Effect of Nb addition on high-temperature oxidation behavior, oxide layer structure, and its exfoliation resistance of Ti-Nb Alloys

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Abstract

The authors proposed an oxide coating on Ti alloys for the dental abutment tooth, and they had reported that Ti-29Nb-13Ta-4.6Zr (TNTZ) alloy forms a dense oxide layer by high-temperature oxidation. On the other hand, CP Ti forms a multilayered oxide consisted of rutile monolayers and the void layer. This morphological change by alloying is supposed to be mainly caused by Nb addition in Ti since the dense oxide layer of TNTZ mainly consists of rutile TiO₂ and TiNb₂O₇.

Therefore, in this study, oxidation behaviors of various range of Nb content of Ti-xNb alloys (x = 1 ~ 32 mol%) were investigated, and exfoliation resistance was evaluated. And in this paper, the oxide/metal interfacial microstructure of oxidized CP Ti, TNTZ alloy, and Ti-Nb alloy was studied by a transmission electron microscopy (TEM) and by a scanning transmission electron microscopy with an electron dispersive spectroscopy (STEM-EDS).

The cross-sectional observations suggested that the substrate was gradually oxidized during heat treatment, and nucleation and grain growth of TiO₂ and TiNb₂O₇ proceed at the metal/oxide interface. Consequently, the gradual oxidation process in TNTZ and Ti-Nb alloys could lead to its continuous interfacial microstructure and dense oxide structure, which can achieve high exfoliation resistance.

1. Introduction

Ti and its alloys are used as a dental material such as artificial teeth, denture base, orthodontic wire, root implant, however, one of the disadvantages is its metallic color which could impair the aesthetic appearance as a dental prosthesis. This aesthetic problem is one of the major reasons for changing the material for dental prostheses from metal to ceramic or resin with the improvement of the patient's QOL consciousness. Another reason is that the manufacturing process of the dental prosthesis is shifting from handmade to CAD/CAM due to the shortage of dental technicians in recent years in Japan. These changes have encouraged the development of ceramics and/or composite resin with better mechanical properties and better usability features. Nevertheless, clinicians and dental technicians still have strong confidence in metallic materials with excellent mechanical properties and dimensional stability.

The authors have proposed the high-temperature oxide coating of CP Ti and Ti-Nb-Ta-Zr alloys to solve the aesthetic problem of metallic dental materials [1-4]. The Ti-Nb based alloy represented by Ti-29Nb-13Ta-4.6Zr alloy (TNTZ) and Ti-36Nb-2Ta-3Zr-0.3O alloy (Gum metal) forms a dense and robust oxide layer consisting of rutile TiO₂ and TiNb₂O₇ by high-temperature oxidation, which has high brightness in color and excellent exfoliation resistance. On the other hand, in the case of CP Ti, the high-temperature oxide layer shows a pie-crust-like structure in which the rutile TiO₂ layer and the void layer overlap, and the exfoliation resistance is very low because of its multilayered structure. When an exfoliation test was conducted with the oxidized CP Ti, exfoliation in the oxide occurred, and the fracture of TiO₂ monolayer was observed. In the case of the fracture surface of oxidized TNTZ after the test, the metal substrate is exposed at the optical microscope (OM) level, however, in the scanning electron microscope (SEM) observation, the thin oxide layer on the substrate was recognized. Thus, the fracture mode of oxidized TNTZ was concluded as a thin layer cohesive fracture (TCF). That is to say, the alloying elements in Ti not only improved the β

stability of the substrate, also caused the phase separation of the oxide, which changed the rate-determining process of the oxidation and oxide microstructures.

Therefore, in this study, oxidation behaviors of Ti-xNb alloys ($x = 1 \sim 32$ mol%) were investigated. In this paper, the oxide/metal interfacial microstructure of oxidized CP Ti, TNTZ alloy, and Ti-Nb alloy was studied by a transmission electron microscopy (TEM) and by a scanning transmission electron microscopy with an electron dispersive spectroscopy (STEM-EDS). From the obtained result, the effect of the alloying element on oxidation behavior in the high-temperature oxidation treatment was discussed [5].

