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EFFECT OF HEAT TREATMENT ON THE SURFACE MORPHOLOGY ON NaOH AND KOH TREATED Ti_6Al_4V

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ABSTRACT

Coating of apatite in biomimetic fluid is an alternative technique in metallic coating. An effective biomimetic apatite coating is depends on the surface material that can be enhancing through a chemical and thermally activated process. In this study, two kinds of alkali with same concentration of 5M NaOH and 5M KOH were used in the surface modification of Ti_6Al_4V at 60°C for 24h. In general, a passive oxide layer covered on Ti_6Al_4V surface changed to form alkali (Na/K) titanate layer which is mechanically unstable. Therefore, alkali-treated Ti_6Al_4V were heat treated at 500-800°C for 1h to consolidate a mechanically stable structure of amorphous alkali titanate layer. Surface morphologies and composition of Ti_6Al_4V before and after heat treatment were characterized using field emission scanning electron microscope (FESEM), equipped with energy dispersive X-Ray (EDX) probe. While, X-ray diffractometry (XRD) was used to examine surface chemical changes. Different alkali used at initial etching process showed a different morphologies structure which to be thought could enhanced bioactive characteristic. Thermal treatment on alkali treated Ti_6Al_4V alloy has limitation as heating above 700°C change porous structure to form a dense and solid non-porous networking structure.

Keywords: Ti_6Al_4V; heat treatment; alkali treatment; bioactive surface

INTRODUCTION

Titanium and its alloy have an excellent corrosion resistance, good biocompatibility and better strength to the weight ratio. The mechanical properties of titanium are an advantage to be widely used as a dental, orthopedic and maxillofacial implant material. However, micro-motion on the implantation site leads to the fibrous tissue encapsulation and drove to loosening effects which cause by indirectly bonding of host tissue to the implant materials[1].

Promotion to the bone healing and cell adherence between metallic implant is enhanced by bioactive coating such as calcium phosphate based material (i.e. hydroxyapatite)[2]. A conventional metallic surface modification has been developed including anodizing[3], electrochemical deposition[4], sol-gel precipitate[5] and plasma spray coating[6]. High processing temperature such as in plasma spray render to decomposition of hydroxyapatite[7]. Intense progress in surface implant modification recently was brought to the biomimetic methods as a promising technique for bioactive coating[8].

The mechanism is conducted at ambient temperature by immersion in simulated body fluid (SBF) and beneficial in promoting a uniform coatings on the porous-complex metal surface. Unfortunately, this process require a pre-treatment on the metallic implant are required to initiate an active surface which beneficial for apatite nucleation in SBF. Various pre-treatment method on titanium surface before immersion has been widely studied, including sandblasting[9], alkali or acid treatment[10], heat treatment[11] or in combination of these three approaches[10],[12]. Chemical surface treatment changed Ti implant surface to form hydrogel layer (alkali titanate layer) that was mechanically unstable while sandblasting cause disordered morphologies and possibility of silicon carbide contamination which might hindered the cell growth[9]. Meanwhile, combination of chemical and thermal become a promising approach in the formation of mechanically stable structure of alkali titanate layer[13]. Hence, bone-like apatite easily deposited on the treated surface due to modification on metallic surface topography. Surface topography such as interconnected porous structure, chemical composition and hydrophilicity was favourable for apatite formation as well as cell apposition.

Thus, the present study aimed to explore the effect of different temperature exposed on Ti metal surface after was treated with NaOH and KOH towards the formation of alkali titanate layer.

EXPERIMENTAL

Materials and methods

Purchased titanium alloy discs (Ø9.4 x 2) mm, Ti_6Al_4V ELI Grade 23 (STC Company, Taiwan) were cleaned in acetone, ethanol and distilled water for 10 minutes each, consecutively in ultrasonic bath (NEYTech, 208H, USA). Then, alkali and heat treatment were applied for surface activation purposes.

