage of 30 KV, magnification of 14x up to 1000000 and resolution for Gun.1n). SEM micrographs were obtained without coating the samples surface under vacuum.

### III. RESULTS AND DISCUSSION

#### A. Change in the surface structure of the Ti-6Al-4V metal after the acid, alkali and heat treatments:

Fig. (2) shows Thin Film X-ray diffraction (TF-XRD) patterns of the surface of Ti-6Al-4V substrate "without any treatment", acid etched, then alkali and thermally treated at various temperatures for 2 h before immersion in SBF. There are four phases were identified in the data of Fig. (2).

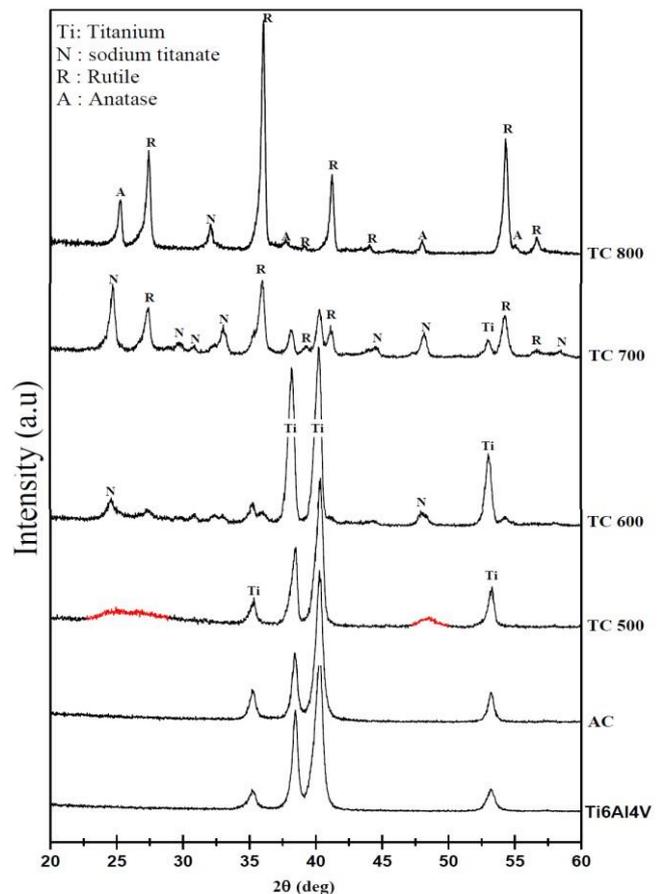
The first of these phases was titanium, Ti-6Al-4V is not included in the Joint Committee on Powder Diffraction Standards (JCPDS) database. Therefore, miller indices and phase determination were derived from the hexagonal α-Ti pattern (JCPDS file #44-1294) and the cubic β-Ti pattern (JCPDS file #44-1288). There are no clear differences between the control and acid treated sample, but after the alkaline-heat treatment, a layer of titanium oxide (rutile and anatase) and sodium titanate ( $\text{Na}_2\text{Ti}_n\text{O}_{2n+1}$ , n = 3, 5, 6) was created on the surface of the metal [2], [9].

From Fig. (2), it can be seen that after alkali and heated treatment at 500°C, broad peaks at 23-30° and 47-49° in 2θ were created, these can be due to an amorphous or a microcrystalline phase. Also, it has been reported that it is the sodium titanate hydrogel layer (JCPDS file #78-1590), formed by alkaline treatment which is responsible for apatite formation [10]. This phase had converted to anatase and rutile after subsequent heat treatments above 600°C.

- ✓ Anatase (JCPDS file #21-1272) peaks are found at 2θ values of 25.29°, 37.81° and 48.05°; these correspond to (101), (004) and (200) crystal planes.

