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Surface characteristics of Ti6Al4V alloy: effect of materials, passivation and autoclaving

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The properties of passivated films for Ti6Al4V alloy prepared by various methods (as-polished, brazed at 970 °C for 2 h and brazed at 970 °C for 8 h) were investigated. Four passivations (non-treated, nitric acid passivation, 400 °C-treated in air, and aged in boiling water), with or without autoclaving treatments, were adopted for evaluating the changes of surface properties, including chemical composition, chemical structure, and oxide thickness. From X-ray photoelectron spectroscopic (XPS) analyses, surface elements of copper and nickel in brazed samples were undetected for non-treated, acid-passivated and boiling water-aged specimens, while they were found in the 400 °C-treated specimen. The relative contents of $Ti^{2+}+Ti^{3+}$ to Ti^{4+} were determined by passivation treatments, but were not related to the experimental materials and autoclaving treatment. Passivation and autoclaving decreased the Ti to Ti^{4+} ratio by virtue of an increase in oxide thickness. Of the four types of passivation treatment, the 400 °C thermal treatment exhibited the lowest content of suboxides and metallic elements and the thickest oxide by XPS analysis; however, this treatment may cause a desorption of the basic OH group in the hydration layer on the surface of titanium alloy.

1. Introduction

The increasingly widespread use of biomedical devices manufactured from titanium or its alloys is due to their favourable corrosion resistance property and biocompatibility, compared to stainless steel and cobalt chromium alloys [1,2]. The reasons for the apparent success of titanium or its alloy implants have been attributed to the existence of a thin, stable passivating oxide layer of TiO_2. The oxide layer of TiO_2 is known to have at least two types of hydroxyl groups, basic and acidic OH, attached to the metal by chemisorption. The acidic hydroxyl groups tend to act as cation exchange sites, while the basic hydroxyl groups may act as anion exchange sites [3–10]. It has been suggested that calcium ions may bind with the acidic groups and phosphate molecules with the basic groups to begin the development of a suitable transition zone for bone growth [11–13]. Meanwhile, the oxide layer of TiO_2 is non-conducting, but electrons can tunnel through the layer, leading to conformational changes and the denaturing of proteins [14].

In order to anchor implants by bone ingrowth, porous coatings have been used for several years [15–18]. Because porous-coated devices have larger surface areas, the problems of ion release and corrosion products of metal become more serious in an aggressive body-fluid environment. In order to increase the corrosion resistance, the ASTM surface passivation protocol, developed for stainless steel and cobalt-based alloy surgical implants [19], was also adopted as one of several tentative passivation treatments for orthopaedic titanium alloy implants [20]. However, the nitric acid-passivated titanium alloy implant has been reported to increase the metal-ion release compared to unpassivated titanium alloy [21,22]. The reconsideration of surface treatment for reducing metal-ion release from the titanium alloy implant has been studied by several researchers [23,24].

In order to fabricate a porous-coated device suitable for bone ingrowth, Ti6Al4V alloy must be heat treated above the beta transus (992 °C) [25,26]. Such treatment at high temperature (around 1250 °C) results in a transformation from equiaxed grain, suggested for surgical implants, to lamellar alpha–beta microstructure, which could alter the biological response in clinical services. Meanwhile, the lamellar alpha–beta structure has been shown to exhibit the worst fatigue properties of the most common structure attainable in Ti6Al4V alloy [26–28]. For solving the

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mechanical properties of titanium-based alloy, Bugle [29] has suggested the diffusion bonding method to manufacture the titanium-porous coating, and Crivella and Stouse [30] adopted a joining agent including copper, which decreased the manufacturing temperature to below the beta transus. By a similar vaccum brazing method, the porous coating can also be manufactured below the beta transus, and the endurance limit of porous-coated Ti6Al4V alloy, under axial loading conditions, was 215 MPa in comparison with 105 MPa by the conventional sintering method (1300 °C) [31]. Meanwhile, the corrosion rates for sintered and brazed specimens were comparable [32].

This work aimed to investigate systematically the surface characteristics of passivation films obtained from variations of combined experimental materials, passivations and autoclaving treatments. It was thought that more data are desirable before a recommendation of surface passivation for titanium alloy can be proposed. In this study, three differently prepared materials (as-polished Ti6Al4V, 2 h brazed Ti6Al4V and 8 h brazed Ti6Al4V) were compared. Each group of materials was subjected to four different surface passivation treatments (as-polished, 34% nitric acid passivation, 400 °C heated in air, and aged in 100 °C de-ionized water) with or without further autoclaving treatment. All the specimens were evaluated for their surface chemistry by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), and by X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Materials

The alloy used in this study was a surgical grade Ti6Al4V alloy (ASTMF136-92). The 0.05 mm thick foil of Ti–15Cu–15Ni (wt %) (m.p. 934 °C) was selected as filler for the vacuum brazing treatment. The foils were placed on 12.7 mm diameter × 2.0 mm Ti6Al4V alloy for brazing treatments which were conducted in a high-temperature vacuum furnace (less than 10^{-5} torr). The brazed specimens were heated at 5 °C min^{-1} to 970 °C, soaked for 2 or 8 h, and followed by furnace cooling to room temperature. Three kinds of experimental materials used in this study were: (a) Ti6Al4V alloy, (b) Ti6Al4V brazed at 970 °C for 2 h, and (c) Ti6Al4V brazed at 970 °C for 8 h. The as-received Ti6Al4V and brazed materials were ground through successive silicon carbide papers to 1500 grit, then subjected to sonication in acetone and rinsed three times in doubly distilled water. The experimental materials after polishing were denoted H, B2 and B8 in accordance with the preparation of experimental materials, respectively, and are also referred to as the as-polished materials.

2.2. Passivation treatment

After polishing and cleaning, each group of specimens was passivated by the following procedure: (a) no passivation treatment, (b) immersed in 34% nitric acid for 1 h (P), (c) 400 °C in air for 45 min (T), and (d) aged in boiling de-ionized water for 24 h (A). After passivation, the passivated samples were denoted by P, T or A in addition to the notations for the experimental materials. After passivation treatment, all the specimens were subjected to sonication five times in de-ionized water. Half of the variously passivated specimens were further examined for the effect of autoclaving on the thickness and composition of titanium oxide, for which the specimens were packed in double-sealed autoclaving bags and steam sterilized at 121 °C for 30 min and dried at 121 °C for 15 min.

2.3. Surface analysis methods

Surface chemical analyses by EDS were carried out for Ti6Al4V and brazed samples prior to passivation and autoclaving treatments. The samples were examined at 20 kV in a Jeol scanning electron microscope (model JSMR 840) equipped with energy dispersive spectrometer (EDS, Link AN 1000/85S).