Alkali treatment was performed by soaking Ti_6Al_4V disc in 50ml of 200g/L NaOH (R&M Chemicals) and 50ml of 280.53g/L KOH (R&M Chemicals) aqueous solution for 24h at 60°C. Then, Ti_6Al_4V discs were rinsed thoroughly with distilled water and dried overnight at room temperature. After alkali-treatment, Ti_6Al_4V discs were heated at 500-800°C for 1h with heating rate of 3°C/min in a CARBOLITE furnace (CARBOLITE, ELF 11/14B, UK), and allowed to cool down in the furnace after the heating process.

Morphology and trace element for all samples of Ti_6Al_4V was observed by using Field Emission Scanning Electron Microscope-Energy Dispersive X-ray (FESEM-EDX, Carl Zeiss, SUPRA 40VP, Germany). The images were captured at magnification of 1k, 5k and 20k at accelerating voltage of 10kV. Surface structural changes on Ti_6Al_4V treated specimen were examined by using X-ray diffraction (XRD, PANanalytical, X'Pert Pro, Netherlands). All specimens were analysed at 2θ angles from 10° to 90° with scan speed of 10° per minute.

RESULTS AND DISCUSSION

The surface morphology and trace element of Ti_6Al_4V before and after alkali treatment with 5M NaOH followed by various heat treatments is shown in
Figure 1 and
Table 1 respectively.