2. Experimental Procedures

Oxidized samples of CP Ti (Grade 2), Ti-29Nb-13Ta-4.6Zr, Ti-13Nb, and Ti-20Nb alloys were prepared for cross-sectional observation. The rod-shaped or rolled-shaped alloys before oxidation was annealed at appropriate heat treatment condition in a vacuum and then sliced in the size of approximately $10 \times 10 \times 1 \text{ mm}^3$. The plate sample was mechanically polished to #1500 with emery paper, washed with ultrasonic wave in acetone, and oxidized in an atmospheric furnace. The oxidation treatment conditions were set to a holding temperature of 1273 K and a holding time of 1.8 Ks, followed by furnace cooling.

The obtained oxide coated sample was identified by X-ray diffraction (XRD). Resin-embedded cross-sectional samples were also prepared and observed by field emission scanning electron microscope (FE-SEM, JSM-7001FA, JEOL, Japan). For TEM observation, micro-sampling was carried out by a focused ion beam (FIB, Quanta3D, FEI, USA). TEM sample was picked up at the substrate/oxide interface. Interfacial microstructures and compositional analyses were performed by TEM (JEM-2100F, JEOL, Japan) and STEM-EDS (JEM-ARM200F, JEOL). Single Crystal (Crystal Maker Software Inc.) and Crystallography Open Database [6] was used for selected area diffraction (SAD) pattern analysis.

3. Results and Discussion

3.1. SEM cross-section observation

The cross-sectional SEM image of the oxide layer formed on CP Ti substrate is shown in Fig. 1. When the thickness of the oxide layer formed on the surface of CP Ti exceeds a specific value, the oxide layer forms a pie-crust-like structure in which the TiO_2 monolayers grow horizontally on the interface, and the void layers alternately overlap. Since the structure contains multiple void layers, fracture occurs easily at the void layer by the external force, and the exfoliation stress is as low as about 2 ~ 4 MPa [1, 4]. However, by introducing a reinforcing material such as SiO_2 glass into the void layer, it is possible to improve the exfoliation stress to about 15 ~ 20 MPa which is durable for practical use [7, 8].

Fig. 1 Cross-sectional SEM images of the oxide layer formed on CP Ti substrate after high-temperature oxidation at 1273 K.

Fig. 2 Cross-sectional SEM images of the oxide layer formed on TNTZ substrate after high-temperature oxidation at 1273 K.

The oxide layer formed on the TNTZ alloy is shown in Fig. 2. In contrast to the pie-crust-like porous structure of the CP Ti oxide layer, the oxide layer on the TNTZ alloy shows a dense oxide layer structure without void, and the oxide microstructure in the vicinity of the interface shows continuous with the substrate microstructure, which means structure patterns of grain boundary and lamellar structure remains in the oxide. The exfoliation stress of the oxide layer is also influenced by the layer thickness, and it shows a high value of about 69 MPa in the maximum average value [4].

The dense and continuous microstructure of TNTZ is considered to be the reason the oxide layer has high hardness, abrasion resistance, and exfoliation stress at the oxide/metal interface. Though not shown here, in the exfoliated surface observation by SEM after the exfoliation test, partial exposure of the metal substrate and fracture in which the oxide layer of submicron thickness was observed, and its fracture mode is concluded to be thin layer cohesive fracture (TCF) which breaks in the oxide layer near the interface. That is, while the exfoliation stress of the oxide layer of CP Ti is defined by the strength of the oxide, the exfoliation stress of TNTZ is defined by the interfacial adhesion of the oxide/metal substrate.

3.2. Interfacial TEM observation

3.2.1 Metal/oxide interface of CP Ti

The bright-field (BF) images of the interface of the oxide layer of CP Ti are shown in Figs. 3 and 4. The oxide layer was confirmed to be rutile type TiO_2 from the results of XRD, etc. In Figures 3 and 4, a 30 ~ 50 nm-thick reaction layer with zonal structure was observed at the interface between CP Ti and oxide in the substrate, suggesting that the oxidation reaction proceeded here. From the SAD image, the crystal orientation of the fine crystals was comparatively similar. As shown in Fig. 4, this boundary layer was composed of long stretched bar-shaped grains parallel to the interface, and fine equiaxed grains with a diameter of several nm to several tens nm were grown beneath the bar-shaped crystalline layer. Fig. 5 shows HRTEM image of the interfacial area between bar-shaped grains and the fine equiaxed grains. Nano-particles in the amorphous were observed in the bar-shaped grain, and crystal grain with a size of several tens of nm exist on the oxide side. Lattice spacings of the nano-particles and the larger crystals were close to rutile TiO_2 . The HRTEM observation suggested that this part of the structure was composed of nanocrystals and amorphous materials.