Shallower surface chemical analyses by XPS were carried out for various specimens subjected to passivation and autoclaving treatments. All analyses were carried out using VG Scientific ESCALAB 210 (analysed area: 0.5 mm diameter), operated at 12 kV and 20 mA in a pressure less than 10^{-8} mbar, using $\mathrm{Mg}K_{\alpha}$ radiation. Measurements of binding energy in the range 0–1000 eV were made at a "take-off" angle 45° with respect to the sample surface. High-resolution scans of titanium, aluminium, vanadium, copper, nickel and oxygen peaks were performed on selected specimens.

XPS data and measurement of peak area ratios were carried out on a personal computer using VGS software. In order to determine the surface composition from XPS data, accurate sensitivity factors (sfs) are required to convert peak area ratios into atomic percentage ratios by VGS software. The binding energy scale was calibrated by the C 1s peak at 284.6 eV.

3. Results

3.1. EDS analyses of surface composition prior to passivation

EDS analyses of chemical composition for as-polished Ti6Al4V and brazed materials are presented in Table I. Compared with Ti6Al4V, the 2 h brazed specimen shows a lower chemical composition (wt %) of aluminium and vanadium, with some additional copper and nickel elements. The longer time of brazing treatment for 8 h results in a reduction of copper and nickel contents compared to the 2 h brazing treatment.

TABLE I Surface chemical composition (wt %) by EDS analyses for as-polished Ti6Al4V and brazed materials prior to passivations

Materials	Ti	Al	V	Cu	Ni
H[a]	90	6	4	–	–
B2	85.28	2.81	2.01	4.45	5.45
B8	86.72	3.33	2.65	3.58	3.72

[a] Nominal.

3.2. XPS analysis of passivated samples

3.2.1. Samples without autoclaving

Broad-range XPS spectra of four passivation treatments for the as-polished Ti6Al4V are shown in Fig. 1.

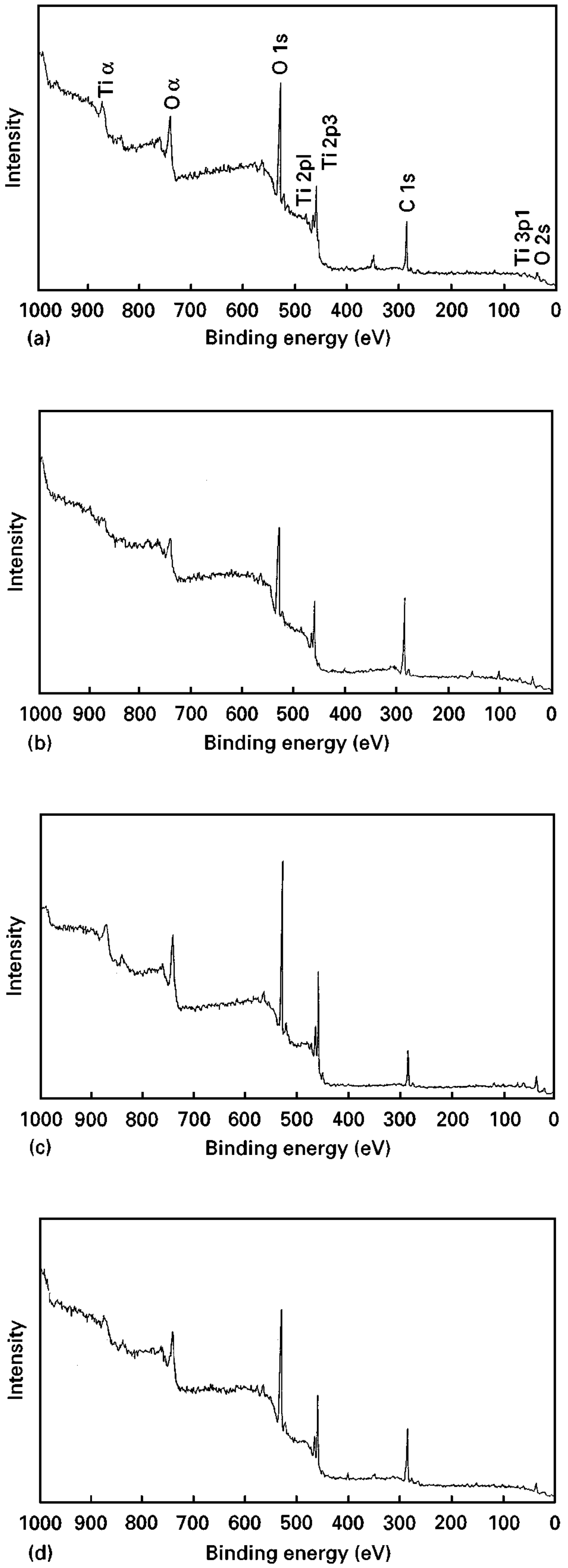

Figure 1 Broad-range XPS spectra of Ti6Al4V without autoclaving: (a) as-polished, (b) 34% HNO_3 passivation treatment, (c) 400 °C thermal treatment for 45 min, and (d) aged in boiling de-ionized water for 24 h.