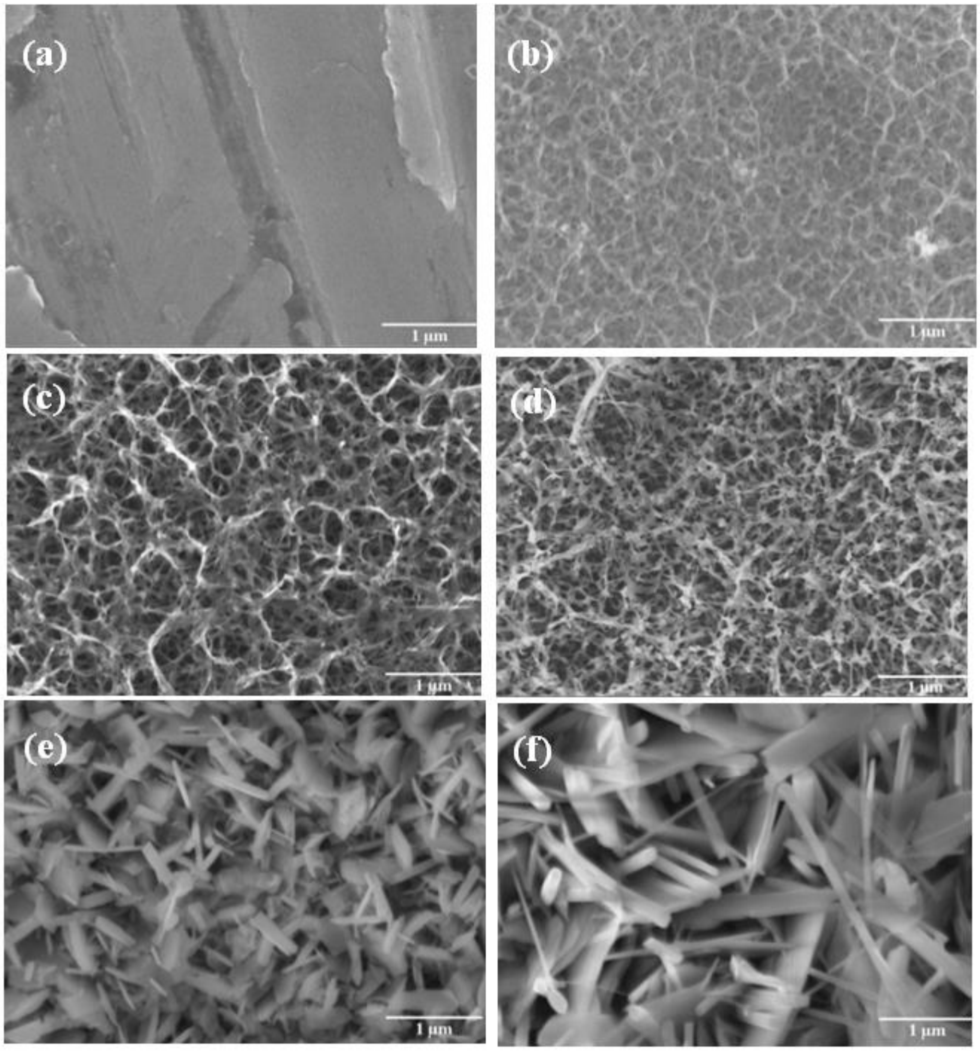

Figure 1 FESEM images at 20k magnification of received Ti_6Al_4V (a); after NaOH treatment (b); after NaOH-heat treated at (c) 500°C, (d) 600°C, (e) 700°C and (f) 800°C

Table 1: Weight percentage of elements detected by EDX analysis at point of FESEM images as in
Figure 1

Element / Sample Image	(a)	(b)	(c)	(d)	(e)	(f)
Ti	90.47	56.00	53.28	55.39	48.52	28.91
Al	5.70	2.39	1.79	1.64	3.37	20.52
V	2.47	1.50	1.56	1.78	2.67	4.10
O	-	34.79	37.09	35.53	39.99	43.73
C	1.35	1.33	1.13	1.19	0.93	0.87
Na	-	3.45	4.33	3.81	3.64	1.09

The result revealed that a smooth surface texture was observed for the untreated Ti_6Al_4V (
Figure **1**(a)). The major element presence at the smooth surface of untreated Ti_6Al_4V is Ti, Al and V. While, alkali treatment of Ti_6Al_4V in NaOH at 60°C for 24h resulted in the homogenous porous network structure covered on its surface as shown in
Figure **1**(b). A similar finding on porous network structure obtain when immersed in 5M NaOH for 24h at temperature between 37°C to 80°C was reported by Kim *et al.* [14], Fatehi [15] and Lee & Yoo[16]. This porous network structure was maintained during heat treatment at 500°C and 600°C as shown in
Figure **1**(c) and
Figure **1**(d) respectively. Similar finding also was reported by Lee and Yoo[16]. However, heating above 700°C, result in the formation of homogenous flake-like shape structure on the NaOH-heat treated surfaces as shown in
Figure **1**(e). Fatehi *et al.*[15] and Wei *et al.* [17] were observed the similar morphology on the SEM photograph of the specimen subjected to 5M NaOH and heat-treated at 700°C. The changes on the morphology structure on the treated surface caused the failure of apatite deposition after 3days immersed in SBF[15],[17]. The EDX result tabulated in
Table **1** detected the presence of Na after NaOH immersion with a great decrease and increase of Ti and O percentage, respectively. This indicates that Na^+ and H_3O^+ in NaOH aqueous solution incorporated into the microstructure of Ti6Al4V surface as supported by Kim *et* al.[14]. The percentage of Na element increased to 4.33% when subjected to 500°C after soaked in NaOH. However, the percentage was decreased after heating at temperature of 600°C. At 800°C, Al and O amount increase with the decrease of Ti and Na content. This might be due to the formation of complex oxide layer (Al_2TiO_5) with an addition of rutile (TiO_2) phase.

The phase structural change due to the heat treatment on NaOH-treated samples was conducted using XRD and the result is reveal in **Error! Reference source not found.**.