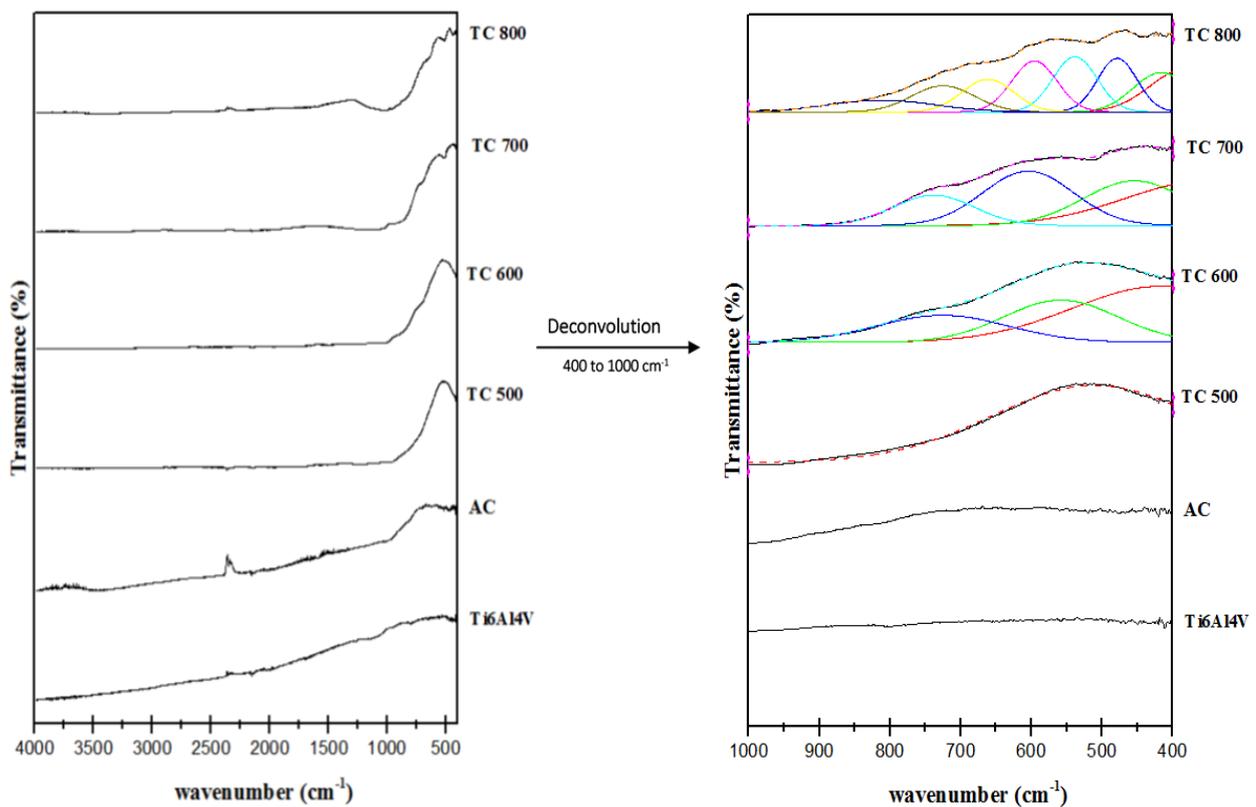
- ✓ Rutile (JCPDS file #21-1276) peaks are found at 2θ values of 27.43°, 36.07°, 39.11°, 41.23°, 44.05°, 54.33°, and 56.67°; these correspond to crystal planes of (110), (101), (200), (111), (210), (211) and (220) [11].

The ratio of rutile to anatase increased with increasing heat treatment [12]–[14]. Fig. (2) shows that 800°C is too high a heat treatment temperature for the sodium titanate layer, which was intentionally formed through alkali treatment to be stable without transformation to titanium oxide.



**Figure 2:** TF-XRD patterns of the surface of Ti6Al4V substrate "without any treatment", Acid treated, then Alkali treated with {10M NaOH}, and heated at various temperatures for 2 h before immersion in SBF. (Ti6Al4V): As Polished Ti control & (Ac): Acid treated & (TC 500, TC 600, TC 700, TC 800): Thermo-Chemically treated at 500,600,700,800°C respectively.

