Effect of Titania Doping on Phase Stability of Zirconia Bioceramics in Hot Water

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The effect of titania doping on tetragonal to monoclinic (t-m) phase transformation of zirconia bioceramics is evaluated by ageing in hot water at 413 K. The examined materials are 3 mol%Y2O3 stabilized tetragonal zirconia polycrystal (3Y-TZP) and 1.5, 3.0 and 7.7 mol%TiO2-doped 3Y-TZP. The t-m phase transformation of 3Y-TZP is accelerated by titania doping in all the specimen examined. However, 7.7 mol%TiO2-doped TZP shows better phase stability than 1.5 or 3.0 mol%TiO2-doped one. This change in phase stability of 7.7 mol%TiO2-doped TZP cannot be simply explained from the difference of grain size or the change in the axial ratio, c/a. XRD analysis reveals that the distance between nearest neighbor anion and cation site significantly decreases only in 7.7 mol%TiO2-doped TZP. This result indicates that the binding energy between dopant and oxygen vacancy affects the phase stability as well as the change in the axial ratio, c/a.

Keywords: zirconia, phase stability, t-m transformation, titania-doping, oxygen vacancy, binding energy

1. Introduction

Zirconia has become a popular alternative to alumina as bioceramics because of substantially higher fracture toughness and strength.1,2) For example, owning to its excellent wear resistance against ultra high molecular weight polyethylene,3) zirconia has been widely used as a femoral head of total hip replacement. Moreover, many dental application of zirconia has been developed.4)

Recently, we have developed the joining technique of zirconia dental bridge by using 7.7 mol%TiO2-doped tetragonal zirconia polycrystal (TZP) as an insert material.5,6) This method is an application of enhanced superplasticity in TiO2-doped TZP,7) which is explained from the balance between the grain size and the increased accommodation length for the stress concentration by diffusion.8,9)

It is well known that zirconia ceramics shows the martensitic phase transformation preferentially at the surface of tetragonal zirconia. It has been shown that tetragonal to monoclinic (t-m) transformation at the surface of zirconia ceramics is accelerated by the presence of water molecules in the environment.10–13) Since the t-m transformation involves volume increase, it induces the formation of microcracks at the surface and an increase of the roughness. Microcracking leads to a decrease of the mechanical properties; this phenomenon is called low temperature degradation of zirconia, which could explain the failure of implants after several years in vivo.

In recent years, t-m phase transformation of zirconia ceramics under the environment where the water exists is investigated frequently, and it has been reported that phase transformation of zirconia is suppressed by adding small amount of cation as dopant in hot water.14–19) Our previous result reveals that the effect of small amount of dopant on phase stability of 3Y-TZP is clearly explained from the valency and ionic radius of the dopant.17–19) For instance, the t-m transformation is promoted when the pentavalent element is added but suppressed when the bivalent element is added. In case the tetravalent element is added, the transformation is promoted if the ionic radius of the element is larger than that of zirconium, and that is suppressed if the element with smaller ion radius is added. However, since this result is obtained only from the small amount of oxide-doped 3Y-TZP less than 2 mol%, the effect of dopant content on phase stability of zirconia has not made clear yet. In this paper, the effect of several amount of titania doping on phase transformation of zirconia bioceramics for dental bridge is evaluated by ageing in hot water at 413 K.

2. Experimental Procedure

The materials used in this study were 3 mol%Y2O3-doped tetragonal zirconia polycrystal (3Y-TZP) and 1.5, 3.0 and 7.7 mol% TiO2-doped 3Y-TZP. The mixed powders were uniaxially pressed into plates at 20 MPa and then cold isostatically pressed at 200 MPa. The specimens were sintered at a temperature between 1673 and 1773 K, so as to have the relative density better than 98% in each material. To evaluate the resistance of the phase transformation in water, accelerated exposure tests were carried out in autoclave at 413 K. XRD analysis were carried out for each sample before and after the exposure tests to evaluate the volume fraction of monoclinic phase. The volume fraction of monoclinic phase was calculated using the following formula proposed by Garvie,20)

\[
m\% = \frac{I_m(11\bar{1}) + I_m(111)}{I_m(111) + I_m(11\bar{1}) + I_t(11\bar{1})} \times 100
\]

where \(I_m(11\bar{1})\) and \(I_m(111)\) refer to the relative intensity of the (11\bar{1}) and (111) planes of the monoclinic phase, respectively; and \(I_t(11\bar{1})\) refers to the relative intensity of the (11\bar{1}) plane of the tetragonal phase. The surface observation was conducted by FE-SEM (Field emission-type scanning electron microscope).