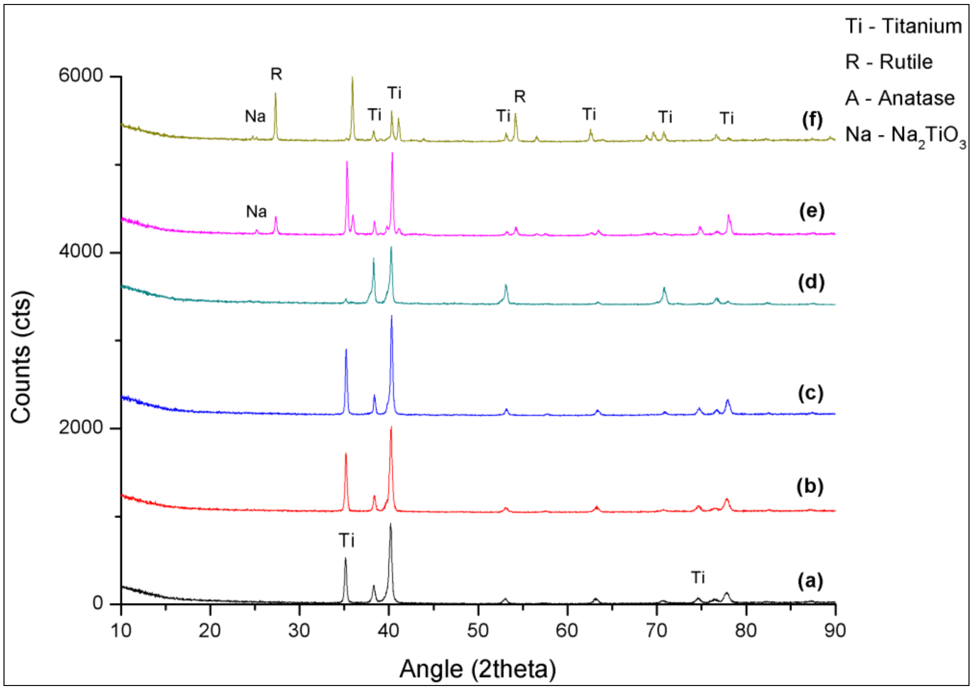

Figure 2: XRD pattern of untreated Ti_6Al_4V (a) and treated with NaOH (b) followed by heat treatment at temperature of 500°C (c), 600°C (d), 700°C (e) and 800°C (f)

The present sharp peak on diffraction pattern of untreated Ti alloy similar to database (ICDD 044-1294) of hexagonal closed-packed α-Ti. The diffraction peaks remain at 2θ angle which corresponding to α-Ti after treated with NaOH (**Error! Reference source not found.**(b)) and subsequent heat treatment at 500°C and 600°C (**Error! Reference source not found.** (c,d). Reported by Lin et al.[18], treatment in 10M NaOH and subsequent heat treated at 500°C show no changes in XRD pattern. However, heat treatment at 600°C results in formation of sodium titanate layer phase ($Na_2Ti_5O_{11}$). Once the temperature increased up to 700°C, a small bump of sodium titanium oxide (Na_2TiO_3) at 2θ = 25° was detected that match with database (ICDD 37-0345) as per **Error! Reference source not found.**e. This indicated that Na_2TiO_3 was formed on the surface due to heat treatment that changes the phase of amorphous layer to slightly crystalline. Along with Na_2TiO_3, newly peak phase was appeared at the pattern 2θ = 27° which indicates the presents of rutile phase. **Error! Reference source not found.**f shows the layer of rutile become thicker as the intensity gets higher and α-Ti peaks gets lower after was heated at 800°C.

The surface morphology and trace element of Ti_6Al_4V before and after alkali treatment with 5M KOH followed by heat treatments at temperature 500-800°C is shown in Figure **3** and Table 2 respectively.