Nano-sized voids were observed in some places between the bar-shaped grain layer and the sub-nano crystal layer. The further area from the interface, a TiO_2 crystal diameter became larger to about 100 ~ 200 nm.

Fig. 3 Bright-field (BF) TEM image of the CP Ti/ TiO_2 interface. Top-half region; metal substrate, bottom-half region: oxide. The SAD pattern in the upper right was obtained in the area surrounded by the dotted line.

Fig. 4 Enlarged BF-TEM image of the CP Ti/TiO₂ interface. Top region; metal substrate, middle region: boundary layer, bottom region: oxide. The SAD pattern in the upper right was obtained from the boundary layer and substrate. $B_{\alpha-Ti} = [10\bar{1}0]$ and $B_{rutile} = [110]$ were indexed.

Fig. 5 HRTEM image of the interface between the boundary layer and the oxide.

In the HAADF image shown in Fig. 6, a clear contrast difference is observed at the interface between the CP Ti substrate and the oxide layer, suggesting that the oxide layer and the substrate have a clear compositional difference. In addition, continuous and isolated voids were scattered between the boundary layer and the sub-micron crystalline area along with the interface. A micrometer-sized TiO₂ crystal layer consisting pie-crust-like layer as seen in the SEM image in Fig. 1 was formed further from the interface, where the void layer was also several hundred nm to several μm . According to the previous result [1], Kirkendall voids are formed during oxidation of CP Ti because Ti has a high solid solubility limit of O and the reaction of Ti-O is faster than the diffusion of Ti atoms to the surface [9]. The observation in Fig. 3 ~ 6 shows that nucleation and growth of TiO₂ crystal proceeded on the oxide side of the oxide layer/substrate interface, supporting the previous report.

Fig. 6 High-angle Annular Dark Field (HAADF) STEM image of the CP Ti/TiO₂ interface. Left region: oxide, and right region: substrate.

3.2.2 Metal/oxide interface of TNTZ

Fig. 7 shows the HAADF image of TNTZ and its oxide layer interface. In the case of TNTZ oxidation, an interfacial reaction layer with fibrous crystals as seen in that of CP Ti was not formed at the oxide/substrate interface, and the compositional contrast between the substrate and the oxide is indistinct compared with that of CP Ti. Instead of that, nano-sized equiaxed oxide crystals dispersed at the interface, and a grain growth layer consisting of oxide particles of several tens nm in diameter was formed toward the surface while maintaining the dense structure.

Fig. 7 HAADF-STEM image of TNTZ/oxide interface. Top region: substrate, and bottom region: oxide.

This grain growth region has a thickness of about 1 ~ 2 μm , and the results of the element mapping by EDS showed the Nb-rich region or Ti-rich region was observed depending on the observed area. In the major region closer to the surface, the average particle size of the oxide is about 200 nm, and the oxide layer above the grain growth layer has almost this particle size when combined with the result of surface observation by SEM. As described above, the oxides of TNTZ have identified as rutile TiO₂ and TiNb₂O₇ from the XRD results.

A cross-sectional sample in which the upper part of the oxide layer was intentionally fractured by quenching after the oxidation treatment was prepared. The results of the elemental mapping of the oxide/substrate interface are shown in Fig. 8. The substrate, which was originally a single β phase before oxidation, is separated into acicular α and fine $\alpha + \beta$ phases, the α phase being Ti-rich and the β phase being Nb and Ta-rich. Zr, which is said to be a neutral element for the phase stability of Ti, is uniformly detected in both phases.

Fig. 8 HAADF-STEM image and its EDS maps of TNTZ/oxide interface. Top left: HAADF-STEM image, top middle: Ta map, top right: Zr map, bottom left: Ti map, bottom middle: Nb map, and bottom right: O.

In the upper part of the image in Fig. 8, a region with a high O concentration was observed, and this region was an internal oxidation region to a grain growth region. In other words, it is suggested that the thermal shock causes the exfoliation in the grain growth region in Fig. 8 on the substrate or at the interface with the upper part of it. In Fig. 8, it is interesting that O diffuses in the depth direction to the lamellar structure of the substrate, and diffuses deeper into the fine $\alpha + \beta$ structure than the α grains.