Fig. (3) shows (ATR-FTIR) patterns of the surface of Ti6Al4V substrates after heat treatment at various temperatures for 2 h following NaOH and acid treatments. Broad-absorptions around 500-800 $\text{cm}^{-1}$ , which are recognized due to short-range O-Ti-O network in amorphous  $\text{TiO}_x$  [15], were observed in the samples which treated with Alkali and thermal from 500 to 800C. This revealed the presence confirming the



**Figure 3:** (ATR-FTIR) patterns of the surface of Ti6Al4V substrates after heat treatment at various temperatures for 2 h following NaOH and acid treatments. before immersion in SBF.

formation of anatase and rutile layer after subsequent heat treatments in agreement with the result of the XRD analysis.

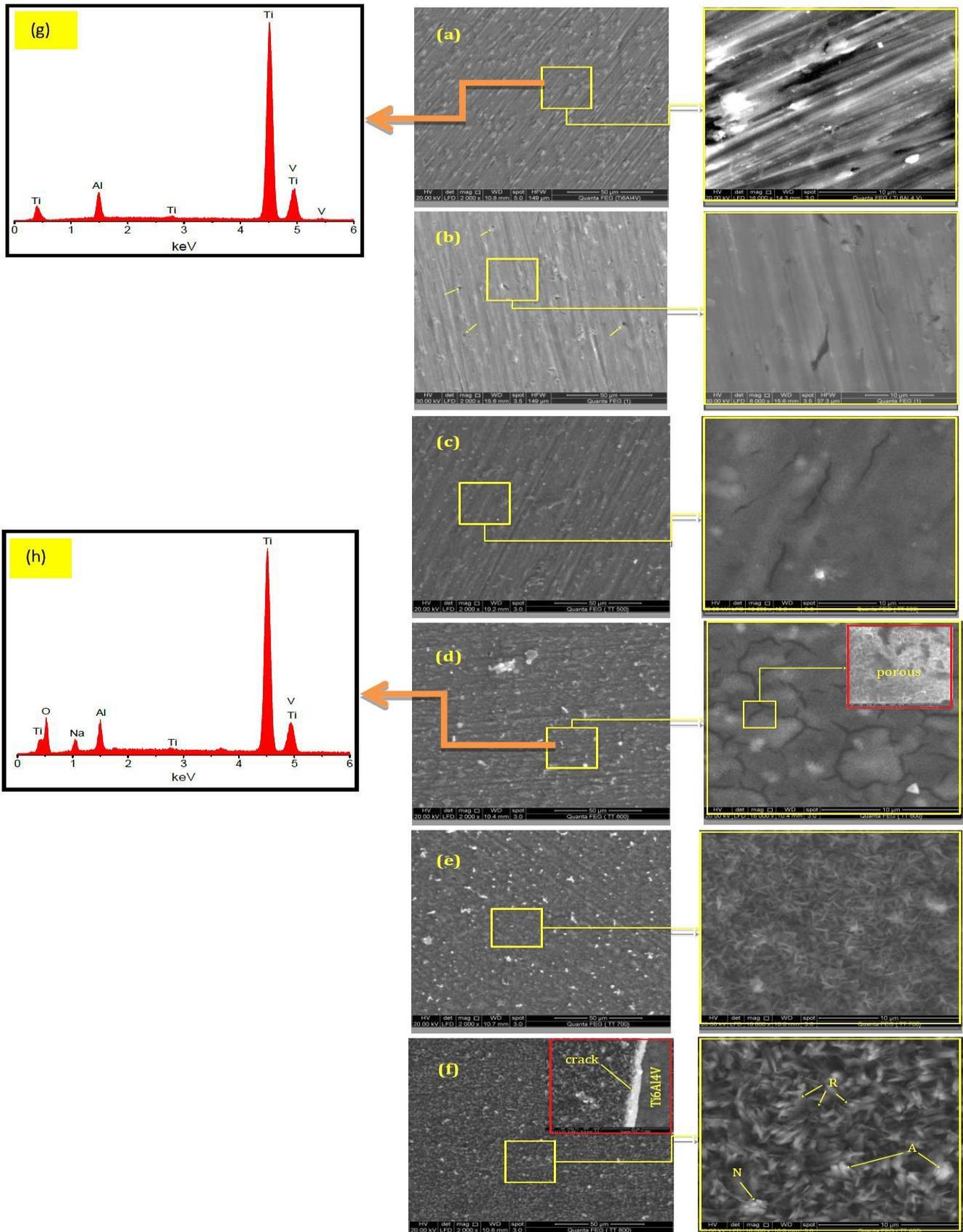
Fig. (4) shows (FE-SEM) photographs and EDS-X spectra of the surface of Ti-6Al-4V metal samples acid etched then subjected to alkali and heat treatments at different temperature before immersion in SBF for comparison with that of untreated Ti-6Al-4V metal. From Fig. 4(a) and 4(b) it can be seen that the acid etched and untreated Ti-6Al-4V control surfaces are dense, Surface morphology for as-polished Ti-6Al-4V typically became rough and irregular after sandblasting, but then after the acid etching treatment the surface is more uniform and small micro pits (1-2 $\mu$ m in diameter) are created, the acid etched sample had a smooth surface and this remained unchanged up to treatments by NaOH and heats at 500°C.

