Low-temperature degradation of high-strength Y-TZP (yttria-stabilized tetragonal zirconia polycrystal)

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The objective of this study was to investigate the low temperature degradation characteristics of 2 types of high strength yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) in order to evaluate its suitability for implant body, implant superstructure or abutment. Disk-shaped conventional Y-TZP (0.25 mass% alumina) subjected to hot isostatic press treatment (HIP-Y-TZP) and Y-TZP/4Al₂O₃ with additional alumina (4.0 mass%) were mirror-polished. Accelerated aging tests with 134°C for 5 h at 0.2 MPa and 180°C for 5 h at 1.0 MPa were performed using an autoclave. Biaxial flexural strength and crystal phases were evaluated. Strength decreased as the proportion of monoclinic phase increased after accelerated aging treatment for both types of high-strength Y-TZPs. Despite the low alumina content, HIP-Y-TZP showed higher static strength and strength after accelerated aging treatment compared to Y-TZP/4Al₂O₃. However, both types of Y-TZP had adequate strength to be used as dental restorations even after accelerated aging treatment, therefore, its clinical suitability was considered high.

Keywords: High strength Y-TZP, HIP treatment, Alumina content, Biaxial flexural strength, Crystal phase

INTRODUCTION

Currently in clinical dentistry, the extensive use of computer-aided design and computer-aided manufacturing (CAD/CAM) systems and the introduction of high strength ceramics, such as tetragonal zirconia polycrystal (TZP) and TZP-alumina composite materials, has allowed the use of all ceramic restorations to accommodate complicated cases involving bridges and connected restorations¹⁻⁴. In particular, TZP is used for implant materials including implant bodies, implant abutments, crowns, and bridge frameworks⁵.

The mechanical properties of TZP is known to degrade in the presence of high temperature and moisture due to low temperature degradation, which is caused by the crystal phase transformation from tetragonal to monoclinic phase^{6,7}. Some studies indicate that low temperature degradation does not occur near body temperature, however in the field of orthopedic surgery, approximately 400 artificial TZP femoral heads placed in 2001 were reported to have undergone damage due to low temperature degradation⁸⁻¹⁰. In order to ensure the long-term success of TZP implant materials in the oral cavity, it is necessary to investigate the characteristics of low-temperature degradation in order to develop high strength TZPs with durability.

Hot isostatic pressing (HIP) and increased alumina content are some methods used to improve the strength of conventional TZP^{11,12}. HIP treatment under high pressure in an inert atmosphere leads to increased strength and translucency by significantly reducing

internal voids^{12,13}. Iijima *et al.* reported that fatigue durability of conventional yttria-stabilized tetragonal zirconia polycrystals (Y-TZPs) was significantly improved by HIP treatment¹⁴, and Koyama *et al.* reported that Y-TZP after HIP treatment possessed superior fatigue characteristics compared to grade 2 titanium¹⁵.

A study reported that the addition of alumina improved strength and fracture toughness by reducing anisotropy in the monoclinic phase¹⁶. Alumina-toughened zirconia (ATZ) and ceria-stabilized tetragonal zirconia polycrystals (Ce-TZP)/Al₂O₃ (NanoZR) with alumina content of approximately 20 mass% has been reported to have high strength and fatigue durability, and these materials are used to manufacture implant materials^{17,18}. Takano *et al.* reported that the fatigue strength of NanoZR was more than twice as high as the standard fatigue strength of conventional TZP (320 MPa), as defined in ISO 13356¹⁹. However, TZP with high alumina content is not suitable for implant superstructure or abutments because translucency significantly declines along with the increase in hardness and Young's modulus²⁰.

ZirTough (Y-TZP/4Al₂O₃) is Y-TZP with an alumina content of about 4.0 mass% with improved resistance to low temperature degradation²¹⁻²³. In addition, since the added amount of alumina is less than ATZ or NanoZR, the translucency, hardness and Young's modulus are relatively similar to conventional Y-TZP, therefore, its application on implant superstructure and abutments is more suitable than ATZ and NanoZR. Accordingly, high strength Y-TZP, Y-TZP treated with HIP (HIP-

Y-TZP) and Y-TZP with 4.0 mass% alumina content (Y-TZP/4Al₂O₃) in this study, seems to be suitable for dental implants as well as fixed dental prostheses.

