

Phase transition and surface hardness improvement of zirconia by hydroxyapatite and β -tricalciumphosphate powder bed sintering

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To improve the surface hardness of zirconia using a phase transition, bed sintering was conducted on 3mol% Y_2O_3 -tetragonal zirconia polycrystal (3Y-TZP) embedded in hydroxyapatite (HA) powder and β -tricalciumphosphate (β -TCP) powder at 1450°C for different times. HA and TCP were decomposed to CaO, which is one of the stabilizers of zirconia at 1400 °C. Various properties of the specimens were analyzed. X-ray diffraction showed that CaO had diffused into ZrO_2 and induced a tetragonal to cubic phase transition during the sintering process. At the same time, the zirconia pellet was densified during the sintering process. The microstructure of zirconia indicated that the thickness of the cubic phase at the surface increased with increasing sintering time. As a result, the Vickers hardness of the specimens processed by powder bed sintering was higher than that of the untreated specimen due to the formation of a cubic phase.

Key words: Bed Sintering, Phase transformation, CaO, Zirconia

Introduction

Ceramics have excellent mechanical properties, such as abrasion resistance, corrosion resistance, and excellent hardness, as well as various electrical characteristics [1, 2]. Because of these advantages, ceramics have a wide spectrum of applications. On the other hand, ceramics are brittle, making them difficult to apply to structural materials [3, 4]. A study of the brittle fracture of ceramics can greatly expand their applications, and the benefits gained from this type of research will be substantial.

Pure zirconia exhibits a monoclinic phase at room temperature. As the temperature increases, it transforms to a tetragonal phase at temperatures approaching 1100 °C and transforms to a cubic phase at approximately 2300 °C [5]. Zirconia exhibits a 3 to 5% volume expansion when it transitions from a tetragonal to monoclinic phase because the monoclinic phase of zirconia is less dense than the tetragonal phase [6]. Therefore, the phase transformed from a tetragonal to monoclinic imposes stresses on zirconia, which can destroy the zirconia structure [7].

Partially stabilized zirconia has a metastable tetragonal structure at room temperature that is resistant to fracture by impact. This property is due to the volumetric expansion by the phase transformation from a metastable tetragonal phase to a monoclinic phase. In general, cracks in ceramics are formed by impact, which propagated gradually, resulting in fracture. On

the other hand, partially stabilized zirconia with a metastable tetragonal phase at room temperature is transformed to a monoclinic phase by external impact. The increase in volume due to the phase transformation causes internal stress, which prevents crack propagation [8, 9].

Fully stabilized zirconia with a cubic phase at room temperature can be fabricated by adding more stabilizer to partially stabilized zirconia. This fully stabilized zirconia has excellent abrasion resistance. Therefore, it is used as cutting tools, such as piercers, slitters, and knives. Despite this, unlike partially stabilized zirconia, brittle fracture occurs easily in fully stabilized zirconia [7, 10–12]. The stabilizer in zirconia has various components, such as Y_2O_3 , MgO, and CaO. Yttria-stabilized zirconia, in which Y_2O_3 is added as a stabilizer, has been used in various fields [13, 14].

Ceramics with both an excellent abrasion resistance surface and toughness in the inner sites can be manufactured by selecting reaction with stabilizer. And this structure can have a range of applications.

Powder bed sintering of 3Y-TZP compacts is performed at 1450 °C. Through this process, the phase transformation of the surface of the pellet by a reaction of zirconia and CaO and the process of densifying the pellet can be performed simultaneously. The source of CaO as a decomposition product varies. A representative CaO source is $CaCO_3$, which is unsuitable for the experiment because of its lower melting point than the sintering temperature of 3Y-TZP. As a raw material of CaO, hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) and β -tricalciumphosphate (β -TCP, $3\beta-Ca_3(PO_4)_2$) are similar to bone [15–17]. Both materials do not melt at the