EDS-X analysis (Fig. 4.(g)) shows the background composed principally of Ti, Al and V atoms (88.7, 9.46 and 1.84 at%, respectively), no oxygen was detected on the control surfaces of the polished samples because the naturally formed oxide layer on Ti6Al4V is only several

nanometers thick [16]. After the alkali treatments, the shoulders of the O K $\alpha$  peak (0.523 keV) were seen in the EDX spectra.

From Fig. 4(c) and 4(d), it can be seen that a fine network structure on the nanometer scale had formed on the surface of the Ti-6Al-4V metal after the NaOH treatment, and this had essentially not changed with the subsequent heat treatment up to 700°C. A porous network was clearly observed in both figures but with a clear and larger porosity in Fig. 4(d) than Fig.4(c).

Lee et al. (2002) [17] reported that the formation of this porous structure on the surfaces of alkali-treated titanium alloys could be because of the local corrosion of Ti-6Al-4V surface by the OH<sup>-</sup> radical. It was also reported [Lee et al., 2002] that titanium alloy exhibits superior corrosion resistance in a strong corroding environment like acids and alkalies because of an excellent passivation film. However, corrosion resistance tends to deteriorate rapidly as the temperature and concentration of the corroding solution increases. So, titanium alloys showed poor corrosion resistance when maintained in a strong alkaline solution with high



**Figure 4:** (FE-SEM) photographs Ti6Al4V, (a) control, (b) Acid T. , (C) TC 500 ,(d) TC600 , (e) TC 700 and (f) TC 800, and EDX profiles of (g) Ti6Al4V "control", (h) TC 700. Before immersing in SBF.

concentration at 60°C and a lot of reacted hydrogen gases were observed on the surface of polished titanium alloy specimens when they were soaked in the alkaline solution.