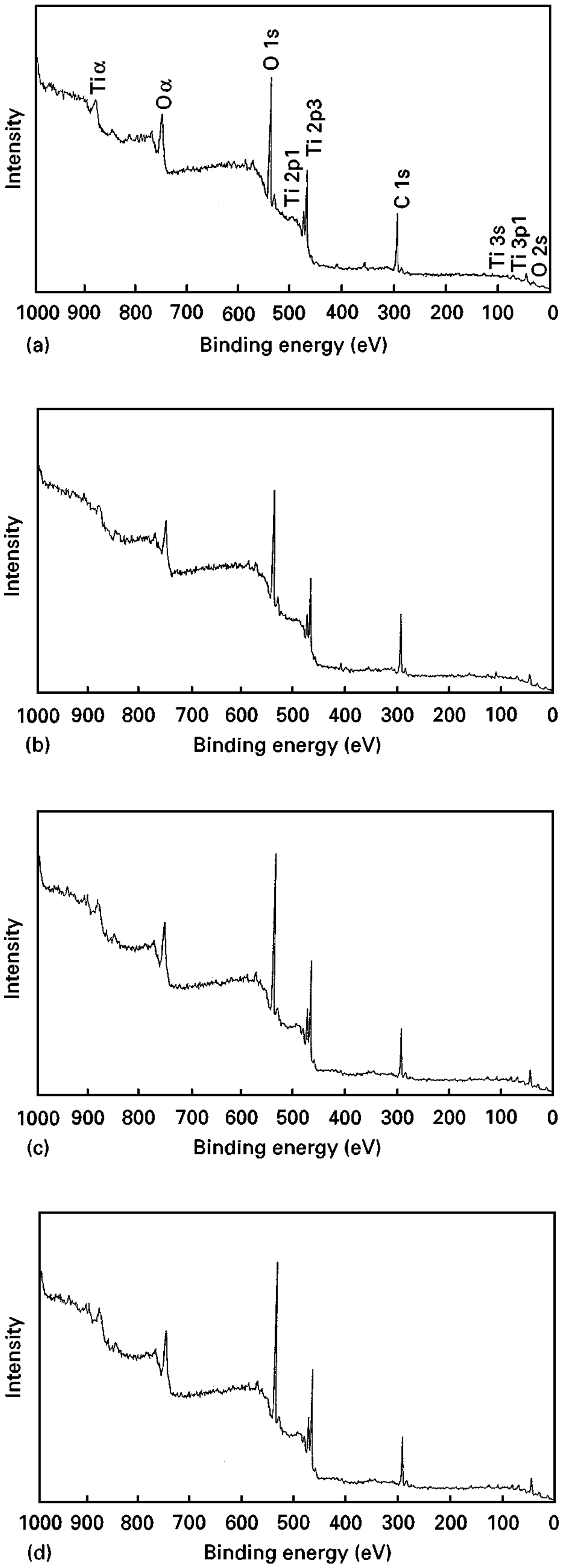

Figure 2 Broad-range XPS spectra of 2 h vacuum brazed Ti6Al4V without autoclaving: (a) as-polished, (b) 34% HNO_3 passivation treatment, (c) 400 °C thermal treatment for 45 min, and (d) aged in boiling de-ionized water for 24 h.

The scans for the four passivation treatments are very similar, with no indication of the presence of vanadium, while the presence of vanadium on the alloy sample can be detected by the V 2p3 peak at 515 eV on a more sensitive scale. As shown in Fig. 2,

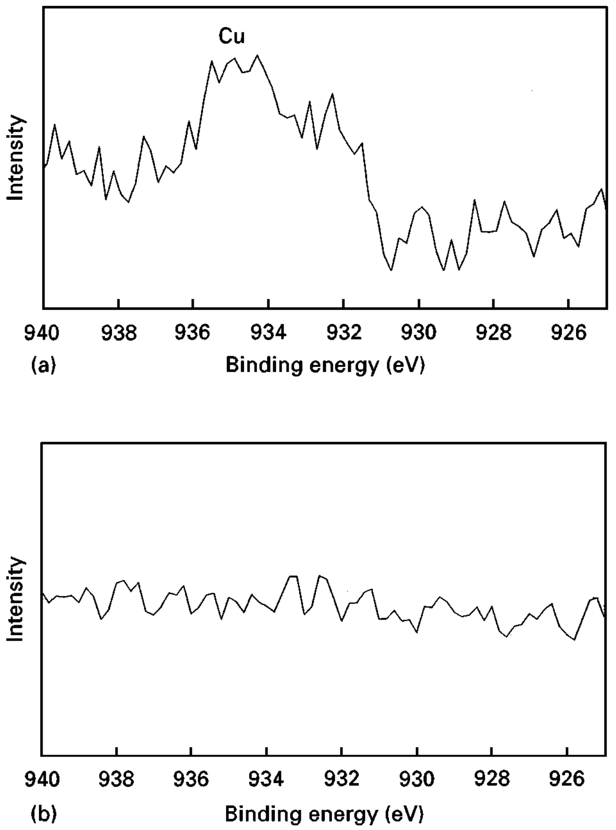

Figure 3 High-resolution XPS spectra of 2 h vacuum-brazed Ti6Al4V without autoclaving: (a) 400 °C thermal treatment for 45 min in which copper is found in the spectrum, and (b) aged in boiling de-ionized water for 24 h in which no evidence of copper is found in the spectrum.

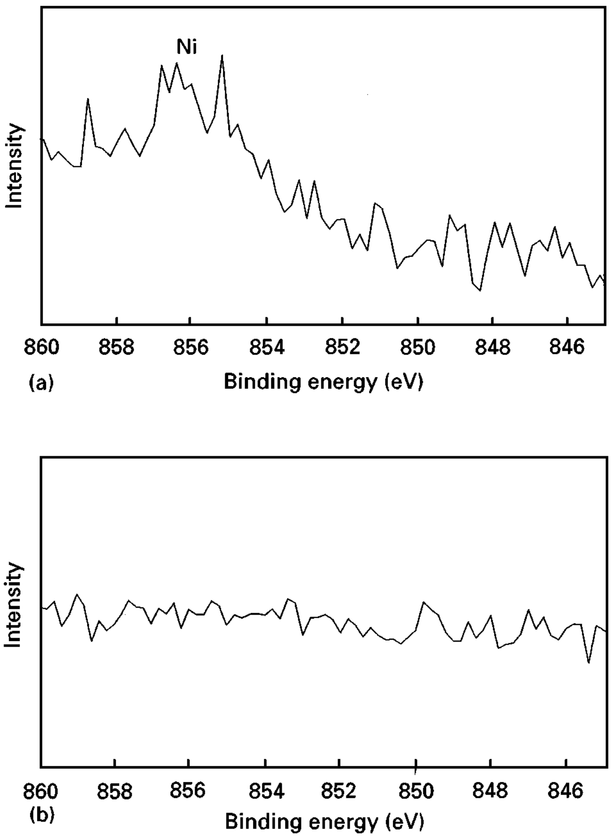

Figure 4 High-resolution XPS spectra of 2 h vacuum-brazed Ti6Al4V without autoclaving: (a) 400 °C thermal treatment for 45 min in which nickel is found in the spectrum, and (b) aged in boiling de-ionized water for 24 h in which no evidence of nickel is found in the spectrum.

the broad-range XPS spectra of the four passivation treatments for the 2 h brazed specimens are similar, and the peaks of copper and nickel can be detected on a more sensitive scale only in 400 °C passivated specimens (B2T) (Figs 3 and 4). The spectra of 8 h brazed treated samples are similar to the 2 h brazed ones, and the presence of copper and nickel is only found in the 400 °C passivated specimens (B8T) on a more sensitive scale. A summary of the surface chemical composition by XPS analyses is given in Table II. As shown in the table, the contents of surface composition from the sample experimental group of materials are similar, in general, irrespective of the passivation treatments. However, for 400 °C thermal treatment, the elements of copper and nickel can be measured in the 2 h brazed treatment samples with values of 6.74 and 4.70 wt %, respectively; the contents are reduced for longer 8 h brazed samples.