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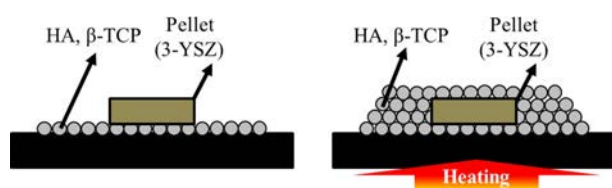


Fig. 1. Schematic diagram of the powder bed sintering process.

sintering temperature of 3Y-TZP, and the CaO is pyrolyzed at same temperatures below ~ 1200 °C, making them suitable as a bed powder. In this experiment, powder bed sintering was carried out using HA and β -TCP powders with different thermal decomposition behaviors and the pyrolysis characteristics were investigated. The phase transformation of the pellet surface was analyzed by microstructure observations, X-ray diffraction (XRD), and surface hardness measurements [18].

Experimental Procedure

3Y-TZP powder (TZ- 3Y, Tosoh, Japan) was compacted uniaxially at 30 MPa to prepare pellets. The density of the pellets was increased by the CIP process for 30 min under a hydrostatic pressure of 1800 bar. To react CaO uniformly with the 3Y-TZP pellet surface, each pellet was covered with HA (Alfa Aesar Co., USA), β -TCP (Alfa Aesar Co., USA) powder, and then heat-treated at 5 °C/min to 1450 °C for various times (HA: 2 hrs-2H, β -TCP: 2, 30 hrs-2, 30T) (Fig. 1). For comparison, the specimens were prepared under the same heat treatment conditions without covering the powder (Without powder 2hours: 2N).

The fabricated specimens were cut vertically to the surface and etched thermally for 30 minutes at 1350 °C. A Pt layer was coated on the cross section to observe the microstructure and analyze the elemental distribution by field emission scanning electron microscopy (FE-SEM, S-4300SE, Hitachi, Japan) and energy dispersive X-ray spectroscopy (EDS). High resolution XRD (HR-XRD, X'pert MRD diffractometer, Philips, Netherlands) was carried out to identify the crystal phase of the pellet surface. The surface of the pellet was polished and then analyzed by XRD with the comparison of the crystal phase inside the pellet. The surface hardness of each specimen was measured using a Vickers hardness tester (Hardness Testing Machine, HM-124, Akashi, Japan). The Vickers hardness was measured at 10 random points of each specimen and the data are represented as the average of each hardness value.

Result and Discussion

Fig. 2(a) presents the T2 and N2 cross-sectional microstructures. In the SEM image, no specific parts of the microstructure was identified. Fig. 2(b) shows an enlarged view of the N2 and T2 specimens. The

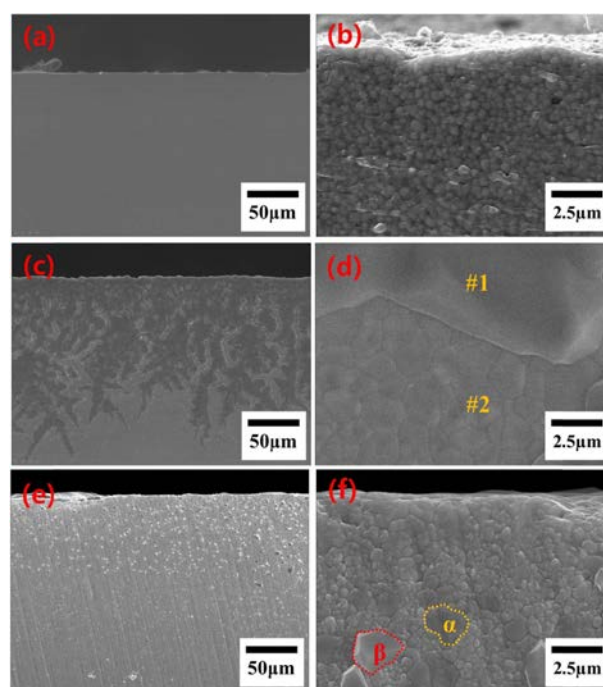
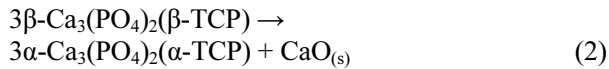
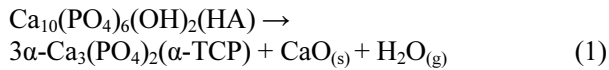