3. Results and Discussion

Figure 1 shows the SEM micrograph of (a) un-doped, (b) 1.5 mol%, (c) 3.0 mol% and (d) 7.7 mol%TiO2-doped 3Y-
TZP. The average grain size is 0.35, 0.43, 0.61 and 0.51 μm, respectively. From the XRD analysis, only tetragonal phase is observed in all the specimens examined in as-sintered state.

Figure 2 shows XRD profiles of 1.5 mol% TiO$_2$-doped TZP before and after the accelerated exposure tests in hot water at 413 K as the typical XRD profiles. The $t$-$m$ phase transformation is observed as the decrease of tetragonal peak and the increase of monoclinic one with time. The phase transformation progresses with time in all the specimens examined.

Figure 3 shows the change in monoclinic fraction with time during accelerated exposure tests in hot water at 413 K of (a) un-doped, (b) 1.5 mol%, (c) 3.0 mol% and (d) 7.7 mol%TiO$_2$-doped 3Y-TZP obtained from XRD profile by using equation (1). The $t$-$m$ phase transformation of 3Y-TZP is accelerated by titania doping in all the specimen examined. However, 7.7 mol%TiO$_2$-doped TZP shows better phase stability than 1.5 or 3.0 mol%TiO$_2$-doped one.

It has been reported that the phase stability of TZP in hot water is highly affected by grain size, i.e., $t$-$m$ transformation significantly promoted with increasing grain size. Then, the effect of grain size on the present result is examined. Figure 4 shows the relationship between average grain size and the monoclinic fraction after the accelerated exposure tests in hot water at 413 K for 60 h. The monoclinic fraction has no clear correlation with the grain sizes. This result
indicates that the accelerated $t$-$m$ transformation in 1.5 and 3.0 mol% TiO$_2$-doped TZP in comparison with that of 7.7 mol% TiO$_2$-doped one cannot be explained from the difference of the grain size.

In order to find a parameter to explain the result that 7.7 mol% TiO$_2$-doped TZP shows better phase stability than 1.5 or 3.0 mol% TiO$_2$-doped one, change in structural parameter with the increase of titania content is examined. Figure 5 shows the relationship between TiO$_2$ content and (a) axial ratio, $c/a$ and (b) unit cell volume estimated from XRD analysis. The axial ratio, $c/a$ increases with the increase of titania content. This result is in good agreement with a previous report.$^{24,25}$ In contrast, the unit cell volume slightly decreases with the increase of titania content until 3 mol%, and significantly decreases by 7.7 mol% addition.

Recently, we have reported that the phase stability of small amount of oxide doped 3Y-TZP such as MgO, CaO, TiO$_2$, HfO$_2$, CeO$_2$, Nb$_2$O$_5$, Ta$_2$O$_5$ is explained from the change in axial ratio, $c/a$, i.e., the decrease in axial ratio results in the increase in phase stability.$^{19}$ The similar result has also been reported in 4–8 mass% yttria-stabilized zirconia.$^{26}$ Figure 6 shows the relationship between axial ratio, $c/a$ and monoclinic fraction after the accelerated exposure tests in hot water at 413 K for 60 h. When the titania content is small, the phase stability decreases with the increase of axial ratio, $c/a$. This result is in good agreement with the previous result. In contrast, the phase stability of 7.7 mol% TiO$_2$-doped TZP is better than that in 1.5 or 3.0 mol% TiO$_2$-doped one although the axial ratio, $c/a$ significantly increases. Another factor must be considered to explain this trend.

As the degradation mechanism of tetragonal zirconia at relatively low temperature (below 673 K), several models have been proposed.$^{11,27–33}$ Among the models, a model proposed by Guo seems to be most commonly accepted.$^{32,33}$ That model consists of the following steps: (i) chemical adsorption of H$_2$O on the ZrO$_2$ surface, (ii) reaction of H$_2$O with O$_2$/C$_0$ on the ZrO$_2$ surface to form hydroxyl ions OH$^-$, (iii) penetration of OH$^-$ into the inner part by grain boundary diffusion, (vi) filling of oxygen vacancies by OH ions, and therefore the formation of proton defects, and (v) occurrence of a tetragonal to monoclinic transformation when the oxygen vacancy concentration is reduced to the extent that the tetragonal phase is no longer stable. In this reaction, the interaction between dopant ions and oxygen vacancies is very important. If the binding energy between dopant ions and oxygen vacancies are strong, the filling of oxygen vacancies by water molecules becomes more difficult and the degradation is suppressed. It has been reported that the degradation of ZrO$_2$ is retarded by the doping of MgO instead of Y$_2$O$_3$.$^{12,34}$ This is because magnesium ions strongly bind oxygen vacancies, which is evident from the low conductivity of MgO-doped ZrO$_2$,$^{35}$ and the very large binding energy between magnesium ions and oxygen vacancies ($\sim 146$ kJ/
2.220
2.221
2.219
Distance of Nearest Neighbor Site / 10^{-10} m