High-resolution Ti 2p spectra were examined to probe the changes in the nature of the oxide layers as a function of passivation. Examples of Ti 2p spectra for passivated Ti6Al4V material are shown in Fig. 5. The predominant oxide phase is TiO_2, and the various suboxide phases, Ti^{2+}, Ti^{3+}, and metallic titanium are also seen in the spectra. As shown in Fig. 5, there is a significant deviation in the suboxide and metallic contribution between the as-polished sample and the other three passivated samples. Passivation treatments exert a similar effect on the spectra of Ti 2p for the brazed samples. Table III summarizes the results of XPS Ti 2p3 spectra of the passivated specimens for different materials. The weight percentage contribution of the metallic and oxide states measured in the surface layer is obtained by calculating the fraction of the fitted areas for each constituent within the Ti 2p3 peak envelope. As shown in Table III, the contents of suboxide phases and metallic titanium are correlated to the passivation treatments, but little to the experimental materials. For as-polished H, B2 and B8 specimens, the weight percentage of suboxide phases and metallic titanium preparation are, on average, 18.3%

TABLE II Surface chemical composition (wt %) by XPS analyses for passivated specimens without autoclaving treatment

Materials	Passivation treatment	Ti	Al	V	Cu	Ni
H		81.85	14.73	3.42	–	–
H	P	80.96	15.29	3.75	–	–
H	T	81.18	14.78	4.03	–	–
H	A	84.94	11.26	3.80	–	–
B2		85.15	12.39	2.46	Nil	Nil
B2	P	85.51	11.74	2.75	Nil	Nil
B2	T	75.85	10.42	2.29	6.74	4.70
B2	A	85.63	11.41	2.96	Nil	Nil
B8		82.45	14.47	3.08	Nil	Nil
B8	P	82.90	13.76	3.34	Nil	Nil
B8	T	75.54	12.45	2.81	5.11	4.09
B8	A	84.32	12.89	2.79	Nil	Nil

and 8.5%, respectively. However, the three experimental materials with 34% nitric acid passivation (P passivation treatment) reduces the values of suboxide phases and metallic titanium to an average of 14.4% and 4.5%, respectively. The 400 °C treatment (T passivation treatment) for the three experimental materials significantly reduces the values of suboxide phases and metallic titanium to an average of 8.2%

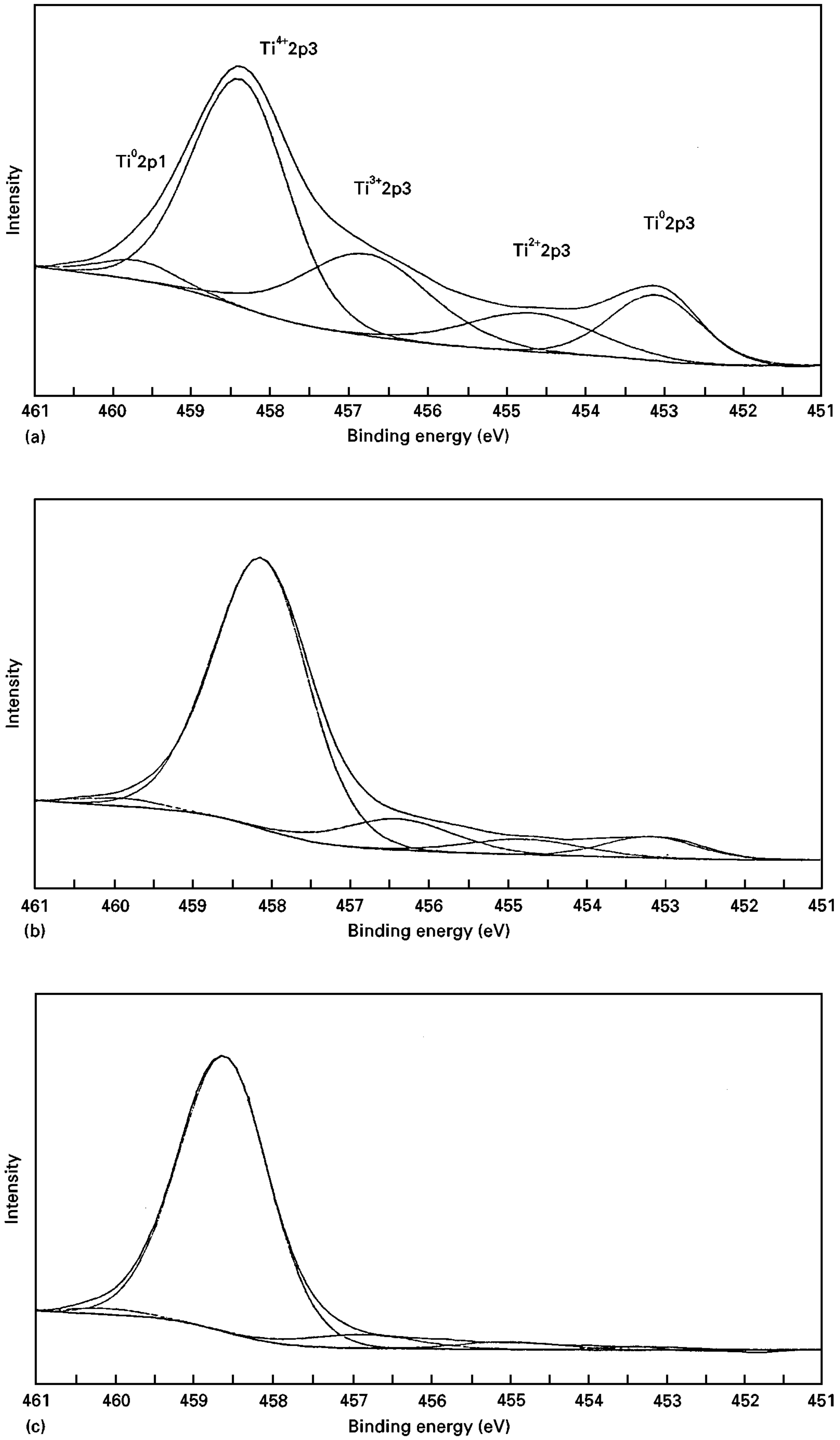

Figure 5 Curve fit of Ti 2p spectra of non-autoclaving treated Ti6Al4V: (a) as-polished, (b) 34% HNO_3 passivation treatment, (c) 400 °C thermal treatment for 45 min, and (d) aged in boiling de-ionized water for 24 h.

