Effect of Adding Diamond Particles on the Fracture Toughness of Apatite Ceramics

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Composite ceramics dispersed through diamond particles with hydroxyapatite as a matrix were prepared by firing at 1250°C under reduced pressure or normal atmosphere. The fracture toughness and physical properties of sintered composite ceramics were examined to determine methods of strengthening hydroxyapatite ceramics. The diamond crystal in composite ceramics was transformed to graphite by firing and the fracture toughness of hydroxyapatite ceramics increased with diamond addition. At 10 wt% diamond, the maximum value for fracture toughness was obtained, and the further addition of diamond particles over 10 wt% caused fracture toughness to decrease. Such increases in fracture toughness were considered the result of microcracking which occurred during the transformation from diamond to graphite.

Key words: Apatite, Diamond, Fracture toughness

INTRODUCTION

Synthetic hydroxyapatite (HAp: Ca₁₀(PO₄)₆(OH)₂) has many uses in dental materials because of its superior biocompatibility. Sintered HAp ceramics are used for artificial tooth roots as bio-active implant materials. However, sintered HAp ceramics has a lower shear strength than other implant materials, since it is essentially a brittle material. To compensate for this brittleness, various methods including plasma-spraying on metal and production or addition of second phase particles to HAp matrix have been proposed. Zirconia dispersed composite ceramics can absorb breaking energy by microcracks which form during the phase transformation of zirconia particles and create an increased fracture toughness. However, in the case of HAp ceramics, unstabilized or partially stabilized zirconia particles are changed to cubic-zirconia by HAp component, i.e. Ca, therefore, the beneficial microcracks do not form.

We used diamond powder in HAp ceramics as a substitute for zirconia. Diamond particles have a volume expansion of about 40% during transformation from diamond to graphite, similar to the expansion of zirconia during tetragonal → monoclinic phase transformation. Noma et al. reported that the fracture toughness of alumina ceramics increased 2 times after the addition of diamond particles.

In the present investigation, HAp composite ceramics containing synthetic diamond powder dispersed through the HAp matrix were investigated as models of dental implant ceramics. We examined the fracture toughness and properties of HAp-diamond composite ceramics, and found that this composite possesses higher fracture toughness than HAp ceramics alone.
MATERIALS AND METHODS

Specimen preparation
HAp powder used for the matrix material was heat-treated at 800°C for 5 hours. After heat treatment, HAp was crushed to a fine powder in an alumina ceramic cell by a vibrating mill*, until a mean particle size of 0.8 μm was obtained. A synthetic diamond powder** with a particle size below 0.5 μm was used as the dispersion particle. The HAp powder matrix and the diamond powder were then mixed in a ball mill# for 1 h without a dispersing agent. Pressures of up to 20 MPa were applied to dry specimens in metal dies using a mechanical press. After press drying, powder compacts were sintered at a heating rate of 5°C·min⁻¹ and a firing temperature of 1250-1300°C for 2 h under a reduced pressure of 1.3 Pa or normal atmosphere.

SEM observations and X-ray diffraction
The microstructure of the fractured surface of the sintered materials was sputtered with gold, and observed with a scanning electron microscope (SEM)##.

The crystal phases in the sintered materials were analyzed with the X-ray powder diffraction (XRD). The diffractometer system employed used Ni-filtered CuKα radiation@. The 2θ range from 10 to 70° was covered at a scanning speed of 1.0 degree·min⁻¹ at 30 kV and 10 mA.

Properties
The firing linear shrinkage of the 8 φ × 10 mm pressed sample was measured during constant heating at a rate of 5°C·min⁻¹ to 1350°C. Firing temperature and heating time of powder compacts were determined by linear shrinkage vs the temperature curve.