From the results of these STEM-EDS observations, it is considered that the oxidation of TNTZ proceeds as follows. By the heat treatment, phase separation to $\alpha + \beta$ occurs in the vicinity of the TNTZ surface of original β single phase by the O diffusion into the substrate, which is α stabilizing element. The O diffusion into the alloy is fast, and the internal oxidation occurs in the substrate in the vicinity of the interface, and O diffusion also causes the phase separation of the substrate into $\alpha + \beta$ structure during the heating process. The β phase would be obtained during duration time, however, redistribution of Nb and Ta atoms into the α phase by diffusion might be slower since β transus increases with increasing O content. Furthermore, phase separation and oxidation at the interface also enhances during cooling. Once oxide formed, the grain growth of the oxide proceeds and phase separation to TiO_2 and TiNb_2O_7 enhanced during heat treatment.

Therefore, Nb, which is the most abundant solid solution element in the Ti alloy, has also a solid solution limit of about 13 mol% in TiO_2 , so that a part of Nb is dissolved in TiO_2 and the excess Nb precipitates as TiNb_2O_7 . It has been reported that the addition of Nb to Ti up to 10 mol% decreases the high-temperature oxidation rate [10, 11]. It is suggested that the slow diffusion rate of Nb relative to Ti and the oxidation reaction to TiO_2 and TiNb_2O_7 controlled the reaction at the interface, and the atomic diffusion and the oxidation reaction rate were consequently balanced. It is considered that the Kirkendall void layer formation as seen in CP Ti was suppressed, and a dense oxide layer and the continuous interfacial structure were formed.

Furthermore, an oxygen concentration gradient exists on the substrate side, and as a result, the hardness gradually increases from the metal substrate toward the oxide layer near the interface [12]. It is suggested that the relaxation of the interfacial stress by the oxygen concentration gradient is one of the reasons for the remarkable increase of the interfacial strength in addition to the high exfoliation resistance of the oxide layer itself by the above-mentioned dense structure and the interfacial structure continuity.

3.2.3 Metal/oxide interface of Ti-Nb

From the previous study, it is suggested that Nb is the key alloying element for densification during oxide growth on TNTZ. Thus, oxidized Ti-Nb binary alloy was prepared and observed by STEM. Fig. 9 shows HAADF images of the cross-section of oxidized Ti-13 mol%Nb and Ti-20 mol%Nb alloy. Exfoliation stress of the oxide layer on Ti-13 mol%Nb and Ti-20 mol%Nb was about 4 MPa and 70 MPa, respectively [13]. In both alloys, highly continuous interfaces without zonal layer and fine voids were observed, while in Ti-13 mol%Nb contained the dispersion of voids of several tens nm size in the oxide. In Ti-20 mol%Nb, nano-sized equiaxed oxide crystals dispersed at the interface, and a grain growth layer consisting of oxide particles of several tens nm in diameter was formed toward the surface while maintaining the dense structure, as well as that in TNTZ. The

Nb-rich region, which was supposed to be the old β grains, was observed as a whitish region in the HAADF image, became unclear on the oxide layer side, while the whitish region was clearly observed on the oxide in Ti-20 mol%Nb. The results indicated that the change of the interfacial microstructure by the Nb addition contributes to the improvement in the exfoliation resistance of the oxide layer, even if the effect of the layer thickness is taken into consideration.

Fig. 9 HAADF-STEM image of Ti-Nb/oxide interface. Top left: Ti-13Nb, right: Ti-20Nb.

4. Conclusions

As a result of interface structure observation of CP Ti oxide layer and TNTZ oxide layer, it became clear that there was a difference in structure and composition continuity in the interface of metal substrate/oxide layer.

1. The reaction layer with several tens nm thickness, consisting of bar-shaped grains, existed at the Ti/oxide layer interface. The reaction layer and the substrate were discontinuous in both the structure and the O concentration distribution.
2. In TNTZ, the clear boundary layer like Ti did not exist, and the O concentration change from the substrate to the oxide layer was also continuous in comparison with Ti.
3. Nb, which diffuses slowly and is phase-separated into TiNb_2O_7 , is considered to be involved in the densification of the oxide layer.

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