In order to use high strength Y-TZP in the oral cavity, in this study, it is necessary to investigate the characteristics of low temperature degradation, however, not many reports have done. Especially, no paper was found the mechanical properties evaluated by biaxial flexural testing instead of fracture toughness, and direct comparison between HIP-Y-TZP and Y-TZP/4Al₂O₃. The objective of this study was to investigate low temperature degradation characteristics of 2 types of high-strength Y-TZP (HIP-Y-TZP and Y-TZP/4Al₂O₃). The biaxial flexural strength of high-strength Y-TZP was determined by subjecting accelerated aging treatment. Phase transformation was also studied using X-ray diffractometry (XRD). In addition, Vickers hardness test and scanning electron microscope (SEM) observation were performed.

MATERIALS AND METHODS

Preparation of TZP specimens

In this study, 2 types of high-strength Y-TZP were used: Y-TZP treated with HIP (HIP-Y-TZP) and Y-TZP with additional alumina (Y-TZP/4Al₂O₃, ZirTough) (Table 1). For HIP-Y-TZP specimens, Y-TZP powder (TZ-3YB-E, Tosoh, Tokyo, Japan) was sintered for 2 h at 1,350°C under atmospheric pressure, subsequently HIP treatment was performed at 1,300°C for 1 h in argon atmosphere (147 MPa). For Y-TZP/4Al₂O₃ specimens, Y-TZP (ZirTough, Kuraray Noritake Dental, Miyoshi, Aichi, Japan) with alumina content of about 4.0 mass% was fired at 1,500°C for 2 h under atmospheric pressure.

Each high-strength Y-TZP specimen was sectioned using a diamond disk to form a disk shape. Both sides of the disk were mirror-polished by a polishing apparatus (Ecomet 250 and Automet 250, Buehler, Lake Bluff, IL, USA) using 9 and 3 µm diamond particles and colloidal

silica of 0.02 µm. The specimens were subjected to ultrasonic cleaning for 10 min with acetone and ethanol then stored in dry atmosphere. The mean roughness (Ra) of the mirror polished surface was less than 0.1 µm.

Accelerated aging treatment

Accelerated aging treatment was performed using an autoclave (Table 2). Accelerated aging treatment consisted of 2 conditions: 134°C for 5 h at 0.2 MPa (HT134)²⁴⁾ and 180°C for 5 h at 1.0 MPa (HT180)^{25,26)}. For HT134, an autoclave (HICLAVE HG-50, Hirayama, Kasukabe, Japan) was used for accelerated aging treatment. For HT180, specimens were immersed in 20 mL of distilled water in a hydrothermal vessel (Shikoku Rika., Kochi, Japan), which consisted of a Teflon® inner vessel and a stainless steel jacket. The vessel was kept at 180°C for 5 h in an electric furnace (KDF90, Denken Highdental, Tokyo, Japan). After the treatment, the specimens were washed with distilled water and dried at 60°C for 24 h. As the control, specimens not subjected to accelerated aging treatment (as-polished) were used.

Flexural strength test

Flexural strength was evaluated through the biaxial flexural test by modifying method of the ISO6872^{27,28)}. Using a universal testing machine (Autograph AG-I 20 kN, Shimadzu, Kyoto, Japan), flexural test was conducted at a crosshead speed of 0.5 mm/min in air at room temperature. Disk specimens having a thickness of 0.5 mm and diameter of 13 mm were placed on 3 steel spheres positioned 120 degrees apart in a circle (8.0 mm in diameter). A flat-end loading cylinder with a radius of 0.8 mm was then applied. Biaxial flexural strength was calculated using the equation listed in ISO6872, with a Poisson's ratio value of 0.25 for each specimen. Six specimens from each group were used under each experimental condition.

Flexural strength distributions were estimated based on Weibull distributions, which were calculated

Table 1 High-strength Y-TZP used in this study

Sample code	Product name	Composition (mass%)	Manufacturer
HIP-Y-TZP	TZ-3YB-E	ZrO ₂ : balanced, Y ₂ O ₃ : 5.16, Al ₂ O ₃ : 0.25, Na ₂ O: 0.021, SiO ₂ : 0.007, Fe ₂ O ₃ : 0.003	Tosoh, Tokyo, Japan
Y-TZP/4Al ₂ O ₃	ZirTough	ZrO ₂ : balanced, Y ₂ O ₃ : 4.5, Al ₂ O ₃ : 4.0, P: 0.8–1.0, SiO ₂ : 0.2–0.4	Kuraray Noritake Dental, Miyoshi, Aichi, Japan

HIP: hot isostatic pressing, Composition is based on manufacturer's information.