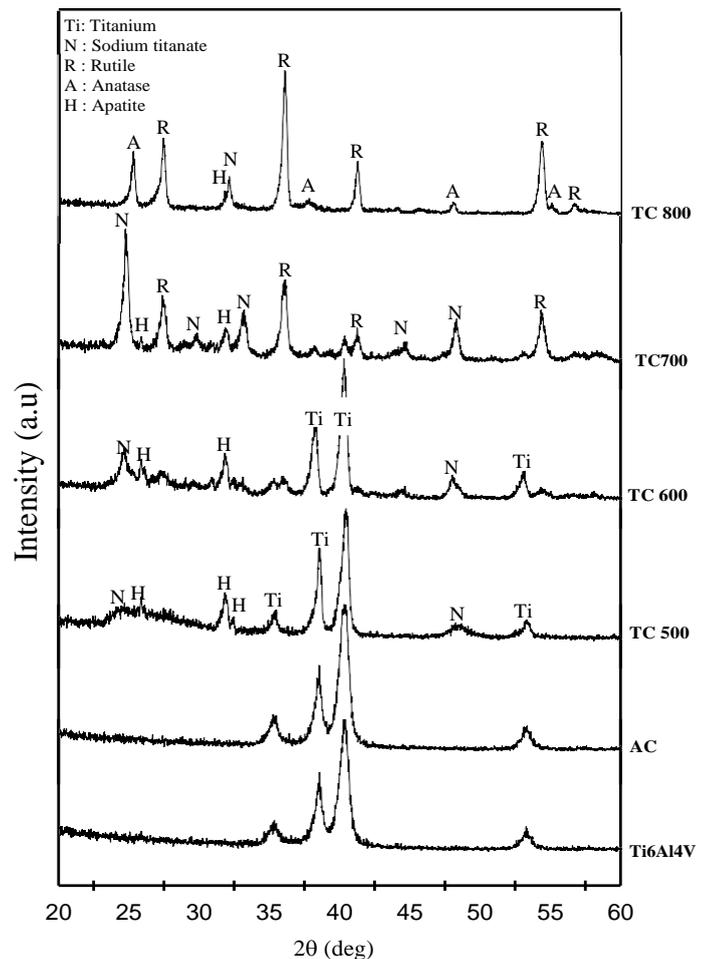
Such treatment produced a layer of approximately few  $\mu\text{m}$  thick containing  $\text{Na}^+$  and  $\text{Ti}^{4+}$  ions, made of  $\text{TiO}_2$  and sodium titanate with some structure growing out of the porous background. This formed layer was mainly composed of sodium titanate according to EDS-X analyses as shown in Fig. 4(h). This revealed the presence of Na, Ti, and O atoms (7.59, 63.29 and 19.47 at%, respectively) confirming the formation of sodium titanate gel layer in agreement with the result of the XRD analysis Fig. (2). From Fig. 4(e) and 4(f), it can be seen that the surface morphology of Ti-6Al-4V alloy after acid etched then NaOH and thermally treated at 700, 800°C respectively, Spallation, newly formed oxide and a crack were observed on the surface of the oxide sample. The magnified image shows that the oxides of the surface were composed of plate-like  $\text{TiO}_2$ . Fig. 4(f) shows that a big crack formed between the thick oxide layer and Ti alloy substrate. Since the rutile  $\text{TiO}_2$  scale is porous, brittle and poorly adherent to Ti alloy substrate, inward diffusion of oxygen and outward diffusion of Ti through oxide layer get very easy, then the oxide scales become thicker and cracks form as a result of thermal and growth stresses during the exposure to elevated temperatures [18].

### B. Change in the apatite-forming ability of the Ti-6Al-4V metal in an SBF after the acid, alkali and heat treatments:

For biocompatibility testing, each sample was soaked in SBF for 30 days for the biomimetic covering method as reported [Kokubo and Takadama, 2006] [19].