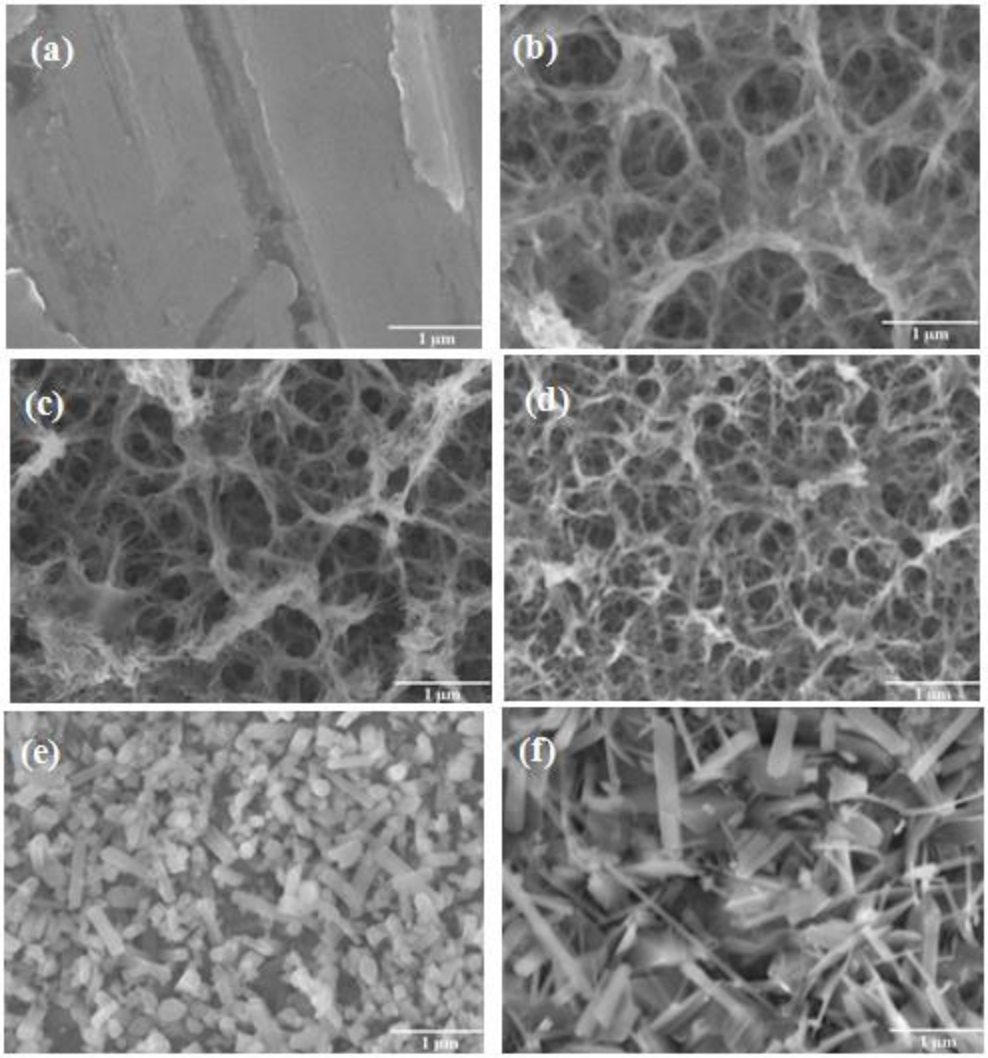

Figure 3: FESEM images at 20k magnification of received Ti_6Al_4V (a); after KOH treatment (b); after KOH-heat treated at (c) 500°C, (d) 600°C, (e) 700°C and (f) 800°C

Table 2 Weight percentage of elements for heat treatment at 500 - 800°C

Element / Sample Image	(a)	(b)	(c)	(d)	(e)	(f)
Ti	90.47	46.89	53.23	46.55	49.48	29.08
Al	5.70	0.30	0.56	0.25	2.84	20.91
V	2.47	1.33	1.04	1.80	2.28	5.70
O		40.67	35.08	38.74	36.70	38.63
C	1.35	0	0	0	0.51	0
K		7.28	9.42	9.23	7.64	3.36