Table 2 Condition for accelerated aging treatment

Condition	Temperature (°C)	Pressure (MPa)	Duration time (h)
as-polished	Room temp.	Atmospheric pressure	—
HT134	134	0.2	5
HT180	180	1.0	5

using the following equation:

$$P(\sigma) = 1 - \exp[-(\sigma/\sigma_{n0})^m]$$

where, $P(\sigma)$ =fracture probability defined by the relation $P(\sigma)=i/(N+1)$, i =rank of strength, N =total number of specimens, σ =strength at given $P(\sigma)$, σ_{n0} =characteristic strength, m =Weibull modulus.

Vickers hardness test

Vickers hardness number (Hv) was obtained using a Vickers hardness tester (Micro Hardness Tester, Shimadzu) with a load of 9.8 N and a loading time of 20 s. Four specimens were tested per condition. Four specimens from each group were used under each experimental condition.

SEM observation

In order to observe the surface of high-strength Y-TZP, thermal etching was performed at 1,350°C for 20 min in atmosphere pressure using an as-polished sample. Then carbon coating was performed and the surface of each sample was observed using a SEM (SU6600, Hitachi, Hitachi, Japan).

Specimens subjected to accelerated aging treatments and fracture tests were also observed after ultrasonic cleaning with ethanol and distilled water for 5 min and carbon coating.

XRD analysis

XRD analysis was carried out on the surface of the specimens subjected to accelerated aging treatment using the θ -2 θ method (analysis depth: 6–10 μm) and the thin film method (analysis depth: approximately 0.5 μm). The θ -2 θ method was a multipurpose X-ray diffractometer (Ultima IV, Rigaku, Tokyo, Japan), and the test conditions were X-ray output: CuK α , 40 kV, 40 mA, and scan speed: 5°/min. For the thin film method, a thin film X-ray diffractometer (Smart Lab, Rigaku) was used. Measuring conditions were X-ray output: CuK α , 40 kV, 30 mA, 1° incident angle, using step scan: 0.02° for 2 s fixed.

The analysis depth (t) on the mirror-polished specimens was calculated by the following equation^{29,30}.

$$t = (Kx/2\mu) \sin \theta$$

where, μ (X-ray adsorption coefficient) for 3Y-TZP=0.0653 μm^{-1} , $Kx=-\ln(0.01)=4.605$ on the assumption that X-ray diffraction intensity is detected to 99% during $2\theta=26\text{--}34^\circ$

for monoclinic and tetragonal phase of zirconia.

The relative amount of monoclinic to tetragonal phase was calculated based on the method of Garvie and Nicholson's method³¹. Three specimens were analyzed for each condition.

Statistical analysis

Two-way analysis of variance (ANOVA) was performed on the biaxial bending strength and Vickers hardness using material type and aging conditions as factors. In addition, Tukey's multiple comparison test was performed after carrying out one-way ANOVA for each material and aging condition. The significance level was set to $\alpha=0.05$.

RESULTS

Flexural strength and Weibull distribution

As a result of 2-way ANOVA, significant differences were observed in biaxial flexural strength when both material and aging conditions were considered (Table 3). Figure 1 displays the biaxial flexural strength of specimens. For HIP-Y-TZP, the flexural strength of as-polished, HT134, and HT180 were $1,881 \pm 172$, $1,730 \pm 166$, and $1,513 \pm 244$ MPa, respectively. For Y-TZP/4Al₂O₃, the flexural strength of as-polished, HT134, and HT180 were $1,546 \pm 101$, $1,414 \pm 93$, and $1,275 \pm 112$ MPa, respectively. HIP-Y-TZP showed greater flexural strength than Y-TZP/4Al₂O₃ under all treatment conditions. In regards to aging conditions, HIP-Y-TZP showed a

Fig. 1 Biaxial flexural strength of as-polished and accelerated aging-treated specimens.

Different letters indicate significant differences on each specimen ($p < 0.05$).