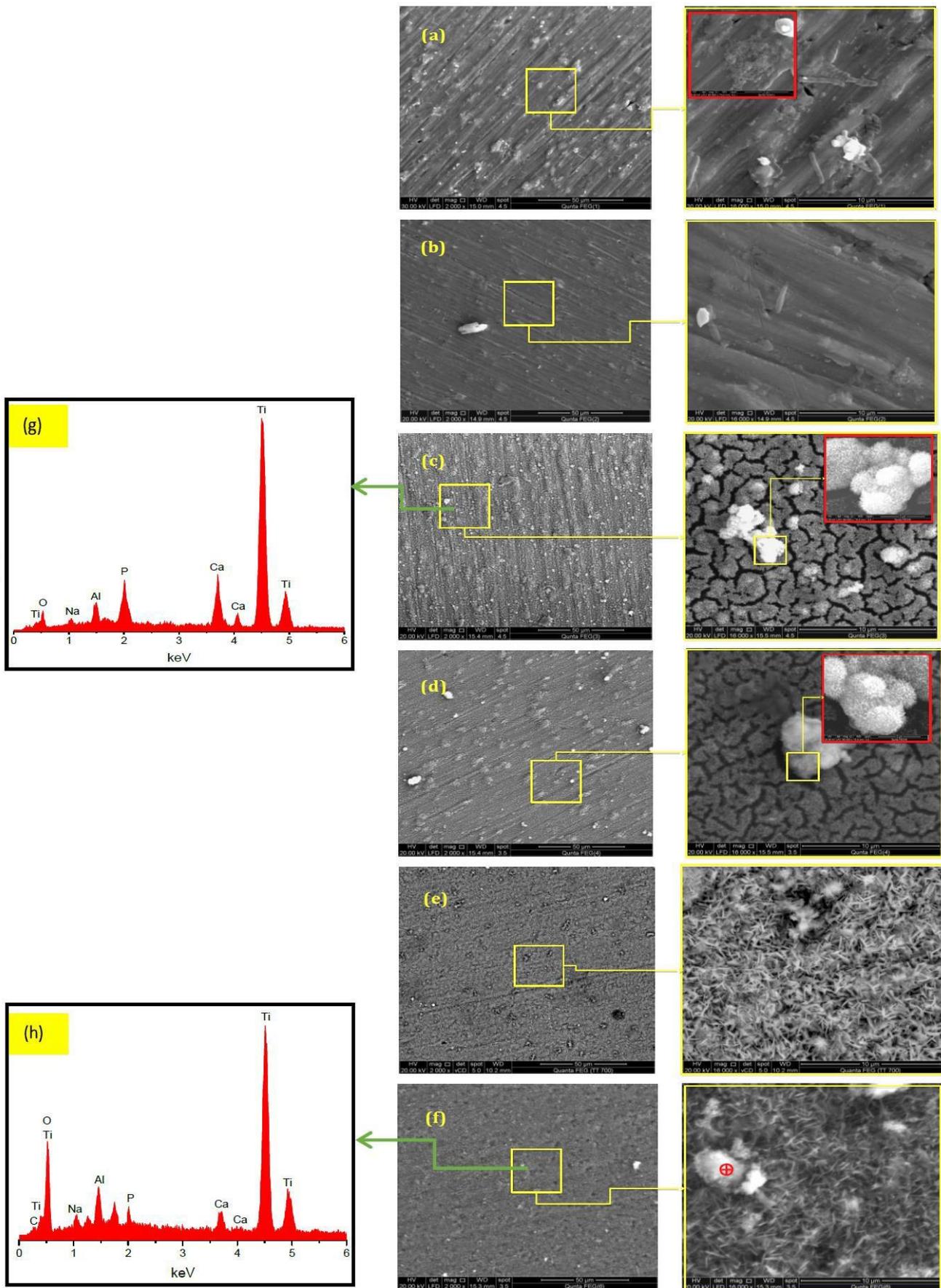
Fig. 5 shows the TF-XRD patterns of Ti-6Al-4V metal samples soaked in an SBF for 30 days after heat treatment at various temperatures following alkali and acid treatments. From Fig.5, it can be seen that apatite (JCPDS file #09-0432) peaks are found at  $2\theta$  values of  $25.88^\circ$ ,  $31.77^\circ$  and  $32.19^\circ$ ; these correspond to (002), (211) and (112) crystal planes, had precipitated on the Ti-6Al-4V metal was thermo-chemically-treated at temperatures in the range 500–700°C. A higher treatment temperature will increase the content of the rutile phase in the titania layer and thus decrease the bioactivity.

These results indicate that the spherical particles observed on the surface of the Ti-6Al-4V metal samples in Fig.6 were composed of apatite.



**Figure 5:** TF-XRD patterns of the surface of Ti-6Al-4V metal samples soaked in an SBF for 30 days after heat treatment at various temperatures for 2 h following NaOH and acid treatments.

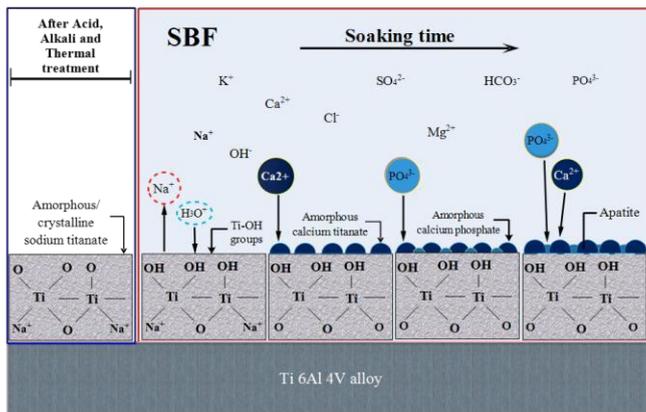
Fig. 6 shows FE-SEM photographs and EDS-X spectra of the surface of Ti-6Al-4V metal samples soaked in an SBF for 30 days after heat treatment at various temperatures following NaOH and acid treatments. From Fig. 6, it can be seen that a small number of spherical particles began to deposit on the surface of the samples treated with NaOH and acid solutions, and the number of these particles increased with increasing heat treatment temperature up to 700°C, and then decreased for a heat treatment temperature of 800°C. Each spherical particle consisted of many tiny particles, which were identified as being crystalline apatite by TF-XRD Fig. 5