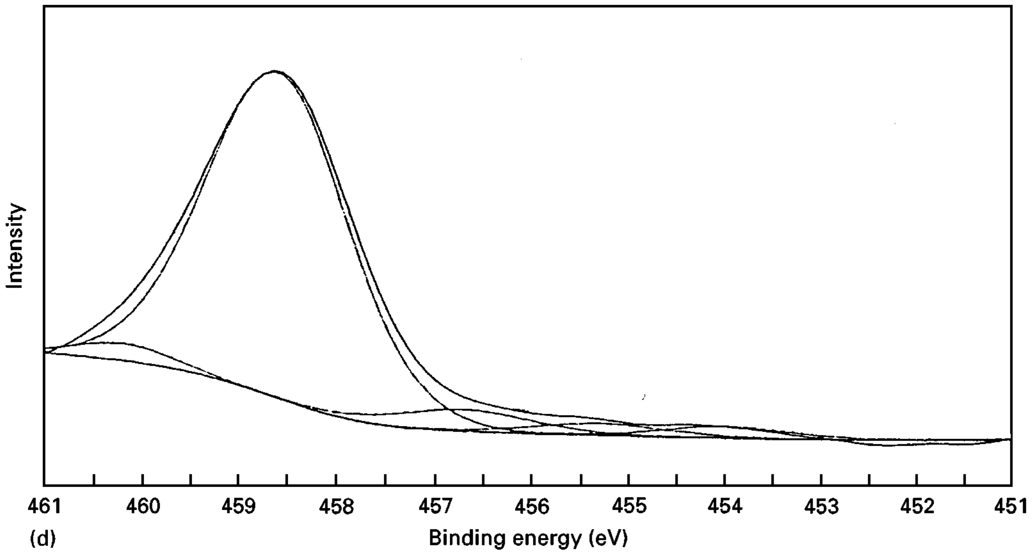

Figure 5 (continued)

TABLE III High-resolution XPS surface chemical analyses (wt %) of Ti 2p3 spectra for passivated specimens without autoclaving treatment

Materials	Passivation treatment	$Ti^{2+} + Ti^{3+}$	Ti	Ti^{4+}
H		19.51	9.11	71.38
B2		18.33	8.32	73.35
B8		17.03	8.13	74.85
H	P	14.79	4.73	80.48
B2	P	14.91	3.99	81.10
B8	P	13.61	4.66	81.73
H	T	8.35	1.18	90.4
B2	T	7.89	1.23	90.88
B8	T	8.26	1.41	90.33
H	A	12.11	3.12	84.77
B2	A	11.02	3.13	85.86
B8	A	11.59	3.20	85.21

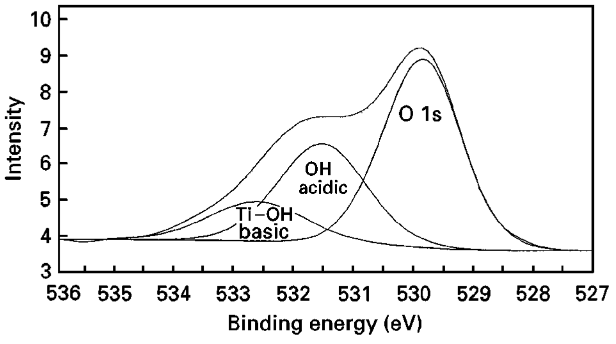

Figure 6 Curve fit of oxygen spectra of as-polished Ti6Al4V without autoclaving treatment.

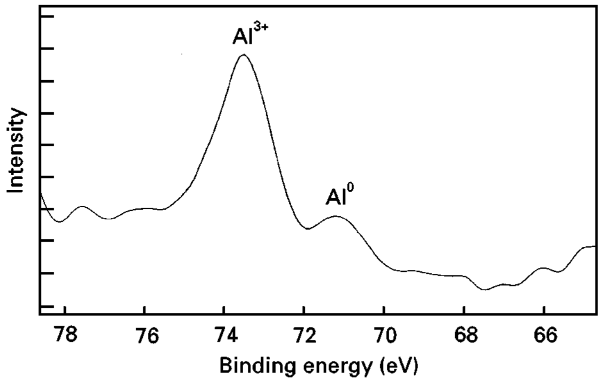

Figure 7 High-resolution XPS spectra of the Al 2p peak from as-polished Ti6Al4V without autoclaving treatment.

and 1.3%, respectively. The measured binding energies of Ti^{4+}, Ti^{3+}, Ti^{2+}, and titanium shows no significant differences between all kinds of samples, e.g. the binding energy of Ti^{4+} was measured between 458.2 and 458.6 eV, irrespective of the kinds of experimental materials and passivation.

As shown in Fig. 6, high-resolution scans of O 1s spectra for as-polished Ti6Al4V (H specimen) show a deviation from the Gaussian fit at higher binding energy edge of the peak. This observation suggests that different oxygen-containing species are present in the oxide. A curve fitting in Fig. 6 indicates that basic and acidic OH groups are formed in the oxide surface by assuming chemisorption, and their chemical nature arises from the way they bond, either to one or two titanium ions. The ratios of basic OH to O 1s and acidic OH to O 1s are 26.4% and 59.5%, respectively. The binding energies of O 1s, acidic OH, and basic OH lie at 529.9, 531.5 and 532.6 eV, respectively. The presence of basic and acidic OH can also be observed in all kinds of passivated specimens for all the materials. The high-resolution XPS spectrum of the Al 2p peak from as-polished Ti6Al4V shows that aluminium exists as the oxidized form of the Al^{3+} in the surface oxide (Fig. 7). The small peak at the lower binding energy is assigned to metallic aluminium, originating from the underlying bulk metal alloy.

3.2.2. Samples with autoclaving

The spectra of surface chemical composition analyses for autoclaved samples are similar to those samples without autoclaving treatment. The presence of

TABLE IV Surface chemical composition (wt %) by XPS analyses for passivated specimens with autoclaving treatment

Materials	Passivation treatment	Ti	Al	V	Cu	Ni
H		82.79	13.96	3.25	–	–
H	P	80.82	15.46	3.72	–	–
H	T	81.69	14.82	3.49	–	–
H	A	81.56	14.60	3.84	–	–
B2		85.00	12.47	2.53	Nil	Nil
B2	P	85.72	11.30	2.98	Nil	Nil
B2	T	76.28	11.31	2.21	5.84	4.36
B2	A	85.40	11.89	2.71	Nil	Nil
B8		82.06	15.06	2.88	Nil	Nil
B8	P	84.22	13.02	2.76	Nil	Nil
B8	T	73.05	14.82	3.19	5.00	3.94
B8	A	84.01	12.94	3.05	Nil	Nil

TABLE V High-resolution XPS surface chemical analyses (wt %) of Ti 2p3 spectra for passivated specimens with autoclaving treatment

Materials	Passivation treatment	$Ti^{2+} + Ti^{3+}$	Ti	Ti^{4+}
H		18.92	4.21	76.87
B2		18.65	4.33	77.02
B8		18.30	4.14	77.57
H	P	14.31	3.67	82.02
B2	P	14.50	3.41	82.09
B8	P	14.68	3.85	81.47
H	T	8.12	0.90	90.98
B2	T	7.49	0.86	91.65
B8	T	7.54	1.04	91.42
H	A	11.54	2.48	85.98
B2	A	11.59	1.96	86.54
B8	A	11.54	2.39	86.07

copper and nickel is still found in the 400 °C brazed and passivated samples (B2T and B8T) on a more sensitive scale, except that the contents of copper and nickel are decreased by autoclaving treatment. A summary of the weight compositions is given in Table IV. Table V summarizes the XPS results of the surface analysis of Ti 2p3 spectra of the passivated specimens for all the materials with autoclaving treatment. The weight percentage of metallic titanium decreases when compared to the non-autoclaved samples, while the contents of suboxide phases remain unchanged (compare Tables III and V). For example, the contents of suboxide phases and metallic titanium of the autoclaved H specimen are 18.92% and 4.21% compared to 19.51% and 9.11% of non-autoclaved samples, respectively. Similar observation of acidic and basic OH is still found in the spectra of autoclaved samples.