Table 3 Results of 2-way ANOVA for biaxial flexural strength

Factor	Sum of squares	df	Mean square	F	p	
Material	616,361.9	1	308,181.0	22.1	<0.01	**
Treatment	789,737.3	2	789,737.3	56.6	<0.01	**
Interaction	15,915.2	2	7,957.6	0.6	0.57	

decrease in strength in the order of HT134 and HT180 as accelerated aging treatment temperature increased when compared with as-polished; a significant difference was indicated between as-polished and HT180 ($p < 0.05$). For Y-TZP/4Al₂O₃, the strength decreased as the temperature of accelerated aging treatment increased, and a significant difference was observed between as-polished and HT134, HT134 and HT180, and as-polished and HT180 ($p < 0.05$).

Figure 2 shows the Weibull distributions of HIP-Y-TZP and Y-TZP/4Al₂O₃ for as-polished and accelerated aging treatment (HT134, HT180). In HIP-Y-TZP, the Weibull modulus (m) of H180 specimens was decreased compared to as-polished and HT134 specimen. In Y-TZP/4Al₂O₃, the Weibull modulus (m) of HT134 and HT180 specimens were decreased compared to as-polished specimens.

Vickers hardness

Results of the Vickers hardness test are shown in Fig. 3. As a result of 2-way ANOVA, significant differences were found only between materials, and no difference was indicated between treatment conditions (Table 4). Under all treatment conditions, Hv of HIP-Y-TZP and Y-TZP/4Al₂O₃ were 1,350–1,400 and 1,250–1,300, respectively.

SEM observation

A typical SEM with secondary electron image of a specimen subjected to thermal etching on as-polished specimen is shown in Fig. 4. HIP-Y-TZP exhibited a surface in which fine crystal grains of equal size were evenly dispersed and almost no voids (#) were observed. On the contrary, Y-TZP/4Al₂O₃ observed to have crystal grains of various grain sizes in addition to voids (#) and

Fig. 3 Vickers hardness number of as-polished and accelerated aging-treated specimens.

Fig. 2 Cumulative Weibull distribution of HIP-Y-TZP and Y-TZP/4Al₂O₃ for as-polished and accelerated aging treatment (H134, H180).
m: Weibull modulus, σ: Weibull characteristic strength

Table 4 Results of 2-way ANOVA for Vickers hardness number

Factor	Sum of squares	df	Mean square	F	p	
Material	789,737.3	1	789,737.3	37.0	<0.01	**
Treatment	7,780.8	2	58,136.9	2.5	0.11	
Interaction	4,679.9	2	2,339.9	1.5	0.25	

particles assumed to be alumina (*) caused by low average atomic number of alumina compared to zirconia.

SEM images of the surface of as-polished and accelerated aging-treated specimens (without thermal etching) are shown in Fig. 5 (Upper: low magnification, Lower: high magnification). Changes in surface morphologies due to accelerated aging treatment were not observed in both materials. In HIP-Y-TZP, surfaces

appeared smooth and homogeneous were and under all conditions. In Y-TZP/4Al₂O₃, black precipitates, which assumed to be alumina particles, were observed on the surface for all conditions.

Figure 6 shows a typical SEM image of the fracture surface after the flexural test of the sample subjected to accelerated aging treatment (HT180). Apparent deterioration layer was not observed on the surface

Fig. 4 Representative SEM images of as-polished high-strength Y-TZP with thermal etching.
#: micro defect, *: alumina particle

Fig. 5 SEM images of as-polished and accelerated aging-treated specimens without thermal etching.
Upper: low magnification, Lower: high magnification

layer of any of the samples by the SEM observation that seemed to be very thin layer.

XRD analysis

Figures 7 and 8 show representative XRD profiles of HIP-Y-TZP and Y-TZP/4Al₂O₃ using the θ -2 θ and thin film method, respectively. In the θ -2 θ method (Fig. 7,

Fig. 6 Representative SEM images of fracture surface of high-strength Y-TZP with accelerated aging treatment (HT180).

Fig. 7 Representative XRD patterns of as-polished and accelerated aging-treated specimens under θ -2 θ method (depth of analysis: 6–10 μ m).
●: tetragonal, ▲: monoclinic

Fig. 8 Representative XRD patterns of as-polished and accelerated aging-treated specimens under thin film method (Approximate analysis depth: 0.5 μ m).
●: tetragonal, ▲: monoclinic

Fig. 9 Monoclinic zirconia (m-ZrO₂) volume fraction (%) of as-polished and accelerated aging-treated specimens.
a) θ -2 θ method (analysis depth: 6–10 μ m), b) Thin film method (approximate analysis depth: 0.5 μ m)

depth of analysis: 6–10 μm), HIP-Y-TZP showed mostly tetragonal peaks; monoclinic peaks were confirmed only in small amounts. In Y-TZP/4Al₂O₃, monoclinic phase was observed in small amounts in as-polished in addition to tetragonal phase, and monoclinic peaks increased with HT134 and HT180 as the temperature of accelerated aging treatment increased.