**Figure 6:** (FE-SEM) photographs and EDS-X spectra of the surface of Ti-6Al-4V metal samples: (a) control, (b) Acid T, (c) TC 500, (d) TC 600, (e) TC 700 and (f) TC 800, and EDX profiles of (g) TC 500 "control", (h) TC 800. After immersing in SBF 30 days.

EDS-X analyses as shown in Fig. 6.(g),(h) revealed the presence of calcium, phosphorus, carbon in addition to sodium, sodium atoms confirming the formation of apatite layer in agreement with the result of the XRD analysis Fig. (5).

Based on the results described above the possible structural changes of titanium surface during chemical treatment and subsequent apatite formation in SBF are as follows Fig. 7. An oxide film that forms spontaneously passivates metal titanium. Its composition is reported to be of a TiO<sub>2</sub> outer layer and a TiOx intermediate layer [20].



**Figure 7:** Possible structural changes of the Ti6Al4V surface after acid etching, alkali treatment and during subsequent apatite formation in SBF.

During acid etching, the passive oxide film degrades. Acid treatment removes the entire passive oxide layer and induces micro roughness on the surface of the sample. It acts as an excellent decontamination agent to a titanium surface because it can readily dissolve titanium salts. Alkaline treatment followed by heat treatment lead to the formation of sodium titanate layer, as shown in Fig.2 & Fig. 4. This kind of morphology can help the integration of the implants due to its porous nanostructured surface, which imitates the natural structures of cortical bone. It, therefore, allows designing titanium implants having reduced risks of failure [21], [22].

During SBF soaking, the Na<sup>+</sup> ions released from the hydrogel layer via exchange with H<sub>3</sub>O<sup>+</sup> or H<sup>+</sup> ions produced in the surrounding fluid resulted in Ti–OH layer formation. This was due to induce apatite nucleation via incorporation of Ca<sup>2+</sup> or increasing the OH<sup>-</sup> concentration. The consumption of H<sub>3</sub>O<sup>+</sup> causes an increase in the pH concentration and an increase in apatite formation. The positively charged Ca<sup>2+</sup> may act

as nucleation sites for carbonate–hydroxyapatite formation by attaching themselves to the negatively charged (PO<sub>4</sub><sup>3-</sup>) and (CO<sub>3</sub><sup>2-</sup>) to form Ca–P enriched surface layer which crystallizes into bone-like apatite (carbonate hydroxyapatite).

The apatite formation on chemically treated titanium seems to be similar to that on bioactive glasses. The exchange of Na<sup>+</sup> from glass by H<sup>+</sup> or H<sub>3</sub>O<sup>+</sup> from the fluid leads to the formation of a Si–OH layer that was described to induce apatite nucleation via incorporation of Ca<sup>2+</sup>. The consumption of H<sub>3</sub>O<sup>+</sup> causes an increase of pH and apatite will be precipitated [23].

#### IV. CONCLUSION

Acid etching of titanium leads to the formation of a uniform micro-roughened surface that provides improved condition apatite formation. After alkali treatment in 10M NaOH the apatite nucleation was homogenous and the thickness of precipitated apatite layer increased. The treatment by a two-step acid and subsequent NaOH treatment seems to be a suitable method for providing the titanium surface with bone-bonding ability.

After alkali and heated treatment at 500°C, broad peaks were created, due to an amorphous sodium titanate hydrogel layer, which converted to crystalline sodium titanate, anatase and rutile after subsequent heat treatments above 600°C. However, 800°C is too high a heat treatment temperature for the sodium titanate layer, which was intentionally formed through alkali treatment to be stable without transformation to titanium oxide.

Among all the Thermo-chemically modified Ti6Al4V alloys, the Ti6Al4V alloys treated at 500-700 °C showed an excellent behaviour in terms of in-vitro bioactivity. The process of apatite formation on chemically treated titanium is supposed to be similar to that on bioactive glasses.

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