Test pieces for the measurement of mechanical properties were made by grinding the surface of the test piece flat and smooth using a diamond rasp (#700) and diamond polishing liquid (0.5 μm diamond powder). The sizes of the test pieces were 4 × 6 × 20 mm³ and 2 × 6 × 20 mm³ for fracture toughness and bending strength tests, respectively. Fracture toughness was measured using the Vickers indentation method with a load of 98 N. Fracture toughness is represented by the following equation: ¹⁵)

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(K_{IC}/H^{1/2})(H/E)^{1/2} = 0.028 (C/a)^{-3/2}
\]

where \( K_{IC} \) is the fracture toughness, \( H \) is the hardness, \( a \) is half the length of the impression diagonal, \( E \) is Young's modulus, \( C \) is the indentation crack length. The fracture toughness (\( K_{IC} \)) is proportional to the indentation crack length (\( C \)), therefore, relative fracture toughness¹² was evaluated from \( C^{-3/2} \). The bending strength was tested by 3-point bending@@ over a 15 mm span at a cross-head speed 0.5 mm·min⁻¹. Hardness of the composite

* T-100 model Vibrating sample mill, Heiko Seisakusyo, Ltd., Fukushima, Japan
** De Beers Co., Johannesburg, South Africa
³ P-7 Planetary micro pulverizer, Fritsch Co., Idar Oberstein, Germany
⁴ S-700 Scanning electron microscope, Hitachi Co., Tokyo, Japan
@ ADG-301, Toshiba Co., Tokyo, Japan
@@ AGS-500A Autograph, Shimadzu Corp., Kyoto, Japan
$ M type, Shimadzu Corp., Kyoto, Japan
ceramics was measured by micro Vickers hardness tester with a load of 4.8 N.

RESULTS AND DISCUSSION

The shrinkage curves of powder compacts of the HAp matrix alone and that of samples with 10 or 20 wt% additions of diamond powder are summarized in Fig. 1. The size of HAp compact sample did not change at 800°C, and then shrank at temperatures above 800°C. The compact demonstrated a linear shrinkage of 20% at 1100°C, but there was no change between 1100°C and 1350°C. Shrinkage curves and sintering temperature of powder compacts containing diamond increased with diamond addition. This result shows that sintering of HAp particles was obstructed with increases in the proportion of diamond particles.

The results of the Vickers hardness measurements are shown in Fig. 2. The Vickers hardness value of HAp ceramics alone was 340 Hv, the values of samples made by the diamond dispersion system were lower than that of HAp matrix alone. In measuring bending strength, HAp matrix alone had a value of 90 MPa, though values of diamond dispersed ceramics were 70–80 MPa at 5-20 wt% diamond additions.

The relative fracture toughness of HAp-diamond composite ceramics sintered under reduced pressure or normal atmospheric pressure are summarized in Fig. 3. The relative toughness of HAp matrix alone was $3.4 \times 10^4$ m$^{-3/2}$. Under atmosphere sintering (○ : B), the relative toughness of HAp-diamond system increased with an increase in diamond content. At 10 wt% diamond, a maximum value of $10.4 \times 10^4$ m$^{-3/2}$ was obtained for relative toughness, while the further addition of diamond over 10 wt% caused toughness to decrease. Relative toughness of HAp–diamond composite ceramics under reduced pressure sintering (● : A)
were similar to those of atmosphere sintering. However, the relative toughness of HAp-diamond composite ceramics in the reduced pressure firing had higher values than those under atmosphere sintering. In particular, the relative toughness of HAp composite with 10 wt% diamond was increased 3 times compared to HAp matrix alone.

The HAp crystal in the HAp-diamond composite ceramics fired below 1250°C was not decomposed, though \( \alpha \)-TCP, produced by a decomposition of HAp, was detected by X-ray diffraction analysis in HAp composite ceramics fired at 1300°C. Some diamond crystal in composite ceramics fired at 1250°C was transformed to graphite (XRD), while a part of the diamond crystal remained in the HAp composite ceramics. The transformation from diamond to graphite did not appear at firing temperature of 1200°C.