In the thin film method (Fig. 8, depth of analysis: about 0.5 μm), the monoclinic phase peak was greater compared to the θ -2 θ method. In HIP-Y-TZP, monoclinic phase was slightly observed in as-polished, and as the temperature of accelerated aging treatment increased, monoclinic peak increased. On the other hand, in Y-TZP/4Al₂O₃, a considerable amount of monoclinic phase was already observed in the as-polished state, and the increase in the peak of the monoclinic phase and the decrease in the peak of the tetragonal phase.

The monoclinic content calculated from the X-ray diffraction analyses is shown in Fig. 9. In the θ -2 θ method for HT180, the proportion of monoclinic phase was less than 4% for HIP-Y-TZP after treatment, whereas this proportion was 25% for Y-TZP/4Al₂O₃. In the thin film method, the proportion of monoclinic phase was approximately 20% for HIP-Y-TZP after accelerated aging treatment of HT180. For Y-TZP/4Al₂O₃, the proportion of monoclinic phase was 40% or more before accelerated aging treatment and 80% after accelerated aging treatment of HT180.

DISCUSSION

This study aimed to clarify the low-temperature degradation characteristics of 2 types of high-strength Y-TZPs by subjecting specimens to accelerated aging treatment. The biaxial flexural strength, Vickers hardness, surface observation, and X-ray diffraction characteristics were examined to compare the influence of accelerated aging treatment among materials.

The thickness of each specimen was established as 0.5 mm in this study. This was because the minimum thickness of TZP prosthesis is approximately 0.5 mm and a report suggested that the influence of low temperature degradation increases as thickness decreases³²⁾. The TZP specimens used in this study were mirror polished. Surface roughness is known to affect the mechanical properties of TZP, therefore an investigation using a roughened surface would be ideal when its application for use as implant materials is considered. However, in order to clarify the low-temperature degradation characteristics of high-strength Y-TZP, it is necessary to investigate surface changes after accelerated aging treatment, therefore mirror polished specimens were used so that changes in surface properties could be easily examined. The characteristics of low temperature degradation on specimens with different surface roughness will be investigated in the future.

In this study, 2 conditions were used for accelerated aging treatment to compare the effects of low temperature degradation. The first condition was done according to the accelerated aging test regulated by

ISO13356²⁴⁾. However, ISO13356 is a standard used for implants in the orthopedic surgical field, therefore the environment in the oral cavity is not considered. In relation to this ISO standard, Chevalier *et al.* calculated the longevity of TZP from the proportion of monoclinic phase and reported that 134°C/5 h/0.2 MPa corresponds to 15 to 20 years in 37°C water^{8,9)}. This report stated that the proportion of monoclinic phase was 20% in 25 years, however, no decrease in strength was indicated. Unlike implants placed in orthopedic fields, dental implants are subjected to harsher conditions in the oral cavity including occlusion, mastication, temperature/pH changes, and oral bacteria, therefore it was necessary to set conditions which were more severe than 134°C/5 h/0.2 MPa. A second condition, 180°C/5 h/1.0 MPa, was used in this study. This is used during the industrial ceramic durability test standardized by ISO10545-11 for ceramic tiles²⁵⁾ and JISA5207 for sanitary ware²⁶⁾. The duration time for this standard is usually 1 h, however, duration time was set to be the same as the first condition at 5 h. If the strength was not reduced under this condition, it can be assumed that this material can function in the oral cavity for long periods of time.

The biaxial flexural test was conducted by modifying method of the ISO6872 in this study. As general flexural test methods, there are the 3-point and 4-point flexural test, however there is a disadvantage that it is difficult to remove the edges of the specimens which significantly affects strength. For this reason, biaxial flexural test is often used to interpret fracture properties of ceramic materials. The biaxial flexural test has also been adopted by the American Society for Testing and Materials to measure the strength of brittle materials such as ceramics, and it is also an international standard for dental ceramics. The biaxial flexural test considers the disadvantage of edge fracture to enable more accurate measurements of strength to be made³³⁾. Furthermore, the biaxial flexural strength was measured using the 0.5 mm thickness specimen in this study, despite the thickness of the specimen was specified as 1.2±0.2 mm in ISO6872. This reason was as follows; 1) zirconia restorations with minimum thickness have been growing in clinical situation due to extremely high strength of zirconia, and thus 2) the 0.5 mm thickness specimens were used in previous study^{14,19)}, and it was reported that the thickness of the specimen had less effect on the failure distribution and increase in thickness had little effect on flexural strength of the material¹³⁴⁻³⁶⁾.