Fig. 2. Cross-section SEM images of (a) N2, (c) H2, (e) T30 and enlarged SEM image of (b) T2/ N2, (d) H2 (f) T30.

specimens had a uniform grain size (~ 0.5 μm) and a dense structure, indicating that the sintering of the pellets had been performed well. H2 was different from N2, grains could be observed on the surface, which decreased in size towards the inside of the pellet. As a result, the grains had two forms, showing a similar shape to tree roots. The tree root shape grains were formed from the surface to 150 μm (Fig. 2(c)). Fig. 2(d) presents an enlarged view of the H2 specimens. Two kinds of grains were observed. #1 was the part that forms the grain shape of the tree root, and #2 consisted of the grains of the remaining part; the grain size was 2–3 μm . The grains were larger than N2. Through these phenomena, it was found that the grain growth rate of each specimen was different. Fig. 2(e) shows the cross-sectional microstructure of T30. Protruding particles were observed in the T30 cross section. In addition, protruding particles were formed from the surface to 120 μm . Fig. 2(f) presents an enlarged view of the protruding particles region in more detail. Each grain had different microstructures, which consisted of 3 types of grains: α (2–3 μm), β , and ~ 0.5 μm sized. Observations of the microstructure of T30 suggested that each grain had different grain growth rates. In addition, protruding particles distributed near the surface were assumed to be β grains, which protruded from the other grains like the #1 grains of H2. Similarly, various grains could be observed in the microstructure of each specimen by bed sintering with HA and β -TCP. These phenomena were caused by the amount of CaO diffused in the 3Y-TZP grain. The grain growth rate is determined by the amount of CaO

diffused into zirconia [19]. These results show that the CaO produced by HA and β -TCP pyrolysis diffused into the zirconia grains. The reactions for the pyrolysis process of HA and β -TCP at 1200 °C are shown below.



α -TCP and CaO were produced as pyrolysis products through a thermal decomposition process. The amount of CaO decomposed thermally from β -TCP was very small at 0.0095 times that of α -TCP [12, 18, 19]. Therefore, the amount of CaO diffused into the zirconia pellets was small, and there was no change in the microstructure. In the case of the protruded grains in H2 and T30, the amount of CaO diffused in the zirconia pellet was large, so that it could be assumed that the grain phase had changed.

Fig. 3 presents the EDS analysis results for analyzing the component distribution of each grain of the T30 specimen. Each grain distributed in T30 contained different Ca contents. The content of Ca in the α , β , and the normal grains was 2.2 at. %, 5.4 at. %, and 0.54 at. %, respectively. EDS confirmed that CaO had diffused selectively into the zirconia grains, and the shape and size of the grains were changed. In other words, the grain growth rate of zirconia grains was dependent on the amount of CaO in the grains. In addition, the β grain could protrude during thermal etching.

Fig. 4 shows the XRD pattern of each specimen surface. The 3Y-TZP powder had a tetragonal phase at room temperature. Typical peaks were divided into two at approximately 35 ° and 60 °. The N2 bed powder had perfectly tetragonal phases like 3Y-TZP powder. These results showed that N2 had not reacted. On the other hand, H2 had a typical cubic phase with only one peak near 35 ° and 60 ° 2 θ . In addition, a CaZrO_3 phase was observed. In the phase diagram of ZrO_2 -CaO, the CaZrO_3 phase is produced when CaO is reacted in zirconia at more than 30 mol%. A large amount of CaO reacted on the H2 surface (Fig. 4(a)) [20]. Fig. 4(b) shows XRD patterns of the T2 and T30 surfaces. T2 had peaks