The nested porous structure was observed on 5M KOH alkali treatment (

Figure **3**(b)) and followed by heat treatment at 500°C and 600°C samples. Similar image was reported by L. Lin *et* al. on SEM surface of Ti foil under hydrothermal treatment[19]. The nested structure becomes smaller as heating temperature increase to 600°C as show in Figure **3**(d). Meanwhile, heating at 700°C after soaking in KOH had changed the surface morphology of Ti_6Al_4V to form a homogenous rod-like shape (Figure **3**e). The porous structure of KOH-treated was fully densified after heat treatment at 700°C. Wang *et* al.[20] and Li *et* al.[21], were reported a similar rod-like structure of potassium hexatitanate ($K_2Ti_6O_{13}$) which produced from a mixing of potassium carbonate/nitrate and titanium dioxide powder as initial. Morphology structure captured by FESEM image of alkali heat treated at 800°C shows the structure had changed progressively to a glassy rod structure with sharp edges (Figure **3**f). Lee & Yoo has reported a similar image capture on NaOH treatment at 700°C of heat treatment[16].

The mass percentage of K detected by corresponding EDX analysis was 7.28% after immersed in 5M KOH. This might be due to the K^+ ion in KOH solution incorporated into surface microstructure. The subsequent heat treatment at 500°C had increased K element to 9.42% and decreased gradually after heating at temperature 600°C. Decreasing in the mass percentage of alkaline metal might be due to a high heating temperature that diminished the element presents on the treated surface by enhanced Al, V, and O. An oxygen mass percentage was increased due to a heat treatment which was oxidized the treated Ti surface to rutile phase, TiO_2. Phase changes on KOH treated Ti6Al4V surface and effects of temperature is shown in **Error! Reference source not found.**.

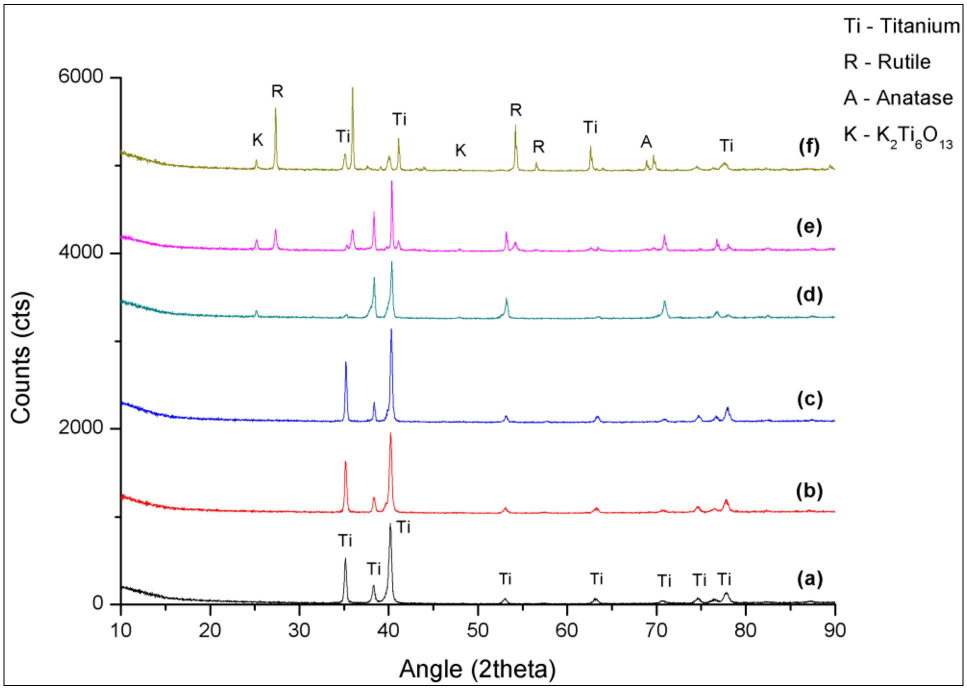

Figure 4: XRD pattern of untreated Ti6Al4V (a) and treated with KOH (b) follow heated at 500°C (c), 600°C (d), 700°C (e) and 800°C (f)