Fracture toughness by methods relying on indentation crack lengths with Vickers indentations was not evaluated in this study. The main reason for this was because the correlation was small between the fracture toughness value and the fatigue strength reported in literature in past dynamic fatigue tests^{4,14,15,19)}. Therefore, it was necessary to evaluate the dynamic fatigue strength as specified in ISO14801 instead of fracture toughness to determine long term material durability in the oral cavity³⁷⁾. In this study, the load value of 9.8 N was used for Vickers hardness test; this did not correspond to the recommended load of 294 N for fracture toughness tests²¹⁾.

The reason for this was because the inner hardness of specimens is reflected when a large load is applied but this is not suitable when measuring the transformation layer on the TZP surface layer where the influence of low temperature degradation is observed. The load of 294 N was used due to the concern that specimens with 0.5 mm thickness would fracture during the hardness test. Since the penetration depth of the Vickers test under the conditions in this study was about 7 μm , it was assumed that the surface transformation layer did not affect the material hardness.

In this study, the flexural strength before accelerated aging treatment (as-polished) for HIP-Y-TZP and Y-TZP/4Al₂O₃ was 1,881 $\pm$ 172 and 1,546 $\pm$ 101 MPa, respectively; these values are greater than the flexural strength of conventional Y-TZP which is approximately 1,000 MPa³⁸. Reports have indicated that the strength of HIP-Y-TZP was about twice the amount of conventional Y-TZP because the degree of voids is reduced after HIP treatment¹⁴. Y-TZP/4Al₂O₃, on the other hand, possess greater strength due to increased compressive residual stress from the increased amount of alumina added³⁹. These results are consistent with a study done by Swain, which reported that volume expansion due to phase transformation from tetragonal to monoclinic phase increases compressive residual stress and improves strength⁴⁰. Inokoshi *et al.* compared Y-TZP/4Al₂O₃ and Y-TZP with a small addition of alumina and reported that the proportion of monoclinic phase were equal after firing alone, whereas when polished with diamond suspension, the proportion of monoclinic phase increased significantly in Y-TZP/4Al₂O₃. This study concluded that compressive residual stress accumulates and strengthens Y-TZP as the monoclinic phase increases on the surface^{22,23,41}. In this current study, more than 40% monoclinic phase was observed on the surface layer of as-polished in Y-TZP/4Al₂O₃. Therefore, it was assumed that Y-TZP/4Al₂O₃ had greater monoclinic phase after mirror polishing leading to increased compressive residual stress and improved strength. In addition, Y-TZP/4Al₂O₃ with about 4 mass% alumina possessed inferior in strength compared to ATZ of Y-TZP type with about 20 mass% alumina, but was similar to the strength of Ce-TZP type NanoZR. Accordingly, it is assumed that the increase in elastic modulus and decrease in the translucency which accompany the increase in alumina content were reduced.

As a result of the flexural test after accelerated aging treatment, both HIP-Y-TZP and Y-TZP/4Al₂O₃, strength decreased in the order of HT134 and HT180 as the temperature of accelerated aging treatment increased. This result was consistent with the report of other accelerated aging tests including a study done by Flinn *et al.* which reported that flexural strength decreased after subjecting to accelerated aging treatment at 134 and 180°C^{22,41}. Low temperature degradation of TZP occurs due to a phase transformation from tetragonal to monoclinic on the surface, causing the surface to swell and crack eventually leading to hydrolysis. Therefore, the greater the transition rate from tetragonal to

Fig. 10 Relationship between biaxial flexural strength and monoclinic volume fraction for 0-20 method (0-20) and thin film method (TF).

monoclinic phase on the surface, the more likely that low temperature degradation will occur.