divided into two at approximately 35 ° and 60 ° like N2 but the XRD patterns were slightly different from N2; the distance between the two peaks was narrower than with N2. T2 was estimated to undergo a tetragonal to cubic phase transition. Although the amount of CaO was small, T2 reacted with the CaO pyrolyzed during the bed sintering process. T30 inside with 100 μm polished from the surface had similar XRD patterns to T2. XRD showed that the phase transition proceeded from tetragonal to cubic. T30 had many peaks compared to the other specimens. The cubic phase and monoclinic phase coexisted at the T30 surface. On the other hand, a tetragonal phase could not be detected. This was caused by the selected grains having a sufficient reaction with CaO and the tetragonal to monoclinic phase transformation. The monoclinic phase is formed

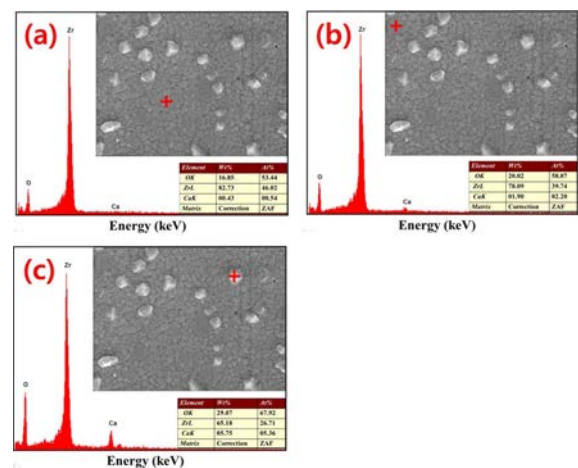


Fig. 3. Elemental distribution of grains in T30. (a) Normal grain, (b) large grain (a), (c) protruding grain (b).

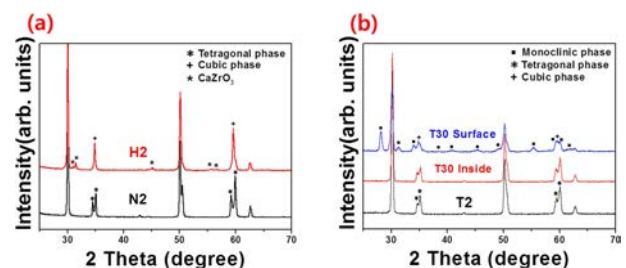


Fig. 4. (a) XRD patterns of H2 and N2. (b) XRD patterns of T2 and T30 at surface and inside.

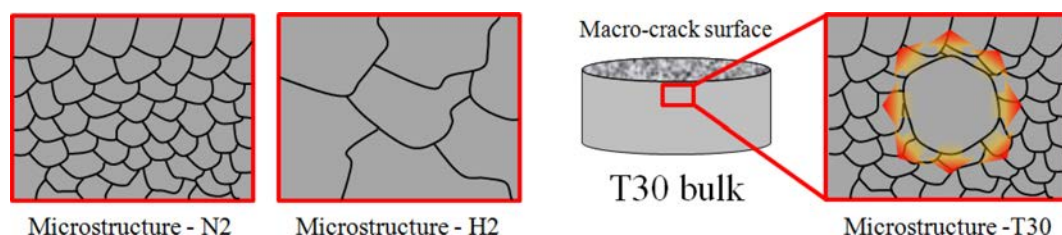


Fig. 5. Schematic diagrams of the microstructure of each specimen and the mechanism of the t-m transformation caused by abnormal grain growth.

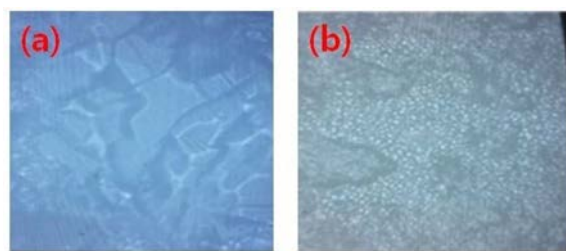


Fig. 6. OM images of the T30 surface taken immediately after sintering without polishing. (a) large grains of the monoclinic phase and (b) small grains of the cubic phase.