The result shows that the pattern remained unchanged on sample treated in KOH and subsequently heat-treated at 500°C. While, heating at temperature of 600°C (**Error! Reference source not found.**d), a small newly peaks of monoclinic potassium hexatitanate ($K_2Ti_6O_{13}$) was detected. The reflection peaks observed around 2θ =25° that similar to ICDD 01-074-0275. A minor increase of $K_2Ti_6O_{13}$ intensity along with the presence of rutile peak might be relative to high heating temperature of 700°C and 800°C (**Error! Reference source not found.**e and **Error! Reference source not found.**f). The weak signals of $K_2Ti_6O_{13}$ detected in **Error! Reference source not found.** can be interpreted as a thin layer of titanate formed on the surface when etching in KOH. Subsequently heated up to 700°C, small amount of rutile (TiO_2) peak around 2θ = 27° were detected for all specimens. These additional peaks indicate that titanium was further oxidized and formed oxide layers with a crystalline rutile structure.

In this study, soaking of Ti6Al4V in KOH at 60°C for 24h results in a grander nested porous network structure compared with soaking in 5M NaOH which formed a cellular-looking morphology at the initial temperature of 60°C. Similar pattern was reported by Kim *et* al. [14]. Porous network structure increases the surface area of treated Ti_6Al_4V which could enhance for a better cell anchoring to adhere on the Ti [22]. Heating above 700°C was changed drastically the porous structure of Ti_6Al_4V to a solid shape of flake-like and rod-like for NaOH and KOH treated surface respectively. This structure was not recommended for further apatite coating in SBF due to the limitation on the porous structure that required for cell ingrowth and good apatite anchoring.

Coating in biomimetic fluid (SBF) is a chemical reaction of ion interchange between Na^+/K^+ with hydronium ion, H_3O^+ in SBF solution. Increase of Na^+/K^+ ion dissociated from titanate at the Ti surface will fasten an attraction of Ca^+ ion due to the negative charge of Ti-OH layer[23]. Hence, the mass percentage of Na/K in the Ti metal surface is important to initiate heterogeneous nucleation towards apatite formation in SBF [24]. In addition, Wei *et* al.[17] claimed that more sodium/potassium ions can be released from thicker sodium titanate layer. This key parameter leads to the apatite formation in SBF as the amount of OH^- release from titanate layer is increased. On the other hand, cell viability study using mesenchymal stem cells, MSCs (MTT assay) on the alkali-heat treated commercial pure Ti (AH-Ti) displayed a significantly higher than untreated commercial pure- Ti (cp-Ti) after cultured for 7days as reported by Cai *et* al.[22]. Follow up from MTT assay, a differentiation of MSCs adhesion (ALP evaluation) on the treated surface observed no significant different on both AH-Ti and cp-Ti. Cai et al.[22] was demonstrated that both Ap-Ti and AH-Ti gave a great potential in promoting MSCs to differentiate.

CONCLUSIONS

In this study, Ti_6Al_4V alkali treated at ambient and heating at 500°C to 800°C has shown a different morphology structure with presents of Na and K titanate layer on the treated surface. Alkali treatment either with NaOH or KOH, subsequently heat-treated at 600°C revealed that a porous network structure successfully formed on the surface of Ti alloy. Heat treatment produced a mechanically stable surface structure for formation of amorphous Na_2TiO_3 and $K_2Ti_6O_{13}$ layer after etched in NaOH and KOH respectively. This present study proved that initial alkali treatment with KOH gave a macroporous network structure. Thus, treated Ti_6Al_4V has a potential to be used as a bone substitute for load bearing application with further in vitro testing in a biomimetic technique using SBF solution.

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