4. Discussion

Increasing the time of brazing treatment from 2 h to 8 h causes a reduction in the contents of copper and nickel by EDS analysis (Table I), and the reduction should be derived from the chemical interdiffusion of copper and nickel and Ti6Al4V substrate at 970 °C.

TABLE VI Oxide thickness of samples, as measured by the relative intensities of the TiO_2 and titanium metal peaks in Ti 2p3 spectra

Materials	Passivation treatment	Oxide thickness (nm)	
		No autoclaving	Autoclaving
H		1.45	2.25
B2		1.55	2.22
B8		1.59	2.27
H	P	2.17	2.45
B2	P	2.36	2.53
B8	P	2.20	2.4
H	T	3.81	4.14
B2	T	3.77	4.20
B8	T	3.61	3.98
H	A	2.66	2.92
B2	A	2.67	3.19
B8	A	2.64	2.97

Although copper and nickel are found upon 400 °C passivation treatment (Table II), they are not detected by XPS on the surface of samples subjected to nitric acid passivation and aged in de-ionized water. The reasons for the observation are rationalized as follows. The copper and nickel elements are electrochemically noble to titanium and aluminium elements in Ti6Al4V alloy in aqueous solution [33]. For nitric acid and de-ionized water passivated specimens at low temperature, it is assumed the titanium and aluminium elements will be preferentially oxidized. These preferentially grown titanium and alumina oxides might screen the shallow-penetrating X-ray from detecting the underlying copper and nickel elements in the substrate [34]. However, for the 400 °C passivated sample, it is likely that copper and nickel elements are simultaneously oxidized together with titanium and aluminium elements to exist as oxides on the surface of specimens in an oxidation environment of air, and hence these elements are detected by XPS analysis. Wood and Stott [35] have suggested that during transient oxidation, oxides of all metal constituents nucleate upon exposure to the atmosphere in proportion to their mole fraction in the alloy.

From XPS analysis, the oxide thickness, d_{oxide}, can be calculated using the formula [8]

$$d_{\text{oxide}} \approx \lambda_{\text{Ti}_{2\text{p}}}^{\text{oxide}} \sin\phi \ln\left(1 + \frac{I_{\text{oxide}}^{d} I_{\text{metal}}^{\infty}}{I_{\text{metal}}^{d} I_{\text{oxide}}^{\infty}}\right) \qquad (1)$$

where $\lambda_{\text{Ti}_{2\text{p}}}^{\text{oxide}}$ is the mean free path of Ti 2p3 electron in the oxide, ϕ is the angle between the sample normal and the take-off direction of the analysed photoelectrons, I_{oxide}^{d} is the Ti 2p3 intensity due to an oxide layer of thickness d_{oxide}, and I_{metal}^{d} is the intensity from the underlying metal. $I_{\text{oxide}}^{\infty}$ and $I_{\text{metal}}^{\infty}$ are the corresponding intensities obtained from a semi-infinitely thick oxide and metal, respectively. We have used a mean free path of 1.7 nm for the Ti 2p3 electrons in TiO_2 adopted by Lausmaa *et al.* [8].

The oxide thicknesses for a number of samples, calculated from the formula above, are given in Table VI. Comparison between specimens with and without autoclaving treatments clearly shows that the thickness of the surface oxides increases during autoclaving procedure. The results indicate a higher growth ratio of the oxide thickness for as-polished samples, and it is possible that the thinner oxide thickness of the as-polished samples provides a shorter distance for diffusion during autoclaving procedure. Among all the passivation treatments, the 400 °C thermal treatment and aged samples with or without autoclaving possess a thicker oxide thickness (Table VI) and lower contents of suboxide phases (Tables III and V), which could reduce ion release from the implant in clinical use. The factors affecting ion release from the oxidized surface of the metal are: (a) the nature and strength of the metal–oxide bond, (b) oxide thickness, (c) defect structure of the oxide (vacancies, interstitial elements, etc.), (d) degree of ordering within the oxide, and (e) anisotropic behaviour due to preferred dissolution sites on the specific crystallographic planes [36].

It has been shown that *in vitro* metal ion release from the nitric acid passivated titanium alloy implant is reduced considerably when the thermal treatments such as ageing in de-ionized water or heating in air are applied before immersion into both the EDTA/saline and bovine serum environment [24, 36]. This reduction in metal-ion release is attributed to a conversion of metastable surface oxide to the stable homogeneous rutile structure. However, the accompanying increased thickness of oxide and lower contents of suboxide phases by thermal surface treatment factors, that might reduce ion release from the sample, were not considered. The effects of various passivations and autoclaving on the oxide state and thickness of oxide were less systematically studied in the literature. The result from the present work suggests that oxide thickness is decided by the factors of passivation treatment and autoclaving procedure, but is little affected by the material preparation, such as brazing treatment (Table VI).

The presence of suboxide phases (Ti^{2+}, Ti^{3+}) and metallic titanium was observed by many researchers [22, 37, 38]. Sodhi *et al.* [37] have investigated the angle-resolved spectra of Ti 2p3 and found the existence of titanium in its lower oxidation state close to the substrate–oxide surface. Fig. 8 plots the relative content of $Ti^{2+} + Ti^{3+}$ to Ti^{4+} as a function of the thickness of oxide. It can be observed that, for specimens without autoclaving treatment (hollow symbols), the ratio of suboxides to oxide is mainly determined by the passivation procedure but not the difference in experimental materials, and the 400 °C treated samples produce the lowest content of suboxide phases as also suggested in Table III and Fig. 8.

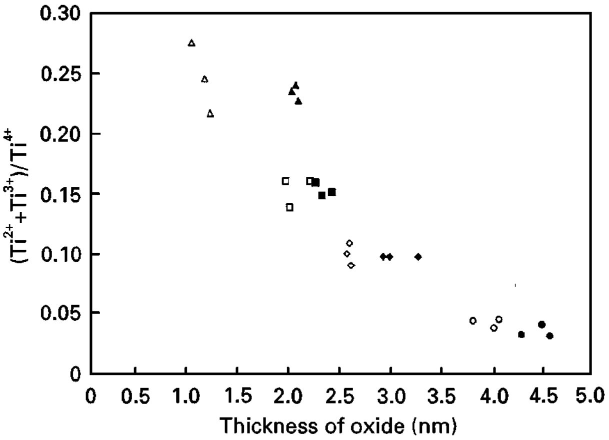

Figure 8 Relative content of $Ti^{2+} + Ti^{3+}$ to Ti^{4+} as a function of the oxide thickness: (△, □, ◇, ○) non-autoclaving, (▲, ■, ◆, ●) autoclaving. The three sets of data belonging to each symbol represent the three experimental materials. (△, ▲) As-polished, (□, ■) passivation, (◇, ◆) aged in water, (○, ●) thermal treatment.