Monoclinic Fraction (%)  
0  
20  
40  
60  
80  
1.5, 3.0 mol% Ti
7 mol% Ti
3Y

Fig. 7 Relationship between distance of nearest neighbor site and monoclinic fraction in 3Y-TZP and TiO₂-doped 3Y-TZP after the accelerated exposure tests in hot water at 413 K for 60 h.

mol) comparing with $-39$ kJ/mol for that between yttrium ions and oxygen vacancies. Similar trend is observed in CaO-doped and CeO₂-doped ZrO₂ in which calcium or cerium ions strongly bind oxygen vacancies. Although the binding energy between the dopant and oxygen vacancies is not clear in this study, the distance between the dopant and oxygen vacancies will affect the phase stability because the distance is inversely related to the binding energy in general.

Since the oxygen vacancy is stable when the binding energy between dopant and oxygen vacancy is large, therefore, the reaction filling of oxygen vacancies by water molecules becomes more difficult; as a result, the degradation of MgO-doped ZrO₂ is retarded. Similar trend is observed in CaO-doped and CeO₂-doped ZrO₂ in which calcium or cerium ions strongly bind oxygen vacancies. Although the binding energy between the dopant and oxygen vacancies are not clear in this study, the distance between the dopant and oxygen vacancies will affect the phase stability because the distance is inversely related to the binding energy in general.

Figure 7 shows the relationship between distance of nearest neighbor site and monoclinic fraction after the accelerated exposure tests in hot water at 413 K for 60 h. The distance of nearest neighbor site is calculated from the lattice parameters assuming that the structure is slightly elongated fluorite structure to the direction of $c$-axis. In the analysis, the oxygen ion's displacement is not considered. When the 1.5 or 3.0 mol% TiO₂ is doped, distance of nearest neighbor anion and cation site is not so different with that of 3Y-TZP, but the phase stability significantly decreases. This result must be explained from the effect of the change in axial ratio, $c/a$ by dopant as has been reported in the previous papers. In contrast, the distance between nearest neighbor anion and cation site significantly decreases only in 7.7 mol% TiO₂-doped TZP, and the phase stability increases in comparison with that in 1.5 or 3.0 mol% TiO₂-doped TZP. The phase stability of large amount of TiO₂-doped TZP has correlation with the distance between nearest neighbor anion and cation site, i.e., phase stability suppressed when the distance between anion and cation site decreases. The similar trend is obtained in the relationship between next nearest neighbor anion and cation site and monoclinic fraction. Since the distance is inversely related to the binding energy in general, this result possibly suggests that the binding energy between dopant and oxygen vacancy affects the phase stability as well as the axial ratio, $c/a$. Detailed analysis of binding energy between dopant and oxygen vacancy will be conducted by ab initio calculation in future works.

4. Conclusion

The effect of titania doping on tetragonal to monoclinic ($t$-$m$) phase transformation of zirconia bioceramics is evaluated by ageing in hot water at 413 K, and the following results are obtained.

1. The $t$-$m$ phase transformation of 3Y-TZP is accelerated by titania doping in all the specimen examined. However, 7.7 mol% TiO₂-doped TZP shows better phase stability than 1.5 or 3.0 mol% TiO₂-doped one.

2. The change in phase stability of 7.7 mol% TiO₂-doped TZP cannot be simply explained from the difference of grain size or the change in the axial ratio, $c/a$.

3. From XRD analysis, it is shown that the distance between nearest neighbor anion and cation site significantly decreases only in 7.7 mol% TiO₂-doped TZP. Since the distance is inversely related to the binding energy in general, this result possibly suggests that the binding energy between dopant and oxygen vacancy affects the phase stability as well as the axial ratio, $c/a$.

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