Table 1. Vicker's hardness of N2, H2, T2, and T30''/T30'.

	N2	H2	T2	T30''	T30'
Hv	1301	1609	1536	1869	964

on the zirconia pellet surface by the abnormal grain growth of the CaO-diffused zirconia grains. The abnormally grown grains form a stress field in the surrounding normal grains. The stress field around the normal grains elevates the surface of the pellet and forms a micro-crack on the surface. Micro-cracks formed on the surface become macro-cracks as the stress increases, causing roughening of the zirconia surface. This crack propagation on the surface causes a tetragonal to monoclinic phase transformation [21-23].

Fig. 5 presents a schematic diagram of a cross-section of each specimen. N2, which was unaffected by CaO diffusion into the grains had smaller grains than the other specimens, whereas HA had large grains. This was caused by the reaction with CaO. T2 reacted with Ca and showed a similar microstructure to N2. The N2 grains were reacted with a small amount of Ca. T30 had various size and shape grains. The 3-Y TZP grains were assumed to have formed from a selected reaction with CaO. The 3-Y TZP grains containing CaO pushed the surrounding grains. Therefore, the surface of T30 formed micro-cracks, which caused a tetragonal to monoclinic phase transformation by the abnormal grain growth of grains on the surface. These phenomena occurred as a result of the grain growth rate from a selected reaction with CaO. The microstructure of the T30 surface was observed by optical microscopy, as shown in Fig. 6. T30 had two types of grains (T30' and T30''). T30' had a large number of cracks, and T30'' had no cracks. T30' with many cracks could be assumed to be a monoclinic phase, and T30'' could be a cubic phase [11-13]. The hardness of each specimen and T30' and T30'' were compared using a Vickers hardness tester (Table 1). The hardness of the specimens N2, T2, and H2 heat treated at the same temperature were 1301 Hv, 1536 Hv, and 1609 Hv, respectively. The hardness of the specimen was improved by increasing the amount of CaO reacting with 3-Y TZP grains. T30 had two types of grains with different hardnesses. The hardness of T30'' and T30' was 1869 Hv and 964 Hv,

respectively. In general, zirconia exhibited various mechanical properties by the phase transition. The cubic phase had excellent hardness and the monoclinic phase of zirconia formed by a crack propagation transformation had very low hardness [13-16]. Therefore, T30'' with higher hardness was estimated to be a cubic phase and T30' with lower hardness and many cracks was estimated to be the monoclinic phase.

Conclusions

This study examined the effects of thermal decomposition of HA and β -TCP on zirconia at high temperature. Each pellet surface had different microstructures because the amount of CaO, which is a pyrolysate of HA and TCP, was different at 1450 °C. The mean grain size of each specimen was different, which suggests that the grain growth rate increases with increasing amount of CaO. The surface of each specimen had a different phase according to XRD, which changed according to the amount of CaO in the grain. The surface of T30 was shown to be a monoclinic phase and cubic phase, and two types of phases could be observed by optical microscopy. The monoclinic phase in T30 was formed by the internal stress of the zirconia pellet. The Vickers hardness of each specimen increased with increasing amount of CaO diffused into zirconia (N2: 1301 Hv, T2: 1536 Hv, H2: 1609 Hv, T30'': 1869 Hv), whereas T30' had a very small hardness of 964 Hv. This was judged to be a monoclinic phase formed by surface crack transitions. Through this study, it was possible to achieve a phase transition of the surface and complete sintering simultaneously. Therefore, ceramics with both an excellent abrasion resistance surface and toughness in the inner sites can be manufactured. This structure can have a range of applications, such as cutting tools.

Acknowledgements

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