The formation process of oxide thin film during autoclaving may occur by (a) dissociation of oxygen molecules into ions and adsorption on the surface, (b) the motion of cation or anion in the scale, and (c) formation of the oxide [39]. Kofstad *et al.* [40] have found that platinum markers have been found at the outer surface of the titanium oxide scales below 900 °C [40], and oxidation is reasoned by inward diffusion of oxygen from outer part of the scale. At the interface of oxide and suboxides, the following competitive reactions may occur: (a) the oxygen ions diffusion inwards through the oxide may react with the suboxide ions to form the new oxide, and (b) the suboxide ions may react with the oxide to grow the new suboxide [41]. After autoclaving treatment (solid symbols, Fig. 8), the relative content of $Ti^{2+} + Ti^{3+}$ to Ti^{4+} is unchanged, but the cause is not exactly understood. It is likely that at low temperature of autoclaving treatment, suboxides are slightly favourably grown relative to oxide. The photoelectrons from predominantly grown suboxides sufficiently compensate the adverse factor of lower emanation from suboxides underneath the oxide.

Similar to the ratio of suboxides to oxide, the relative content of metallic titanium to Ti^{4+} is significantly influenced by the passivation procedure but not the difference in experimental materials, as shown in Fig. 9. Autoclaving treatment, however, decreases the ratio of titanium to Ti^{4+} by XPS analysis, particularly for the case of the as-polished three experimental materials. In Figs 8 and 9, the symbols for the experimental materials such as H, B2 and B8 associated with a particular passivation are not differentiated, for the reason that the differences in measurements between them are relatively small. As the estimated maximum depth from which the photoelectrons emanate is much less than 4.97 nm at take-off angle of 45° [13], the decrease of titanium relative to Ti^{4+} as a function of passivations and autoclaving procedure may only reflect the lesser emanation from the bottom titanium substrate with an increase in oxide thickness by such procedures (Table VI, Fig. 9). Thus the ratio of Ti/Ti^{4+} decreases monotonically with the thickness of oxide.

High-resolution scans of oxygen spectra have shown the existence of basic and acidic OH groups. The presence of basic and acidic OH groups is derived from the hydrated titanium oxide exposed to ambient moisture. Hydration minimizes the surface potential by forming amphoteric OH sites. In the case of TiO_2, basic and acidic OH groups are formed by chemisorption. Meanwhile, the magnitude of these peaks

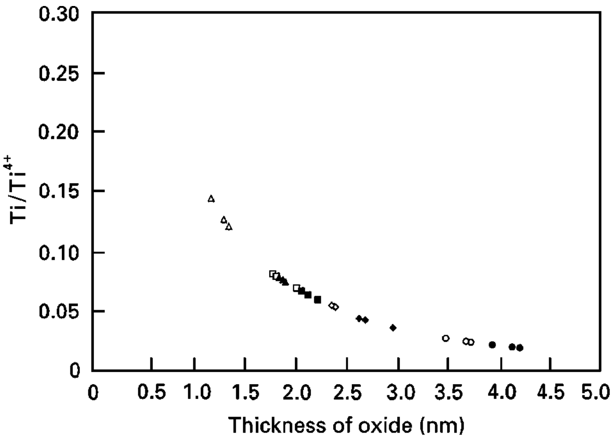

Figure 9 Relative content of titanium to Ti^{4+} as a function of the oxide thickness: (△, □, ◇, ○) non-autoclaving, (▲, ■, ◆, ●) autoclaving. (△, ▲) As-polished, (□, ■) passivation, (◇, ◆) aged in water, (○, ●) thermal treatment.

increases with the reflection from smaller angles of incidence, suggesting a high concentration of those groups at the outermost oxide surface [23]. These groups may play an important role in oxide/biomolecule integration. High-resolution XPS surface chemical analyses of oxygen spectra for passivated specimens without autoclaving treatment, shown in Table VII, indicates no apparent difference in amphoteric OH groups for brazed materials with respect to the Ti6Al4V alloy for each kind of passivation treatment, implying the surface of brazed materials might still react with calcium and phosphate binding biomolecules to begin the development of a suitable transition zone for bone growth. It has been found that the 400 °C passivated specimens might possess the characteristics of the lowest suboxides and metallic element in the surface and the highest oxide thickness. Nevertheless, these specimens, brazed or not, indicate a desorption of basic OH group in the hydration layer on the surface of titanium alloys due, presumably, to the debonding of the group at this temperature (Table VII). The loss of basic OH cannot be recovered by the autoclaving treatment in steam at 121 °C for 30 min as shown in Table VIII.

TABLE VII High-resolution XPS surface chemical analyses (at %) of oxygen spectra for passivated specimens without autoclaving treatment

Materials	Passivation treatment	Ti–OH basic	OH acidic	O 1s
H		14.21	32.01	53.78
B2		12.58	27.59	59.83
B8		16.52	24.79	58.68
H	P	11.34	26.05	62.61
B2	P	10.05	23.76	66.19
B8	P	12.76	32.32	54.92
H	T	9.57	26.09	64.34
B2	T	8.70	27.85	63.45
B8	T	6.86	24.69	68.46
H	A	14.34	21.46	64.20
B2	A	9.83	26.59	63.58
B8	A	8.50	26.20	65.30

TABLE VIII High-resolution XPS surface chemical analyses (at %) of oxygen spectra for passivated specimens with autoclaving treatment

Materials	Passivation treatment	Ti–OH basic	OH acidic	O 1s
H		10.76	21.66	67.58
B2		12.70	17.19	70.11
B8		16.96	27.74	55.30
H	P	12.22	27.93	59.86
B2	P	20.33	22.47	57.20
B8	P	14.45	30.50	55.05
H	T	9.37	23.31	67.32
B2	T	8.07	26.70	65.23
B8	T	6.73	23.46	69.81
H	A	15.59	20.04	64.37
B2	A	18.08	27.18	54.74
B8	A	17.81	24.30	57.89

5. Conclusions

Work was carried out to characterize the properties of passivation films of titanium alloys obtained from the variations of combined experimental materials, passivations and autoclaving treatment. Three experimental materials and four methods of passivation were attempted with or without autoclaving treatment. The results from this study can be concluded as follows.