From the X-ray diffraction analysis, HIP-Y-TZP showed a large proportion of tetragonal in as-polished specimens and an increased peak of monoclinic phase after accelerated aging treatment. On the other hand, in Y-TZP/4Al₂O₃, the proportion of monoclinic crystals was more than 40% in as-polished specimens, which increased to approximately 80% after accelerated aging treatment at 180°C for 5 h. Therefore, it was confirmed that the proportion of monoclinic phase increased in both HIP-Y-TZP and Y-TZP/4Al₂O₃ as the condition of treatment became severe. These results are consistent with the report by Flinn *et al.* that flexural strength decreases with the increase in monoclinic phase. It is also supported by the scatter plot graph of strength *vs.* monoclinic phase fraction that showed high relationship between biaxial flexural strength and monoclinic volume fraction (Fig. 10). It can be assumed that volume expansion occurred on the surface of the TZP due to accelerated aging treatment, which formed microcracks where moisture entered and resulted in decreased flexural strength due to hydrolysis. In addition, since the increase in proportion of monoclinic phase was significant in the thin film method (0.5 μm from surface), it is apparent that accelerated aging treatment affects only the surface layer of TZP.

This was also supported by the fact that no change in hardness was observed after accelerated aging treatment. In addition, apparent deterioration layer was not observed on the surface layer of any of the samples by the SEM observation (HT180, Fig. 6). Accordingly, deterioration phenomena were evaluated by XRD analysis with thin film method as above mentioned.

On the contrary, a study reported that compressive residual stress on the surface in fact, increases when the proportion of monoclinic phase is high, which improves low temperature degradation³⁹. Furthermore,

Munoz-Tabares and Anglada reported that the 10–20 nm microcrystalline layer present under the surface of polished zirconia was a transition layer from tetragonal to monoclinic phase, and this layer, along with residual compressive stress, is reported to play an important role for low temperature degradation resistance⁴²⁾.

As described above, phase transformation to monoclinic phase can be influenced by both reduction in strength by hydrolysis and improvement in strength by compressive residual stress, and the dominant cause cannot be unconditionally determined.

Clinical implication

As a result, both types of high-strength Y-TZP decreased in strength as a result of accelerated aging treatment due to increase in proportion of monoclinic phase. In addition, decrease of Weibull modulus (m) in the severe condition of 180°C for 5 h (1.0 MPa) is remarkable in HIP-Y-TZP compared to Y-TZP/4Al₂O₃, indicating that HIP-Y-TZP is prone to be subjected with low temperature degradation compared to Y-TZP/4Al₂O₃. However, even in the severe condition of 180°C for 5 h (1.0 MPa), the strength for HIP-Y-TZP and Y-TZP/4Al₂O₃ were 1,513 MPa (19.6% reduction compared to as-polished) and 1,275 MPa (17.5% reduction compared to as-polished), respectively. In contrast to conventional Y-TZP, where some of the same products could have up to 40% lower strength under the similar conditions, the strength reduction of high-strength Y-TZP used in this study was minimal compared to conventional Y-TZP²²⁾. It can be assumed that high strength was due to internal defects being reduced by HIP treatment for HIP-Y-TZP, and increase in alumina content for Y-TZP/4Al₂O₃¹⁶⁾. By substituting these values into the equation to obtain the biaxial flexural strength, then calculating the fracture load at 1 mm thickness from the obtained flexural strength, fracture loads for HIP-Y-TZP and Y-TZP/4Al₂O₃ were 895 and 756 N, respectively. The occlusal force is reported to be approximately 250–400 N in the molar region and 140–170 N in the anterior region⁴³⁾, and maximum biting forces is reported to be approximately 700 N⁴⁴⁾, indicating that both types of high-strength Y-TZP could withstand occlusal forces in the oral cavity.

Among the materials used, HIP-Y-TZP was demonstrated to have higher strength than Y-TZP/4Al₂O₃ when subjected to accelerated aging treatment. This material is suitable for use as implant bodies, in addition to anterior prosthesis, because high translucency and sufficient elastic modulus is maintained due to its low alumina content.

CONCLUSIONS

1. Strength decreased as the proportion of monoclinic phase increased after accelerated aging treatment for both types of high-strength Y-TZP (HIP-Y-TZP, Y-TZP/4Al₂O₃).
2. Despite low alumina content, HIP-Y-TZP had higher static strength and strength after accelerated aging treatment compared to

Y-TZP/4Al₂O₃.

3. Both types of high-strength Y-TZP had sufficient strength as implant materials even after accelerated aging treatment, therefore, clinical suitability was considered high.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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