Increase in fracture toughness seemed to coincide with the microcracking\(^{4,10}\). For example, the microcracks in zirconia dispersed ceramics are formed by the expansion of zirconia particles during transformation from tetragonal to monoclinic phase\(^{4,6,9,10}\). This microcrack formation develops with the tensile stress of the matrix phase, around the zirconia particles. The diamond particles in HAp-diamond ceramics expand during the transformation of diamond \( \rightarrow \) graphite phase, similar to the transformation of the zirconia particles. Therefore, increased fracture toughness is considered the result of microcracks in the HAp matrix produced by the expansion during diamond transformation\(^{12-14}\). The
16 TOUGHENING OF APATITE CERAMICS

Fig. 4 Microstructure (SEM) of sintered ceramics of HAp matrix alone and HAp-diamond composite.
Sintering conditions: at 1250°C for 2 hours under a reduced pressure.

The decrease in fracture toughness when more than 10 wt% diamond is added may be related to large cracks that form as some microcracks join. The difference in fracture toughness under various sintering conditions is considered affected by the graphite volume formed during transformation.

Scanning electron microscopy (SEM) was used to observe the microstructure of the surface of fractured composite ceramics. As shown in Fig. 4, deflection and bowing of the cracks occurred before destruction. Microcracks due to transformation of the diamond phase were not observed by SEM. However, deflection and bowing of cracks on fractured surfaces increased compared with that of HAp alone. This phenomena may show that a microcrack zone formed in the HAp matrix.

CONCLUSIONS

Diamond powder dispersed ceramics with hydroxyapatite as the matrix were prepared as models of dental implant material to study increases in the fracture toughness of hydrox-
apatite ceramics.

The relative fracture toughness of hydroxyapatite and diamond composite ceramics was 3 times higher than that of hydroxyapatite matrix alone with the addition of 10 wt% diamond. The addition of diamond had little effect on the bending strength and hardness. Increases in fracture toughness were considered due to the microcracking effect caused by the transformation of diamond to graphite.

REFERENCES

本号掲載論文の和文抄録

バリウム・ポロシリケートガラスフィラーを含む
試作光硬化型 X 線不透過性コンポジットレジンへの
フッ素化芳香族ジメタクリレートの応用
——耐水性の向上——
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バリウム・ポロシリケートガラスをフィラーとする試作光硬化型 X 線不透過性コンポジットレジンの耐久性、特に耐水性、の向上を目指した。この目的を達成するため、従来から用いられているベースモノマーの典型的な成分である Bis-GMA に換えて撥水性を賦与するために Bis-GMA-F を用いた。
その結果、約 2 万回のサマルサイクリング後において、Bis-GMA を含むコンポジットレジンは圧縮強さ、ダイヤモンド柄張り強さ、曲げ強さ、曲げ弾性係数が初期の 60〜70％に低下した。一方 Bis-GMA-F を含むコンポジットレジンは曲げ強さを除く圧縮強さ、ダイヤモンド柄張り強さ、曲げ弾性係数に関してほとんど低下しなかった。これはマトリックスレジンとしての Bis-GMA-F と Bis-GMA の吸水に関する性質が反映したものと考えられた。

アバタイト焼結体の破壊靭性に及ぼすダイヤモンド添加の影響

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歯科用インプラント材料としてハイドロキシアバタイト焼結体の高靭化を試みる目的で、ハイドロキシアバタイト粉末にダイヤモンド微粒子を分散させた複合焼結体を作製した。この複合焼結体の破壊靭性などに及ぼすダイヤモンド粒子添加の影響を調べた。その結果、アバタイト・ダイヤモンド複合焼結体の強さおよび硬さはアバタイト単独の焼結体に比較してわずかに低下したが、破壊靭性はダイヤモンドを添加することにより向上することとがわかった。特に 10 wt%ダイヤモンド添加時に極大値を示し、相対靭性値でアバタイト単独の焼結体より 3 倍向上することがわかった。破壊靭性が向上した理由はアバタイト複合焼結体中のダイヤモンド粒子が焼成温度で黒鉄に転移することによりアバタイトマトリックス相にマイクロクラックを生成させたためであると推察された。