1. Passivation by 400 °C thermal treatment for all the materials investigated exhibits the lowest content of suboxides and metallic elements in the surface and the highest oxide thickness. Nevertheless, this treatment may cause a desorption of the basic OH group in the hydration layer on the surface of the titanium alloy.
2. Passivation by 400 °C thermal treatment may not be suitable for the brazed materials which reveal copper and nickel elements in the surface by XPS analysis. For specimens passivated by other methods, no such elements are detected.
3. The oxide thickness is decided by the factors of passivation treatment and autoclaving procedure, but not by the experimental materials in this study. The content of suboxide phases (Ti^{2+} and Ti^{3+}) by the XPS method is determined by the passivation treatments, but not by the experimental materials and autoclaving treatment.
4. The ratio of titanium to Ti^{4+} decreases monotonically as a function of the thickness of oxide which, in turn, is related to passivations and autoclaving. The preparation of an experimental material, such as brazing, has little influence on the ratio.

References

1. J. GALANTE, W. ROSTOKER, R. LUECK and R. D. RAY, *J. Bone Joint Surg.* **53A** (1971) 101.
2. T. ALBREKTSSON, P. I. BRANEMARK, H. A. HANSSON, B. KASEMO, K. LARSSON, I. LUNDSTORM, D. H. McQUEEN and R. SKALAK, *Ann. Biomed. Engng* **11** (1983) 1.
3. P. A. MAEUSLI, P. R. BLOCH, V. GERET and G. STEINEMANN, in "Biological and Biomedical Performance of Biomaterials", edited by P. Christel, A. Meunier and A. J. C. Lee (Elsevier, Amsterdam, 1986) p. 57.

4. C. JOHANSSON, J. LAUSMAA, M. ASK, H-A. HANSSON and T. ALBREKTSSON, *J. Biomed. Engng* **11** (1989) 3.
5. J. LAUSMAA, M. ASK, U. ROLANDER and B. KASEMO, *Mater. Res. Symp. Proc.* **110** (1989) 647.
6. J. LAUSMAA, L. MATTSSON, U. ROLANDER and B. KASEMO, *ibid.* **55** (1986) 351.
7. B. KASEMO and J. PROSETH, *Dent.* **6** (1983) 832.
8. J. LAUSMAA, B. KASEMO and H. MATTSSON, *Appl. Surf. Sci.* **44** (1990) 133.
9. K. HEALY and P. DUCHEYNE, *J. Biomed. Mater. Res.* **26** (1992) 319.
10. P. A. LEE, K. F. STORK, B. L. MASCHOFF, K. W. NEBENSY and N. R. ARMSTRONG, *Surf. Interf. Anal.* **17** (1991) 48.
11. T. K. SHAM, and M. S. LAZARUS, *Chem. Phys. Lett.* **68** (1979) 426.
12. L. J. MENG, C. P. MOREIRA, DE DA, and M. P. DOS SANTOS, *Thin Solid Films* **239** (1994) 1117.
13. K. E. HEALY and P. DUCHEYEN, *Biomaterials* **13** (1992) 553.
14. D. S. SUTHERLAND, P. D. FORSHAW, G. C. ALLEN, I. T. BROWN and K. R. WILLIAMS, *Biomaterials* **14** (1993) 893.
15. R. M. PILLIAR, *J. Biomed. Mater. Res. Appl. Biomater.* **21 A1** (1987) 1.
16. J. J. CALLAGHAN, *J. Bone Joint Surgery*, **75-A** (1993) 299.
17. J. D. BOBYN, R. M. PILLIAR, H. U. CAMERON and G. C. WEATHERLY, *Clin. Orthop.* **150** (1980) 263.
18. J. J. CALLAGHAM, R. D. HEEKIN, C. G. SAVORY, S. H. DYSTAR and W. J. HOPKINSON, *Clin. Orth.* **282** (1992) 132.
19. Annual Book of ASTM Standards 13.01 (American Society for Testing and Materials, Philadelphia, PA, 1992) p. 44.
20. R. W. REVIE and N. D. GREENE, *Corros. Sci.* **9** (1969) 763.
21. B. F. LOWENBERG, S. LUGOWSKI, M. CHIPMAN and J. E. DAVIES, *J. Mater. Sci. Mater. Med.* **5** (1994) 467.
22. B. W. CALLEN, B. F. LOWENBERG, S. LUGOWSKI, R. N. S. SODHI and J. E. DAVIES, *J. Biomed. Mater. Res.* **29** (1995) 279.
23. M. BROWNE, P. J. GREGSON and R. H. WEST, *J. Mater. Sci. Mater. Med.* **7** (1996) 323.
24. A. WISBEY, P. J. GREGSON, L. M. PETER and M. TUKE, *Biomaterials* **12** (1991) 470.
25. S. YUE, R. M. PILLIAR and G. C. WEATHERLY, *J. Biomed. Mater. Res.* **18** (1984) 1043.
26. S. D. COOK, F. S. GEOGETTE, H. B. SKINNER and R. J. HADDAD, *ibid.* **18** (1984) 497.
27. S. D. COOK, N. THOMGPREDA, R. C. ANDERRSON and R. J. HADDAD, *ibid.* **9** (1988) 287.
28. C. A. STUBBINGTON and A. W. BOWEN, *ibid.* **9** (1974) 941.
29. C. D. BUGLE, US Pat. 4854496 (1989).
30. C. CRIVELLA and L. A. STOUSE, US Pat. 4650109 (1987).
31. C. H. YEN, Master Thesis, National Cheng Kung University (1995).
32. T. M. LEE, E. CHANG and C. Y. YANG, *J. Mater. Sci. Mater. Med.* **9** (1998) 429.
33. D. A. JONES, in "Principles and Prevention of Corrosion", edited by D. A. Jones (Macmillan, New York, 1992) p. 43.
34. S. HOFMANN, in "Practical Surface Analysis, Vol. 1, Auger and X-ray Photoelectron Spectroscopy", edited by D. Briggs and M.P. Seah (Wiley, Chichester, UK, 1994) p. 151.
35. G. C. WOOD and F. H. STOTT, *Mater. Sci. Technol.* **3** (1987) 519.
36. M. BROWNE and P. J. GREGSON, *Biomaterials* **15** (1994) 894.
37. R. N. S. SODHI, A. WENINGER and J. E. DAVIES, *J. Vac. Sci. Technol.*, **A9** (1991) 1333.
38. M. ASK, J. LAUSMAA and B. KASEMO, *Appl. Surf. Sci.* **35** (1998) 283.
39. B. SIEMENSMEYER and J. W. SCHULTZE, *Surf. Interface Anal.* **16** (1990) 309.
40. P. KOFSTAD, K. HAUFFE and H. KJOLLESDAL, *Acta Chem. Scand.* **12** (1958) 259.
41. N. BIRKS and G. H. MEIER, "Introduction to High Temperature Oxidation of Metals" (Edward Arnold, London, 1983).

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